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Tissue S/N ratios and stable isotopes (δ^{34}S and δ^{15}N) of epilithic mosses (*Haplocladium microphyllum*) for showing air pollution in urban cities in Southern China

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Tissue S/N ratios and isotopes of mosses

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ABSTRACT

In urban cities in Southern China, the tissue S/N ratios of epilithic mosses (*Haplocladium microphyllum*), varied widely from 0.11 to 0.19, are strongly related to some atmospheric chemical parameters (e.g. rainwater SO_4^{2-}/NH_4^+ ratios, each people SO_2 emission). If tissue S/N ratios in the healthy moss species tend to maintain a constant ratio of 0.15 in unpolluted area, our study cities can be divided into two classes: class I (S/N > 0.15, S excess) and class II (S/N < 0.15, N excess), possibly indicative of stronger industrial activity and higher density of population, respectively. Mosses in all these cities obtained S and N from rainwater at a similar ratio. Sulphur and N isotope ratios in mosses are found significantly linearly correlated with local coal δ^{34}S and NH_4^+–N wet deposition, respectively, indicating that local coal and animal NH_3 are the major atmospheric S and N sources.

1. Introduction

Both nitrogen and sulphur play important roles in development of acid rain, since their oxides form chemical compounds which serve to increase the acidity of water. Deposition of acid compounds and inorganic-nitrogen (N) from the atmosphere has increased in some Chinese area during recent decades (e.g. Lü and Tian, 2007), and there is increasing concern that deposition of these compounds is damaging the forest 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). The main anthropogenic sources for NO_x emissions are transport, industry, and energy production. Ammonia emissions arise mainly from agriculture, particularly livestock farming and animal wastes, which is widespread in the city surroundings (Asman et al., 1998).

Dijkshoorn et al. (1960) postulated that since most of the organic S and organic N in plants is used in protein synthesis, the composition of the proteins largely determines the ratio of organic S/N in the plant material. On theoretical grounds the S and N contents are related and it is important to consider this in assessing the S and N status of foliage. Because of the strong inter-dependence of N and S metabolism, it is not surprising that plants tend to maintain a relatively constant ratio of organic N to organic S, particularly in their vegetative tissues (Dijkshoorn and van Wijk, 1967).

Plants growing under optimum conditions can contain significant quantities of inorganic-N (as nitrate-N) and inorganic-S (as sulphate-S) (Stanford and Jordan, 1966). The S/N ratios have been used to assess the S status in foliage subject to S emissions (Malcolm and Garforth, 1977). In Western Europe, for example, S deficiency has become more common as a result of cleaner air over the last decade. As a consequence, the mean S/N ratios in plants decreased from 0.083 in 1981/1982 to 0.0625 in 1992/1993 (Zhao et al., 1995). Accordingly, the S/N ratios can be used to assess the intensity of pollution to which plant foliage is exposed and could, therefore, be used to monitor the effect of S emissions before damage was detected visually (Malcolm and Garforth, 1977).

Mosses, being sensitive to both acid deposition and N fertilization, have been shown to be outstanding bioindicators in a wide

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range of air pollution studies (Hutchinson and Scott, 1988; Nygaard and Abrahansen, 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). 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 (Conti and Cecchetti, 2001). In areas with high N deposition, the N content of the bryophytes is increasing and the bryophyte communities are declining (Baddeley et al., 1994; Pitcairn et al., 1995).The results reported by Mäkipää (1998) also indicated that addition of ammonium sulphate increased the N concentration in *Pleurozium schreberi* and *Dicranum polysetum*.

Sulphur isotope ratios ($\delta^{34}S$) 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 sulphur sources and, consequently, to assess the relative contribution and impacts of the different sources (Ohizumi et al., 1997; Novák et al., 2001; Xiao and Liu, 2002; Pruett et al., 2004). Moreover, isotopic signatures can give us a better understanding of mixing processes, transport pathways, deposition of sulphur and history of pollutant sulphur in the environment (Krouse, 1977; Xiao and Liu, 2002; Pruett et al., 2004; Gislason and Torssander, 2006). 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).

Industrialized cities in South China have been confronted with the consequences of acidic deposition since 1980s. Some studies have shown that atmospheric S in Chinese industrialized regions mainly came from S bearing coal through industrial and domestic burning (Galloway et al., 1987). Because northern Chinese coals usually have been reported to have higher S isotopic ratios than southern Chinese coals (Hong and Zhang, 1992), atmospheric S with a low $\delta^{34}S$ value over most southern Chinese urban cities was believed emitted from local coal-burning power stations according to the very limited data available (Mukai et al., 2001; Xiao and Liu, 2002).

