

Tracing sources of coal combustion using stable sulfur isotope ratios in epilithic mosses and coals from China

Hua-Yun Xiao,* Cong-Guo Tang, Ren-Guo Zhu, Yan-Li Wang, Hong-Wei Xiao and Cong-Qiang Liu

Received 24th January 2011, Accepted 20th April 2011

DOI: 10.1039/c1em10073d

In China, coal combustion is the most important source of atmospheric sulfur pollution. Moss sulfur isotopic signatures have been believed to hold source-specific information that can serve as a fingerprint to identify atmospheric sulfur sources. In cities where only local coals were combusted, we observed a good correspondence of average sulfur isotope ratios in urban mosses (*Haplocladium microphyllum*) to the values of local coals ($\delta_{\text{coals}} = 1.455\delta_{\text{mosses}} - 3.945$, $R^2 = 0.975$, $p = 0.01$). But if different types of coals were combusted, we did not know whether moss sulfur isotope ratios can indicate mixed coals. To confirm this, using a mixing model we estimated the ratios of imported coal to local coals at cities where both coals were used. We found that the estimated ratios at large cities (>1 million people) where both coals were used were similar to the reported ratios in their respective provinces. For small cities (<0.5 million people) in Jiangxi Province and other provinces, the estimated ratios were higher than the reported ratios because the relatively cheaper local coals were less used in all the small cities except in cities where local coal deposits were found nearby. The comparison results showed that moss sulfur isotope is a useful tool for indicating coal-derived sulfur even in cities where mixed coals were combusted.

Introduction

China is rich in coal resources. Coal is the main energy source in China both at present and in the future. Most of the coals in China are mined to be used in power plants and in the cement industry. Sulfur in the atmosphere occurs in a variety of gaseous, liquid and solid chemical forms. Major inputs in heavily industrialized areas are anthropogenic SO₂ mainly due to the combustion of fossil fuels in the form of coal.^{1–3} In remote regions, natural sources such as biogenic emissions in the form of dimethyl sulfide (DMS) and H₂S, volcanic SO₂, and sea salt sulfate are the dominant origins of atmospheric sulfur compounds.^{4–6} SO₂ plays an important role in the generation of acid rain. Deposition of acid compounds from the atmosphere has increased in some Chinese areas during recent decades.⁷ High

sulfur deposition has resulted in sulfur accumulation in forest soils, which will further acidify surface waters.⁸

Since numerous potential sources are likely to 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. Moreover, atmospheric isotopic signatures can tell us about mixing processes, transport pathways and deposition of sulfur in the environment.^{9–11} Except for those in atmospheric samples, measurements of sulfur isotopic ratios in mosses have been exploited in the study of atmospheric sulfur pollution on a regional scale.¹² Xiao *et al.*¹³ reported that present moss sulfur isotopic ratios were comparable to those of present rainwater. They also used moss sulfur isotopic ratios to indicate the atmospheric sulfur sources in Southern Chinese mountainous areas.¹⁴ 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, natural gas): petroleum

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

Environmental impact

Owing to the scarcity and high-cost of physical monitoring, bio-indicator, an easy and less costly alternative, is increasingly used to study atmospheric sulfur sources. In this paper, a mixing model was established using moss sulfur isotopes to calculate the ratios of coals of different origin. The paper evidenced that moss sulfur isotope is a useful tool for assessing the use of coals from different areas.

natural gas, -20 to $+30\text{‰}$; coal, -35 to $+30\text{‰}$.¹⁵ 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.¹⁶

Industrialized cities in Southern China have been confronted with the consequences of acidic deposition since the 1980s. Some previous studies have shown that atmospheric sulfur in Chinese industrialized regions mainly came from sulfur bearing coals through industrial and domestic burning.¹⁷ Because Northern Chinese coals usually have been reported to have higher sulfur isotopic ratios than Southern Chinese coals,¹⁶ atmospheric sulfur with a low $\delta^{34}\text{S}$ value over most southern Chinese urban cities was believed to be emitted from local coal-burning power stations.^{3,10} In a recent study on urban mosses, regional differences in moss sulfur isotopic ratios were also observed between Southern China and Northern China.¹⁴ Since mountainous areas in Southern China are usually surrounded by industrialized cities, sulfur coming from local cities was believed to contribute much to these areas.¹⁸

The proportion of coal combustion in the total energy demands is high in China. Coal consumption changed little between 1990 and 2001, but has rapidly increased since 2001 (Fig. 1). With the increase of economic development in Chinese cities and transport capacity by train, coals from Northern China (mainly from Shanxi Province) are introduced into most of the Southern Chinese provinces except for Anhui Province, Guizhou Province and Chongqing City (Table 1). So, although atmospheric sulfur pollution in Chinese cities is still dominated by coal combustion, the contribution of local coals might be changed. These maybe consequently change isotopic values of atmospheric sulfur. So it is important to know whether sulfur isotopes in mosses sampled in cities where mixed coals were combusted can effectively indicate coal-derived sulfur. In order to confirm this, we estimated the proportions of local coals and imported coals that combusted in Southern Chinese cities with moss sulfur isotope and compared them with reported values.

Materials and methods

A sampling plan of coals was designed based on the distribution of coal yields in Southern Chinese provinces (Fig. 2). Coal samples were collected by a channel sampling method as

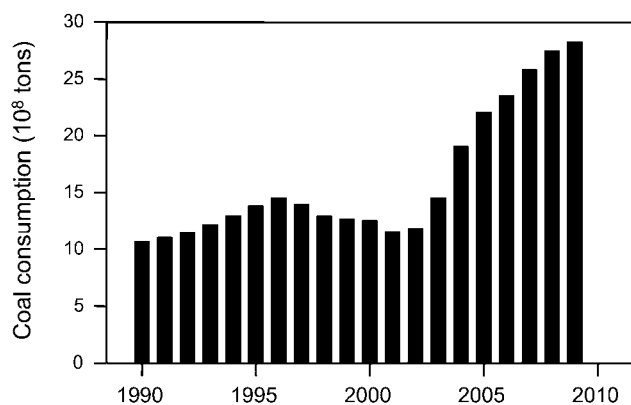


Fig. 1 Temporal changes of coal consumption from 1990 to 2009 in China.

described in the Chinese national standard GB481–93.²⁰ First, the weathered surface of a coal exposure was removed, and the face of coal fields was evened. Then, a channel sample (approximately 15 cm in diameter and 5 cm deep) was taken from the top to the bottom of the coal bed, excluding dirt partings thicker than 3 cm. More than 10 samples were collected in each coal deposit. Coal samples were dried at 70 °C and re-dried after being ground separately into fine powders using a mortar and pestle.

The moss materials *Haplocladium microphyllum* (Hedw.) in large cities of Southern Chinese provinces were collected in 2006 (Fig. 2). In order to compare the use of local and imported coals between large (>1 million people) and small (<0.5 million people) cities, we also sampled mosses in 6 small cities in Jiangxi Province, Southern China. We did not collect mosses in Shanxi Province because of arid climate there. Urban mosses were mainly collected around parks or hills. Because wild plants are often cleared away from city parks, urban mosses we sampled are one to two years old. All mosses were obtained from natural rocks (avoiding the influence of soil sulfur) without canopies or overhanging vegetation ensuring they were not 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. A 5–10 g moss sample was selected and prepared for analysis. In order for the sampling to be representative for these sampling sites, more than 10 samples were collected in each city (5 samples at YCH). 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.*,²¹ samples were gently rinsed with 1.5 mol L⁻¹ HCl solution, then sonicated and washed with deionized water for several times until no SO₄²⁻ was detected in the washed water. 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.

Sulfur contents in mosses and coals were measured by an elemental analyzer (Model PE-2400 II, USA) with an analytical precision of 1%. It operates by flash combustion of the specimen encapsulated in tin cups or disks whereby the specimen is completely combusted at a temperature of 960 °C. The resulting gases are chemically scrubbed of the halogens (and of sulfur in the CHN mode) and are separated in a GC column. Detection is conducted by a thermal conductivity detector (TCD). Calibration of the instrument with cystine standard (N141–0324, provided by Perkin Elmer) was carried out. Accuracy and recovery of sulfur were checked by analyzing a sample of this standard material after each set of eight moss or coal analyses.

Both moss and coal samples were oxidized in a Parr bomb to convert all forms of sulfur present to sulfate.²² To assure complete conversion, hydrogen peroxide was added to all washings. HCl solution was then added to acidify the washings (pH < 2). Sulfate was recovered from moss or coal washings by precipitating as BaSO₄ with enough 2 mol L⁻¹ BaCl₂ solution. After precipitation for 24 h, the mixture was filtered through a 0.22 μm acetate membrane filter. The precipitates (BaSO₄) on

Table 1 Coal consumption in some provinces of South China and in Shanxi Province^b