Isotopic data for atmospherically derived nitrogen are increasingly used in assessing the sources of inputs to a wide variety of soil and plant environments (Evans and Ehleringer, 1993; Durka et al., 1994). 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).

The aims of the work reported here were firstly, to understand the effects of environmental parameters (e.g. rainwater, SO_2 emission) on tissue S/N ratios of epilithic moss *Haplocladium microphyllum* (Hedw.) and, secondly, to identify S and N sources in the atmosphere using moss stable isotopes.

2. Materials and methods

2.1. Study area

The industrial cities chosen are listed in Table 1, including 12 industrial cities and 1 remote city (Lhasa). Lhasa is believed having clean atmosphere, while at Guiyang and Chongqing (SW China) acid rain has been observed since 1980s. At that time,

Table 1
Sampling site description.

Sites	Lat.	Long.	Altitude (m)	Population in 2005 ($\times10^3$)	SO_2 emission in 2005 (tonsyr^{-1})	Wet deposition				SO_4^{2-}/NH_4^+ molecule ratios in rainwater
						SO_4^{2-} (kg S ha^{-1} yr^{-1})	NH_4^+ (kg N ha^{-1} yr^{-1})	NO_3^- (kg N ha^{-1} yr^{-1})	$NH_4^+ + NO_3^-$ (kg N ha^{-1} yr^{-1})	
Suzhou (SZ), Jiangsu Province	31°18′N	120°37′E	3	1810	242 400	69.7	14.3	2.2	16.5	2.1
Hangzhou (HZ), Zhejiang Province	30°18′N	120°12′E	42	2540	125 844	52.3	13.9	2.7	16.6	1.6
Nanjing (NJ), Jiangsu Province	32°02′N	118°50′E	9	3730	149 171	67.1	21.3	2.9	24.2	1.4
Hefei (HF), Anhui Province	31°51′N	117°18′E	30	1720	24 264	45.4	16.4	4.5	20.9	1.2
Nanchang (NC), Jiangxi Province	28°39′N	115°53′E	22	1840	27 002	39.5	17.5	5.5	23.0	1.0
Wuhan (WH), Hubei Province	30°37′N	114°21′E	23	5080	133 442	44.6	18.5	10.2	28.7	1.1
Changsha (CS), Hunan Province	28°12′N	112°59′E	45	2200	58 887	41.5	15.6	5.2	20.8	1.2
Guilin (GL), Guangxi Autonomous Region	25°15′N	110°18′E	150	760	56 345	32.9	12.0	3.8	15.8	1.2
Guiyang (GY), Guizhou Province	26°34′N	106°42′E	1100	1560	220 297	49.8	18.1	0.8	18.9	1.2
Zunyi (ZY), Guizhou Province	27°42′N	106°53′E	1300	710	67 597	58.3	15.0	2.7	17.8	1.7
Chongqing (CQ)	29°32′N	106°31′E	300	4350	683 162	79.2	23.4	4.3	27.7	1.5
Chengdu (CD), Sichuan Province	30°40′N	104°04′E	500	3470	156 760	88.2	23.0	6.9	29.9	1.7
Lhasa (LS), Tibet Autonomous Region	43°05′N	86°49′E	3659	270	300	2.1	1.1	0.6	1.7	0.9

Wet deposition is calculated based on NH_4^+, NO_3^- and SO_4^{2-} concentrations in rainwater (Hu et al., 2002; Li, 1999; Liu et al., 2005; Mei et al., 2005; Wang et al., 1992; Xiao and Liu, 2002, 2004; Zhou et al., 2003) and annual precipitation (Chinese Environmental Protection Bureau, 2006). SO_2 emission in 2005 is cited from Chinese Environmental Protection Bureau (2006).

SO_2 concentrations at Guiyang reached 400–500 μg/m^3 on the ground (Wang, 1993). In 2004, rainwater in all these industrial cities was found at pH < 5 (Fig. 1) although SO_2 emission rates are declining as a result of the introduction of sulphur control legislation. In 2006, ambient SO_2 concentration at Guiyang was only 73 μg/m^3 and pH of the rainwater reached 6.0 (Guiyang Environmental Protection Bureau, 2007). Wet deposition of nitrogen and sulphur in these cities was calculated from the concentrations in rainwater in the literature and annual precipitation.