No.	Provinces	Cities studied ^a	Coal production in 2007 (10 ⁴ tons)	Coals imported (-) and outputted (+) in 2007 (10 ⁴ tons)	Coal consumption in 2007 (10 ⁴ tons)	Imported/local ratios in 2008
1	Jiangsu	NJ, SZH	2457	-5653	8111	2.30
2	Zhengjiang	HZH, JH	12	-3577	3589	298.06
3	Anhui	HF	9370	+514	8856	—
4	Jiangxi	NCH, GZH	2703	-342	3045	0.13
5	Hubei	WH, YCH	1107	-2421	3529	2.19
6	Hunan	CHS	5415	-384	5799	0.07
7	Guizhou	GY, ZY	10864	+2471	8393	—
8	Chongqing	CHQ	4203	+723	3480	—
9	Sichuan	CHD	9558	-832	10390	0.09
10	Shanxi	—	63000	+55000	—	—

^a Abbreviations of the sampling sites are presented in Fig. 2. ^b — means only local coal was used.

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 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. For each sample, sulfur isotope analyses were performed by burning a mixture of 10 mg BaSO₂ with 200 mg V₂O₅ and SiO₂ at 950 °C in a vacuum line.²³ The SO₂(g) produced was analyzed with a Finnigan MAT-252 mass spectrometer (a dual micro-volume inlet system, electromagnet, 24× multiport manifold interfaced with a Pentium PC). The δ³⁴S values are given in permil [‰] units, in reference to V-CDT international standard. SO₂ gas prepared from the NBS-127 standard (barium sulfate) was analyzed for normalization of rough delta values. The

standard deviation for the δ³⁴S analysis of NBS127 (barium sulfate) was better than ±0.2‰ (*n* = 5).

Results and discussion

Characteristics of coal δ³⁴S

Isotopic composition of sulfur in Southern Chinese coals varied widely from -8.1 to +7.6‰ (Table 2), with a mean of +2.0 ± 3.9‰. Among these coals, the most ³⁴S-depleted occurred in Guizhou Province (-8.1 to -4.7‰) and then in Jiangxi Province (-3.1‰), while coals in the east province showed more positive δ³⁴S values. The δ³⁴S values (+2.0 ± 3.9‰) in most coals of Southern China were significantly lower (*p* < 0.001) as compared