2.2. Sample collection and treatment

The moss materials *H. microphyllum* (Hedw.) at all study sites were collected in 2006 (Fig. 1). Moss *H. microphyllum* (Hedw.) was selected because of its widespread distribution in the study area. Urban mosses were mainly collected around parks or hills. All mosses were obtained from natural rocks without canopies or overhanging vegetation ensuring no influenced by throughfall N compounds and by soil solution (Liu et al., 2007). 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.

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.

Coal samples were collected from the main coal deposition in the respective province except in Zhejiang Province and Tibet Autonomous Region, where no large coal deposition was found, and stored in cleaned plastic bags enroute to the laboratory. Then they were dried in a vacuum oven at 70 °C and re-dried after being ground separately into fine powders using a mortar and pestle.

2.3. Chemical analyses

Sulphur and N contents in mosses and coals were measured by an elemental analyzer (Model PE-2400 II, USA) with an analytical precision of 1%.

Moss and coal samples were oxidized in a Parr bomb to convert all forms of sulphur present to sulphate (Siegfriedt et al., 1951). 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 $BaCl_2$ solution. After precipitated for 24 h, the mixture was filtered through a 0.22nbsp;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 of mosses and coals 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‰.

2.4. Statistical analysis

Statistical analysis was conducted by SPSS 11.5, and graphs were mainly created with SigmaPlot 2000 software (both SPSS Science, Chicago, USA).

3. Results

3.1. Moss sulphur and nitrogen contents

The mean S contents of epilithic mosses in the study varied from 0.31 ± 0.04% in Hefei (HF) to 0.55 ± 0.05% in Suzhou (SZ) (Fig. 2). The mean S contents of urban mosses changed linearly with SO_4^{2-}–S wet deposition ($p < 0.05$) (Fig. 3a and Table 2).

Among all these mosses, those sampled in Wuhan (WH) had the highest mean tissue N content (3.21 ± 0.27%), then those in Changsha (CS: 3.12 ± 0.37%) and in Nanchang (NC: 2.93 ± 0.20%). Mosses in two cities of Guizhou Province, Zunyi (ZY) and Guiyang (GY), showed the lowest values, being 1.89 ± 0.18% and 2.26 ± 0.32%, respectively (Fig. 2). There is no significantly linear relationship between mean N contents of mosses and NH_4^+–N wet deposition or NO_3^-–N wet deposition or (NH_4^+–N + NO_3^-–N) wet deposition (Fig. 3b–c and Table 2).

If a mean S/N ratio of mosses sampled in remote forests (e.g. Gongga Mountain: S/N = 0.15; Xiao unpublished data) can be considered as a normal S/N ratio, the study cities are separated into two classes by the line S/N = 0.15 (Fig. 2): class I shows excess S in the tissue (S/N > 0.15) such as in Suzhou (SZ), Hangzhou (HZ), Chongqing (CQ), Chengdu (CD) and Zunyi (ZY), while class II shows excess N in the tissue (S/N < 0.15).

3.2. $\delta^{34}S$ and $\delta^{15}N$ in Mosses

Among all these mosses (Fig. 4), the lowest mean $\delta^{34}S$ values occurred in Guiyang (GY: −3.1 ± 1.7‰), then in Guilin (GL: −0.5 ± 1.2‰). The highest mean $\delta^{34}S$ values were found in Hefei (HF: +7.9 ± 4.0‰) and in Wuhan (WH: +7.5 ± 2.8‰).

Epilithic mosses showed negative $\delta^{15}N$ signatures except for some sampled in Lhasa (LS: +4.2 ± 2.5‰), Chongqing (CQ:

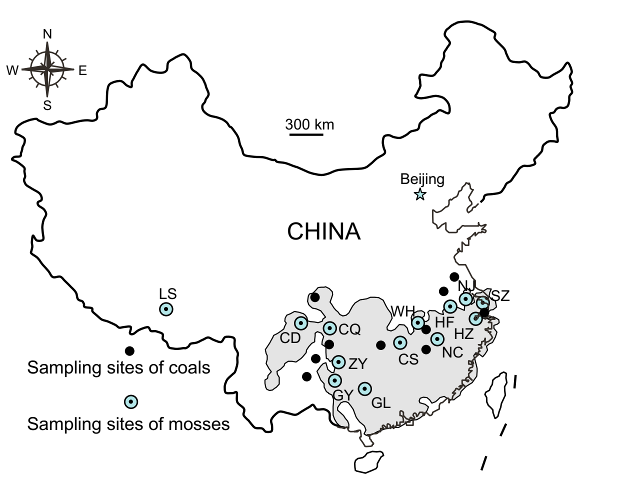

Fig. 1. Map of China showing the sampling sites in cities in South China and acid rain distribution (pH < 5) in 2004 (revised from Chinese Environmental Protection Bureau, 2005). The shaded regions represent areas where acid rain was measured. The abbreviations of the sampling sites are presented in Table 1.

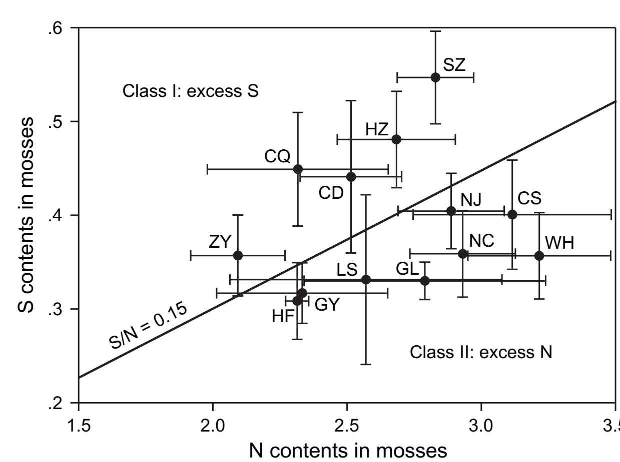

Fig. 2. Chemical composition and stable isotopes of epilithic mosses vs. wet deposition in cities. (a) $\delta^{34}S$ and %S vs. SO_4^{2-}–S deposition; (b) $\delta^{15}N$ and %N vs. NH_4^+–N deposition; (c) $\delta^{15}N$ and %N vs. NO_3^-–N deposition; (d) $\delta^{15}N$ and %N vs. (NH_4^+–N + NO_3^-–N) deposition.