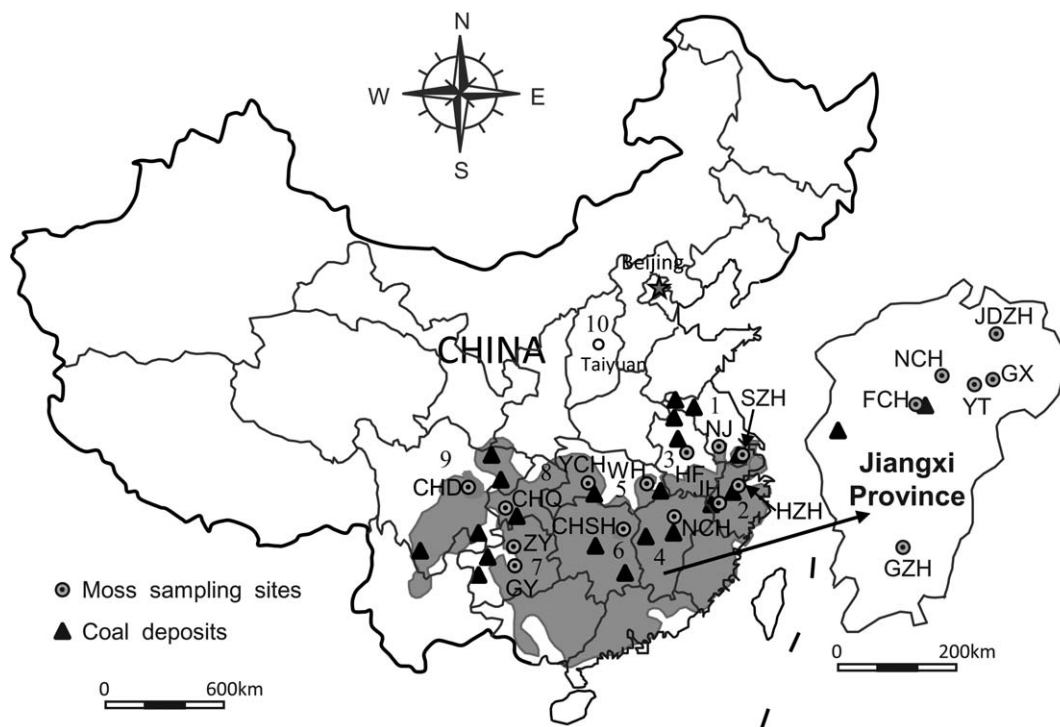


Fig. 2 Map of China showing the sampling sites of coals and mosses in Southern China. NJ-Nanjing; SZH-Suzhou; HZH-Hangzhou; JH-Jinhua; HF-Hefei; NCH-Nanchang; GZH-Ganzhou; WH-Wuhan; YCH-Yichang; CHSH-Changsha; GY-Guiyang; ZY-Zunyi; CHQ-Chongqing; CHD-Chengdu. The Arabic numbers in the provinces are the same as the No. in Table 1. The shaded regions represent areas where acid rain was measured (pH < 5) in 2004 (revised from ref. 19).

Table 2 The $\delta^{34}\text{S}$ values of coals and urban mosses in Southern China and Shanxi Province

No.	Provinces	$\delta^{34}\text{S}$ values of coals (‰)		Cities ^a	$\delta^{34}\text{S}$ values of mosses (‰)	
		Mean	Std		Mean	Std
1	Jiangsu	5.4	1.0	NJ ^b	5.6	0.7
		3.0	1.1	SZH	4.7	0.4
2	Zhejiang	2.5	2.2	HZH ^b	7.4	1.5
				JH	6.5	1.4
3	Anhui	7.6	2.9	HF ^b	8.0	3.1
4	Jiangxi			NCH ^b	0.3	1.7
				FCH	-3.3	0.4
				YT	2.3	2.5
				GX	2.5	0.6
				GZH	3.6	0.2
				JDZH	7.1	—
				WH ^b	6.5	1.6
5	Hubei	-4.3	1.9	YCH	5.4	0.6
				CHSH ^b	5.2	0.6
6	Hunan	3.1	0.4	GY ^b	-3.1	1.7
7	Guizhou	-8.1	3.0	ZY	0.5	2.0
		-4.7	2.6	CHQ ^b	1.8	1.5
8	Chongqing	-0.3	1.2	CHD ^b	3.3	2.0
9	Sichuan	0.5	2.4			
10	Shanxi	9.7	5.2			

^a Abbreviations of the sampling cities are presented in Fig. 2. ^b The large cities in the respective provinces.

with those in Shanxi Province (averaging +9.7‰), the largest coal production province in China (Table 1). These are consistent with the results reported by Hong and Zhang¹⁶ and Maruyama *et al.*²⁴ According to their previous reports, Northern Chinese coals (averaging +3.7‰) have higher sulfur isotope ratios than Southern Chinese coals (averaging -0.3‰). Our results are relatively higher than their reported values of Southern Chinese coals possibly because coals in ten Southern Chinese provinces were sampled in this study while Hong and Zhang¹⁶ only selected six provinces for coal $\delta^{34}\text{S}$ determination.

The difference in coal $\delta^{34}\text{S}$ values makes it possible to distinguish them from each other in a given city in order to assess their use. Although we did not find a quantitative isotopic correlation between coals and atmospheric sulfur in our studied cities, a similar changing trend between atmospheric sulfur isotopes and those of coals used in those areas was reported.^{3,13} For instance, Mukai *et al.*³ found that sulfur isotope ratios in the atmosphere were observed significantly higher in northern Chinese cities than in southern Chinese cities. So, regional isotopic differences of atmospheric sulfur in some Chinese industrial cities were believed to be strongly associated with those in fossil fuels (mainly coals) used in those areas.³ Our recent studies also found that regional patterns of sulfur isotope ratios in rainwater corresponded well to that in coals.¹³

Characteristics of moss $\delta^{34}\text{S}$

Mosses in Southern Chinese cities showed a wide range of $\delta^{34}\text{S}$ values (-3.3 to +7.9‰, averaging +3.6‰), with the highest occurring at Hefei (HF: +7.9‰) and the lowest at Fengcheng (FCH: -3.1‰) (Table 2). As compared to those in Southern Chinese forested and remote areas (averaging +4.4‰¹⁴), $\delta^{34}\text{S}$ values of urban mosses are relatively lower. In Jiangxi Province, the city (FCH) that is closest to local coal deposits showed the lowest moss $\delta^{34}\text{S}$ values

(-3.3 ± 0.4‰). Mosses sampled at the northern city (JDZH) in Jiangxi Province had the highest mean $\delta^{34}\text{S}$ value (+7.1‰).