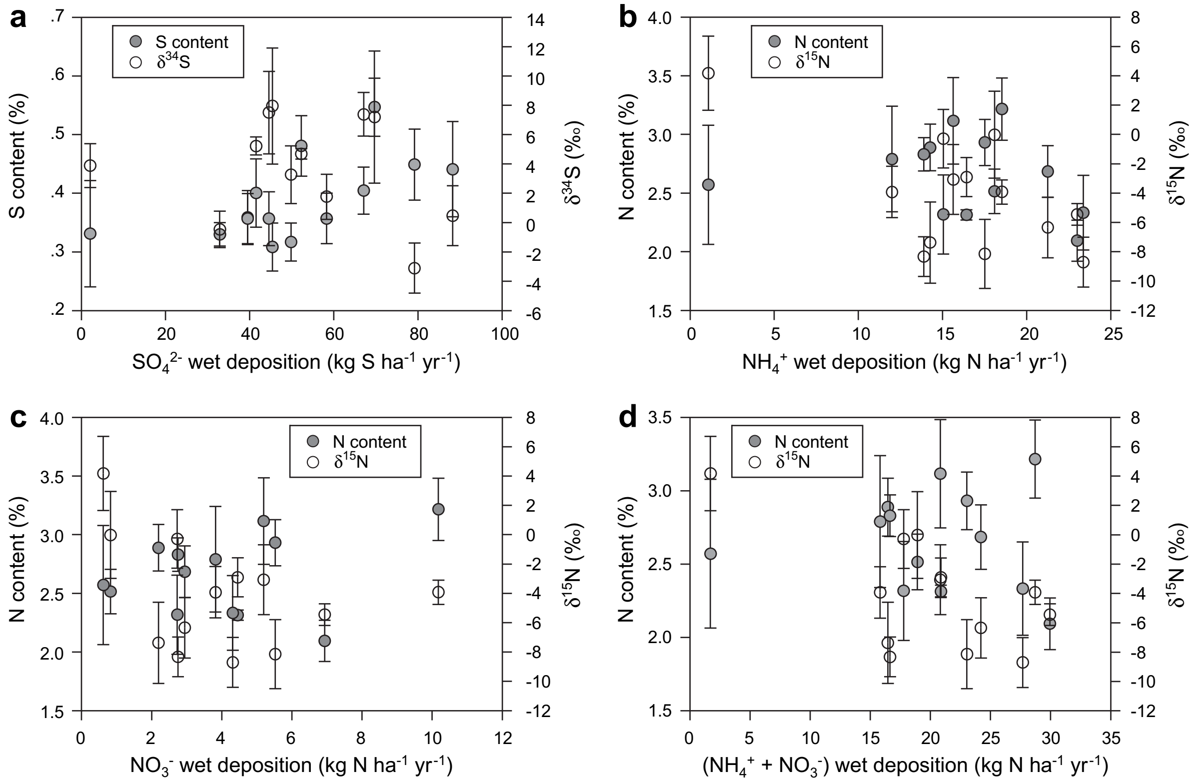

Fig. 3. %S vs. %N in mosses. The line $S = 0.15N$ is found in an unpolluted forest (Gongga Mountain, China; Xiao unpublished data).

$-0.8 \pm 2.0‰$) and Chengdu (CD: $0.0 \pm 3.0‰$) (Fig. 4). Epilithic mosses in Suzhou (SZ), Nanjing (NJ), Nanchang (NC) and Guiyang (GY) showed very negative mean δ^{15}N values ($<-7‰$). The δ^{15}N signatures agreed well with the estimated NH_4^+–N deposition in South China ($p < 0.05$) (Fig. 3b and Table 2).

As shown in Fig. 4, three classes of cities can be divided: high δ^{34}S values in the east cities (HF, WH, HZ, NJ and CS), high δ^{15}N values in the northwest cities (LS, CD and CQ), and low δ^{34}S and low δ^{15}N values in Southwest cities (GY, ZY and GL). It is interesting that it is almost divided by natural geographic location except for Nanchang (NC), which belongs to the east cities while has relatively low δ^{34}S and low δ^{15}N values.

3.3. δ^{34}S and δ^{15}N in coals

The δ^{34}S values in coals ranged widely from -8.1 to $+5.4‰$ in South China. The most ^{34}S-depleted coals occurred in Guizhou Province ($-8.1 \sim -4.7‰$) and then in Jiangxi Province ($-3.1‰$), while coals in the east province and in Sichuan Province have positive δ^{34}S values (Table 3). A significantly linear correlation between mosses and coals sampled in the same provinces was observed for δ^{34}S values ($y = 0.77x + 3.17$, $R^2 = 0.85$, $p < 0.001$) (Fig. 5a).

The δ^{15}N values of coals fell within a relatively narrow range of $-3.1 \sim +1.1‰$. Most of the coals were found δ^{15}N negative except in Jiangsu Province and Hubei Province ($+1.0‰$ and $+1.1‰$, respectively). For δ^{15}N values, we did not observe a significantly linear correlation between mosses and coals in the same provinces ($p > 0.05$; Fig. 5b).

Table 2
t-Value test on linear correlation between wet deposition and isotopic ratios or contents.

Samples	Wet deposition	*t*	*p*
Moss S contents	SO_4^{2-}	2.552	0.027*
Moss N contents	NH_4^+	−0.680	0.511
	NO_3^-	0.987	0.345
	$NH_4^+ + NO_3^-$	−0.186	0.856
Moss δ^{34}S	SO_4^{2-}	−0.558	0.588
Moss δ^{15}N	NH_4^+	−2.701	0.021*
	NO_3^-	−1.222	0.247
	$NH_4^+ + NO_3^-$	−2.579	0.026*

* indicate that there are significantly linear correlation between them at $\alpha = 0.05$.

4. Discussion

4.1. Tissue S/N ratios in Mosses

The S/N ratios for several sensitive plant species in unpolluted atmospheres have been used to calculate the excess S found in

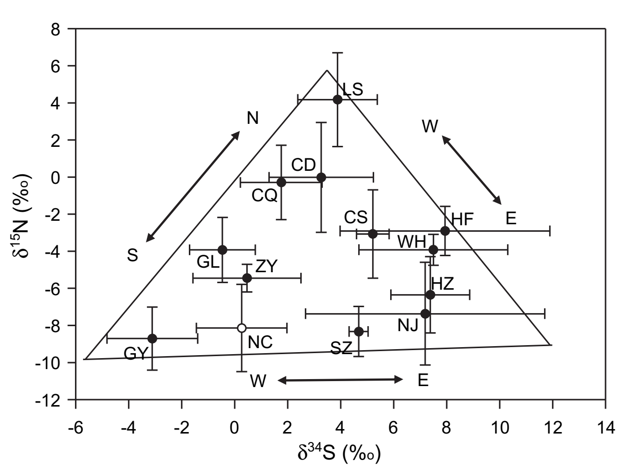

Fig. 4. δ^{15}N vs. δ^{34}S in mosses.