Because mosses acquire S chiefly from the atmosphere and their rhizines and rhizoils serve mainly for attachment, moss isotopic method plays a critical role in the biomonitoring of atmospheric sulfur sources,¹² which represents an important supplement to instrumental monitoring methods. Our recent study found that epilithic mosses assume sulfur isotopic signature close to that of the surrounding atmosphere.¹³ This indicated that characteristics of atmospheric sulfur can be obtained by analyzing the moss $\delta^{34}\text{S}$ values. Thereby, we guessed that $\delta^{34}\text{S}$ values of atmospheric sulfur were lower at Guiyang city and higher at Hefei city. The former is confirmed by previous studies on atmospheric sulfur isotopes at Guiyang city.^{3,10}

Isotopic relationship between coals and mosses

In most of the Southern Chinese cities, coals were imported from Northern China, mainly from Shanxi Province, the largest coal production province. We did not find an isotopic correlation between mosses and local coals because both imported coals from Northern China and local coals were used at some of these studied cities (Table 1). Nevertheless, in those cities where only local coals were used, there is a significantly linear correlation between them ($\delta_{\text{coals}} = 1.455\delta_{\text{mosses}} - 3.945$, $R^2 = 0.975$, $p = 0.01$) (Fig. 3). This indicates that mosses $\delta^{34}\text{S}$ indeed can be used to trace sources of coals combustion. But if inputted coals are also used, they reflected the mixing coals. The isotopic relationship between coals and mosses is associated with coal combustion and plant assimilation.

Isotopic fractionation might be expected in the process of coal burning.²⁵⁻²⁷ The SO_2 gas produced was ^{34}S -depleted while the soluble sulfate in the ash was enriched in ^{34}S , in reference to the total sulfur of the original coal samples. In spite of that, Kawamura *et al.*²⁸ observed that the $\delta^{34}\text{S}$ values of the sulfur oxides collected at Fukuoka (Japan) were close to those of fossil fuels. Although we do not have enough data to get an isotopic correlation between coals and atmospheric sulfur in our studied cities, a similar changing trend between atmospheric sulfur isotopes and those of coals used in those areas was reported.^{3,13} The isotopic fractionation that occurred during coal combustion may cause the relation of atmospheric $\delta^{34}\text{S}$ to moss $\delta^{34}\text{S}$ to deviate from the 1 : 1 line.

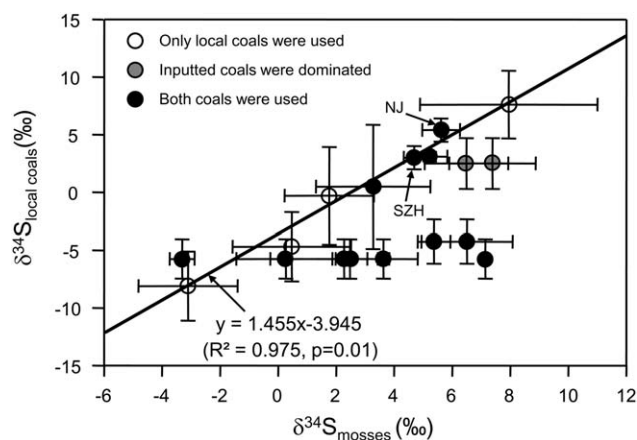


Fig. 3 $\delta^{34}\text{S}_{\text{coals}}$ vs. $\delta^{34}\text{S}_{\text{moss}}$ in some Southern Chinese cities.

There is some evidence that assimilation of atmospheric sulfur by some plants discriminates against ^{34}S resulting in lower $\delta^{34}\text{S}$ values (-1 to -2‰).²⁹ For instance, Novák *et al.*³⁰ found that Norway spruce (*Picea abies*) was lighter than atmospheric sulfur, on average by 2‰ , and *Sphagnum* exhibited 0.7‰ lighter than bulk (open area) precipitation. The moss' magnitude is smaller in comparison with spruce. In spite of this, it is generally believed that most biological assimilation of SO_4^{2-} results in little isotopic fractionation.³¹ This was confirmed by Wadleigh and Blake.³² Van Stempvoort *et al.*³³ also observed that the $\delta^{34}\text{S}$ values of white cedar foliage were similar to that of the local atmospheric sulfur, or slightly depleted in ^{34}S at the Paris site. Although Liu *et al.*²¹ reported that moss sulfur isotopic value under some canopies was different to the average atmospheric sulfur isotopic value, it has been demonstrated that little isotopic fractionation accompanies sulfur assimilation by mosses as they acquire sulfur chiefly from the atmosphere and they have no cuticles to block atmospheric inputs.^{34–36}