Table 3
The isotopic composition in coals.

location	$\delta^{34}S$ (‰)[a]	$\delta^{15}N$ (‰)
Jiangsu Province	+5.4 (Nanjing) +3.0 (Suzhou)	+1.0
Zhejiang Province	+2.5	n.d.
Anhui Province	+3.8	−1.1
Jiangxi Province	−3.1	−0.4
Hubei Province	n.d.	+1.1
Hunan Province	n.d.	−4.0
Guizhou Province	−8.1 (Shuicheng) −4.7 (Dafang)	−2.1
Chongqing	−0.3	−0.7
Sichuan Province	+3.2	−3.1

[a] The $\delta^{34}S$ values are cited from Hong and Zhang (1992) and Maruyama et al. (2000). n.d. means no data.

foliage subject to S emissions (Malcolm and Garforth, 1977). To use the S/N ratio as an indicator of pollution it is necessary to know those contents that might be expected in an unpolluted environment. Very few estimates of the normal or healthy S/N ratios in unpolluted areas have been published for epilithic moss *H. microphyllum*. 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 N to organic S, particularly in their vegetative tissues (Dijkshoorn and van Wijk, 1967). In this study, we used S/N = 0.15 obtained from remote forested mosses in Gongga Mountain (Xiao unpublished data) as the healthy value. Different to the constant ratios in unpolluted area, tissue S/N ratios in these industrial cities varied widely from 0.11 to 0.19.

As shown in Fig. 2, our study cities are separated into two classes by the line S/N = 0.15. Mosses in the first class of cities (class I: S/N > 0.15) are capable of absorbing a relatively greater amount of atmospheric S (S excess) whereas those in the second class (class II: S/N < 0.15) are believed to be S deficient or N excess. When S supply is greater than that required for protein synthesis (class I), 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 (class II), N will be accumulating, resulting in an S/N ratio smaller than the healthy. This is because that limiting S availability has been shown to favour the synthesis and accumulation of S-poor or low-S storage proteins such as ω-gliadin, and even accumulation of non-protein such as amides occurs. For example, in a study on wheat, Stewart and Porter (1969) found that where a lack of S was limiting growth, there was an accumulation of nitrate, amides and amino acids. When S was added to soil at high rates, there was an accumulation of sulphate.

The correlation between mean S/N ratios in mosses and in rainwater was seldom reported before and in this study a significantly linear correlation was found (Fig. 6). It suggested that rainwater SO_4^{2-}/NH_4^+ ratios played important roles in regulating the moss S/N ratios. But the ratios of SO_4^{2-}/NH_4^+ in rainwater were almost 14-fold of S/N ratios in mosses, indicating that about 1 part of S for every 14 parts of S in rainwater was obtained for protein synthesis in mosses (*H. microphyllum*).

In Fig. 6, class I cities and class II cities are separated by two lines: $S/N_{moss} = 0.15$ and $S/N_{rainwater} = 1.375$. The second line was obtained by the first line and the linear correlation between mosses and rainwater. The higher ratios of SO_4^{2-}/NH_4^+ in rainwater, the higher ratios of S/N mosses obtained from rainwater. In class I cities, higher ratios SO_4^{2-}/NH_4^+ in rainwater resulted in higher S/N ratios in mosses, the excess S was stored in tissues as sulphate, while in class II cities, lower ratios of SO_4^{2-}/NH_4^+ in rainwater resulted in lower S/N in mosses, the excess N was stored in tissues as nitrate.

4.2. Sources of atmospheric S in cities

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). They reported that S isotope ratios in the atmosphere were observed significantly higher in northern Chinese cities than in southern Chinese cities. This regional difference in mean atmospheric S isotope ratios was considered to correspond well to those of their source coals. 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

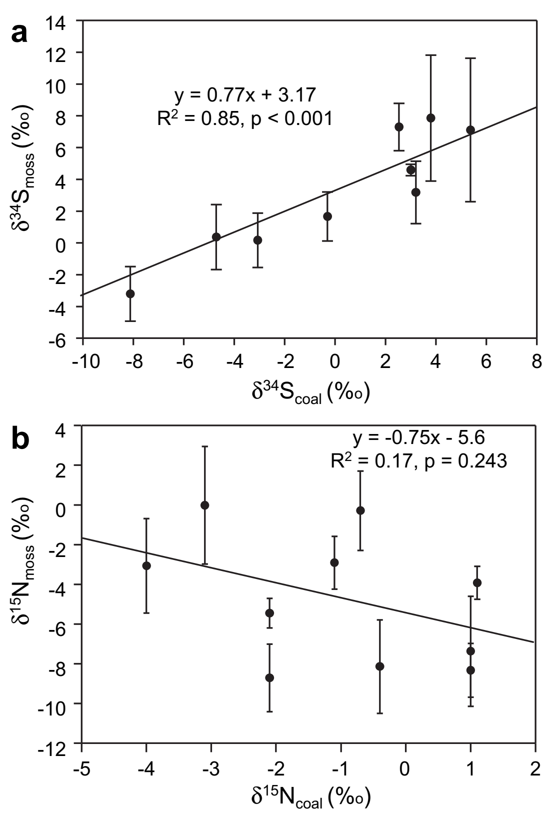

Fig. 5. Isotopic relationship between mosses and coals. (a) $\delta^{34}S$; (b) $\delta^{15}N$.

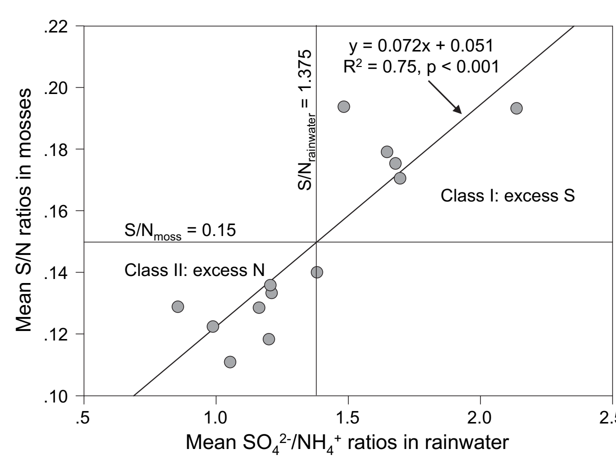

Fig. 6. Linear relationship between S/N ratios in mosses and SO_4^{2-}/NH_4^+ ratios in rainwater. The line S/N = 0.15 is found in an unpolluted forest (Gongga Mountain, China; Xiao unpublished data).

southern Chinese coals (averaging −0.32‰). In South China, regional difference in coal δ^{34}S values also exists (Table 3). Positive δ^{34}S values occurred to the coals in the east provinces and Sichuan Province whereas two obvious negative δ^{34}S values were found in coals of Guizhou Province and of Jiangxi Province. According to these limited rainwater δ^{34}S data recently reported in the literature (Mukai et al., 2001; Xiao and Liu, 2002; Zhang et al., 2002; Li et al., 2006a,b; Xiao et al., 2009), we found that regional pattern of S isotope ratios in rainwater corresponded well to that in coals. For example, among all the rainwater δ^{34}S data, the most ^{34}S-depleted rainwater occurred in Guiyang (−3.3 ± 2.8‰) and then in Nanchang (+0.5 ± 2.4‰), consistent with the characteristic of coal δ^{34}S.

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). Our recent study has further demonstrated that epilithic mosses assume sulphur isotopic signature close to that of the surrounding atmosphere because they acquire sulphur from the atmosphere and their rhizines and rhizoils serve mainly for attachment (Xiao et al., 2009). It is difficult to test the correlation of δ^{34}S values between rainwater and moss due to the very limited δ^{34}S values in rainwater.

Because present moss sulphur isotopic ratios were comparable to those of present rainwater (Xiao et al., 2009), correlation may be exists between coals and mosses. In a study on mosses in forests, we also found a δ^{34}S increase from southern Chinese mountains to northern Chinese mountains just like that for coal δ^{34}S (Xiao et al., 2008). In this study, indeed we found a good correspondence of average S isotope ratios in urban mosses to the values of source coals (Fig. 5a). The similar changing trend between coals and mosses in cities suggested a considerable contribution of local coal combustion to the atmospheric S. And this can be used to well explain the regional δ^{34}S difference shown in Fig. 4 except in Lhasa city, where atmospheric S may be more related to ^{34}S-enriched oil combustion (Maruyama et al., 2000; Zheng and Gao, 2006) than to coal combustion.