An earlier comparison by Winner *et al.*³⁷ showed that moss sulfur isotope ($+24\text{‰}$) around natural gas smelters closely reflected the influence of SO_2 from smelts ($+25\text{‰}$). A conclusion was also drawn by Nriagu and Glooschenko¹² that *Sphagnum fuscum* on low hummocks in ombrotrophic bogs acquired $\delta^{34}\text{S}$ values similar to those found for atmospheric SO_2 . It has further been shown by Krouse³⁸ and his co-workers³⁹ that mosses acquire $\delta^{34}\text{S}$ values similar to those found for atmospheric SO_2 . This is also right at Guiyang city where the average $\delta^{34}\text{S}$ value of epilithic mosses was found to be -3.1‰ in this study (Table 2), very similar to the average $\delta^{34}\text{S}$ value (-3.1‰) of aerosol sulfate and SO_2 reported by Mukai *et al.*³ Because the $\delta^{34}\text{S}$ values in summer rainwater of Guiyang city ($-4.9 \pm 2.8\text{‰}$)¹⁰ are comparable to the summer average S isotope ratios for SO_2 and sulfate ($-4.0 \pm 3.6\text{‰}$) in the atmosphere reported by Mukai *et al.*,³ our recent study found that moss $\delta^{34}\text{S}$ values were also comparable to those of rainwater at this city (13). Similar results were also observed at Emei Mountain (SW China) and at Nanchang city (NC) where moss isotopic ratios averaged $+4.6\text{‰}$ and $+0.1\text{‰}$, respectively, much closer to the reported mean values of rainwater sulfate ($+4.7\text{‰}$ and $+0.46\text{‰}$, respectively).^{13,18} These indicated that moss sulfur isotopic ratios preserved the average $\delta^{34}\text{S}$ signal of total sulfur deposition and thereby could reliably reflect sulfur in the atmosphere.

Based on the above discussion, it is likely that an isotopic correlation exists between coals and mosses. In this study on mosses in urban areas where only local coals were used (*e.g.* Hefei, Guiyang, Zunyi and Chongqing), indeed we found a significantly linear correlation between average sulfur isotope ratios in urban mosses and the values of local coals used (Fig. 3). The consistence between mosses and coals in these cities suggested a considerable contribution of local coal combustion to the atmospheric sulfur. However, combustion of local coals mixed with imported coals would bring about the differences in $\delta^{34}\text{S}$ values between mosses and coals.

Assessing the use of coals from different areas

Although moss $\delta^{34}\text{S}$ has been shown as a useful tool to trace the use of local coals as discussed above, we did not know whether sulfur isotopes in mosses sampled in cities where mixed coals

were combusted can effectively indicate coal-derived sulfur. The best way to confirm it is to estimate the proportions of different coals combusted and to compare the estimation results with reported values. A simple estimation using moss sulfur isotopes was carried out in some Southern Chinese cities to assess the use of coals from different areas (local or imported coals). Assuming that the relative proportion of local coals to total coals used is x and that of imported coals is y , the y/x ratios can be resolved in the following way:

$$y/x = (\delta_{\text{local coals}} - \delta_{\text{mixed coals}})/(\delta_{\text{mixed coals}} - \delta_{\text{imported coals}})$$

Substituting $\delta_{\text{mixed coals}}$ with $1.455\delta_{\text{mosses}} - 3.945$ (Fig. 3), then the equation can be rewritten as

$$y/x = (\delta_{\text{local coals}} - 1.455\delta_{\text{mosses}} + 3.945)/(1.455\delta_{\text{mosses}} - 3.945 - \delta_{\text{imported coals}})$$

In the equation, $\delta_{\text{imported coals}}$ is set at $+9.7\text{‰}$, which is the average $\delta^{34}\text{S}$ value in Shanxi Province. Using the equation, we can estimate the ratios of imported to local coals (y/x) at cities where both coals were used. The results are shown in Fig. 4 and 5.

The estimation of relative proportions of different coal types was evaluated by comparing them with the reported values. With regard to the estimation in large cities where both local and imported coals were used (NCH, WH, CHS and CHD), the estimated ratios of imported to local coals (y/x) were similar to the reported ratios in their respective provinces (Fig. 4). This indicated that the use of coals from local deposits or imported coals in the four large cities could represent the average ratios in the provinces because they all are the largest coal consumers in their respective provinces. The comparison results showed that moss sulfur isotope is a useful tool for indicating coal-derived sulfur even in cities where mixed coals were combusted.