4.3. Sources of atmospheric N in cities

Studies by Pearson et al. (2000) in the London area and Gerdol et al. (2002) in northern Italy have found that moss δ^{15}N values can effectively decipher atmospheric N sources from urban NO_x (relatively positive signature) and from rural NH_3 (relatively negative signature). For example, some very negative δ^{15}N values of mosses appeared in the Netherlands, Denmark, Switzerland, and Italy, reflected a major role of local ammonia emitted from excretory wastes (Asman et al., 1998). Our recent studies in Guiyang area further showed that moss δ^{15}N value was a good indicator for different sources of NH_3 in atmospheric deposition (Liu et al., 2008).

Due to the high population density and intensive industries, anthropogenic N emissions from cities have inevitably become prominent sources for elevated regional N pollution, which influences the air quality of cities and poses threats to surrounding ecosystems (Jung et al., 1997; Krupa, 2003). As an important S source as discussed above, regional coal combustion is not an important N source of these urban atmospheres because there is no significantly linear correlation between δ^{15}N values of coals and mosses (Fig. 5b).

Except for oxidized forms (NO_x) from fossil fuel combustion during transport, industry, and energy production, the most abundant reactive N compounds in the atmosphere are represented by reduced forms (NH_x) from animal excrement, soil emissions and fertilizer application (Dentener and Crutzen, 1994). According to the δ^{15}N inventories of these potential N sources (Moore, 1977; Freyer, 1978; Heaton, 1987, 1990), N deposition in these southern Chinese cities mainly came from NH_x emissions from excretory wastes because of their relatively negative δ^{15}N values. As listed in Table 2, there is significantly linear correlation between δ^{15}N values and wet deposition of NH_4^+–N or NH_4^+–N + NO_3^-–N while not for NO_3^-–N ($p < 0.05$). This further indicated that NH_4^+–N was the major N source for mosses. 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. Our previous studies showed that negative δ^{15}N signatures of urban mosses in Guiyang city 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), suggesting that urban mosses in the city were more influenced by the reduced form of N (NH_x–N) than by the oxidized N species (NO_x–N) (Xiao and Liu, 2002, 2004). Because moss δ^{15}N values in the Guiyang area were mainly regulated by NH_x–N from urban sources (excretory wastes: −15 ∼ −5‰) and rural soil sources (−5.8 ∼ −3.3‰), it was believed that variation of moss δ^{15}N values from the urban to the rural area was controlled by the ratios of urban-derived NH_x to soil-derived NH_x in N deposition (Liu et al., 2008). Mean S/N ratios in mosses were found significantly linearly correlated with each people SO_2 emission (Fig. 7) but not with annual SO_2 emission, suggesting that NH_x in the atmosphere is strongly related to population in cities. The relatively positive δ^{15}N values in mosses of Chongqing (CQ), Chengdu (CD) and Lhasa (LS) shown in Fig. 4 may be due to higher contribution of NO_x–N.

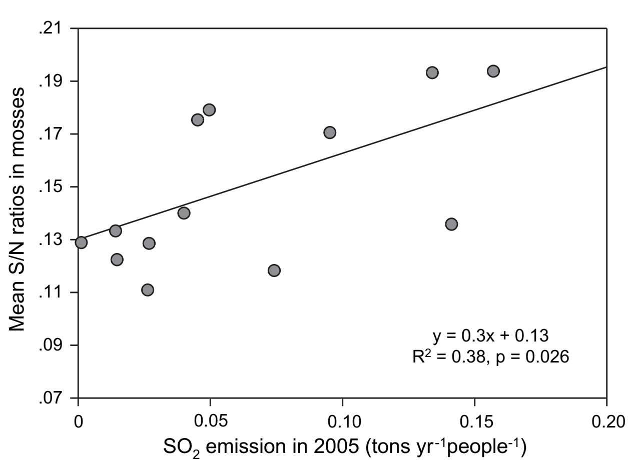

Fig. 7. Linear relationship between S/N ratios in mosses and each people SO_2 emissions.

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