With regard to the estimation in small cities in Jiangxi Province, the estimated ratios were higher relative to the reported ratios for all the small cities except Fengcheng (FCH) (Fig. 5) which is near local coal deposits (Fig. 2). Similarly, lower

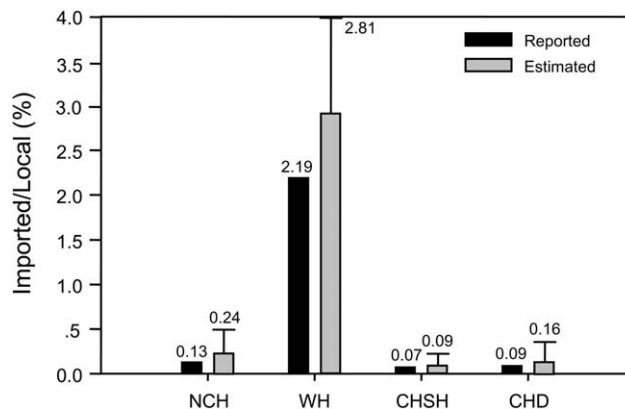


Fig. 4 Estimates of imported to local coal ratios at cities where both local and imported coals were used and the reported ratios in their respective provinces.

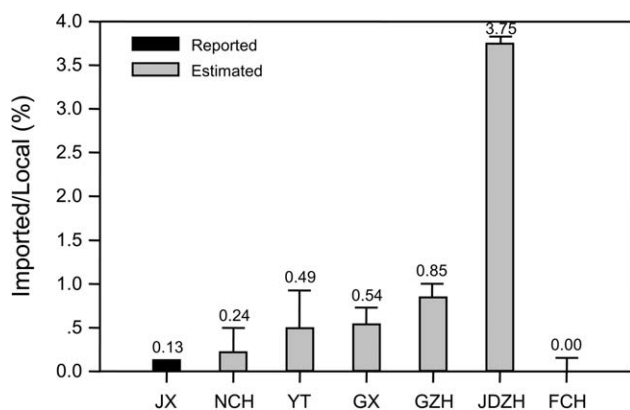


Fig. 5 Estimates of imported to local coal ratios at some cities in Jiangxi Province.

estimated ratio (1.43 ± 0.33) than the reported ratio of Hubei Province (2.19; Table 1) was also found for Yichang (YCH; in Hubei Province), which also lies close to local coal deposits (Fig. 2). Therefore, the potential explanations for the differences were that if local coal deposits were found near a city (e.g. FCH, YCH), it can provide more local coals for the city and thus the city's energy sources were more dependent on the local coals. The relatively high estimated ratio at Jingdezhen (JDZH) suggested that imported coals were dominated there.

We did not estimate the ratios in Jiangsu Province (NJ and SZH) and Zhejiang Province (HZH and JH). In Jiangsu province, the points of NJ and SZH lie much closer to the regression line ($\delta_{\text{coals}} = 1.455\delta_{\text{mosses}} - 3.945$) in Fig. 3, and thus the estimated ratios approached zero, different to the reported ratio of the province (2.3; Table 1). This suggested that the estimated ratios might be inaccurate for cities where local coals had the similar isotopic values to that of imported coals. Because local coal production was very low (12×10^4 tons) in Zhejiang Province, imported coals (3577×10^4 tons) were dominated (Table 1). So, we cannot use the estimation method to assess the use of imported coals in these cities.

Conclusions

Moss sulfur isotopic signatures have been believed to hold source-specific information that can serve as a fingerprint to identify atmospheric sulfur sources. In cities only local coals were combusted, indeed we observed a good correspondence of average sulfur isotope ratios in urban mosses to the values of source coals used ($\delta_{\text{coals}} = 1.455\delta_{\text{mosses}} - 3.945$, $R^2 = 0.975$, $p = 0.01$). But we did not find an isotopic correlation between mosses (*Haplocladium microphyllum*) and local coals because imported coals from other areas and local coals were both used at some of the studied cities.

To confirm whether moss $\delta^{34}\text{S}$ can be used to trace sulfur from mixed coals that combusted, a mixing model was used to estimate the ratios of imported coals to local coals in some Southern Chinese cities. We found that the estimated ratios at large cities (>1 million people) where both coals were used were similar to the reported ratios in their respective provinces, while at small cities (<0.5 million people) in Jiangxi Province and other provinces where the relatively cheaper coals (local coals, saving

transportation fee) were less used, the estimated ratios were higher than the reported ratios. The study indicated that moss sulfur isotope is a useful tool for indicating coal-derived sulfur even in cities where mixed coals were combusted. But if sulfur isotopic values between local and imported coals are similar, we cannot discriminate the atmospheric sulfur sources by sulfur isotope.

Acknowledgements

This study was kindly supported by the National Natural Science Foundation of China through grants 41073016 and 40573006 (H.Y. Xiao) and 40721002 (C.Q. Liu), and by West Light Foundation of The Chinese Academy of Sciences (H.Y. Xiao).

References

- W. W. Kellogg, R. D. Cadle, E. R. Allen, A. L. Lazrus and E. A. Martell, The Sulfur Cycle. Man's contributions are compared to natural sources of sulfur compounds in the atmosphere and oceans, *Science*, 1972, **175**, 587–596.
- Y.-F. Li, Y.-J. Zhang, G.-L. Cao, J.-H. Liu and L. A. Barrie, Distribution of seasonal SO_2 emissions from fuel combustion and industrial activities in Shanxi province, China, with $1/6^\circ \times 1/4^\circ$ longitude/latitude resolution, *Atmos. Environ.*, 1999, **33**, 257–265.
- H. Mukai, A. Tanaka, T. Fujii, Y. Zeng, Y. Hong, J. Tang, S. Guo, H. Xue, Z. Sun, J. Zhou, D. Xue, J. Zhao, G. Zhai, J. Gu and P. Zhai, Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites, *Environ. Sci. Technol.*, 2001, **35**, 1064–1071.
- J. O. Nriagu, D. A. Holdway and R. D. Coker, Biogenic sulfur and the acidity of rainfall in remote areas of Canada, *Science*, 1987, **237**, 1189–1192.
- Z. Yang, K. Kanda, H. Tsuruta and K. Minami, Measurement of biogenic sulfur gases emission from some Chinese and Japanese soils, *Atmos. Environ.*, 1996, **30**, 2399–2405.
- D. Shooter, Sources and sinks of oceanic hydrogen sulfide – an overview, *Atmos. Environ.*, 1999, **33**, 3467–3472.
- C. Lü and H. Tian, Spatial and temporal patterns of nitrogen deposition in China: Synthesis of observational data, *J. Geophys. Res.*, 2007, **112**, D22S05, DOI: 10.1029/2006JD007990.
- L. Duan, S. D. Xie, Z. P. Zhou and J. M. Hao, Critical loads of acid deposition on soil in China, *Water, Air, Soil Pollut.*, 2000, **118**, 35–51.
- T. Ohizumi, N. Fukuzaki and M. Kusakabh, Sulfur isotopic view on the sources of sulfur in atmospheric fallout along the coast of the sea of Japan, *Atmos. Environ.*, 1997, **31**, 1339–1348.
- H. Y. Xiao and L. Q. Liu, Sources of nitrogen and sulfur in wet deposition at Guiyang, Southwest China, *Atmos. Environ.*, 2002, **36**, 5121–5130.
- L. E. Pruett, K. J. Kreutz, M. Wadleigh and V. Aizen, Assessment of sulfate sources in high-elevation Asian precipitation using stable sulfur isotopes, *Environ. Sci. Technol.*, 2004, **38**, 4728–4733.
- J. O. Nriagu and W. A. Glooschenko, Isotopic composition of sulfur in mosses across Canada, *Environ. Sci. Technol.*, 1992, **26**, 85–89.
- H. Y. Xiao, C. G. Tang, H. W. Xiao, X. Y. Liu and C. Q. Liu, Identifying the Change of Atmospheric Sulfur Sources in China Using Isotopic Ratios in Mosses, *J. Geophys. Res.*, 2009, **114**, D16304, DOI: 10.1029/2009JD012034.
- H. Y. Xiao, C. G. Tang, X. Y. Liu, H. W. Xiao and C. Q. Liu, Sulfur isotopic ratios in mosses indicating atmospheric sulfur sources in southern Chinese mountainous areas, *Geophys. Res. Lett.*, 2008, **35**, L19807, DOI: 10.1029/2008GL034255.
- H. Nielsen, Sulfur isotopes in nature, In *Handbook of Geochemistry*, K. H. Wedepohl, ed., Springer-Verlag: Heidelberg. 1978, Vol. II/2, pp. 1–40.
- Y. T. Hong and H. B. Zhang, Sulfur isotope characteristic of coal in China and isotopic fractionation during coal burning, *Science in China (B)*, 1992, **00B**(8), 868–873(in Chinese).
- J. N. Galloway, D.-W. Zhao, J.-L. Xiong and G. E. Likens, Acid rain: China, United States, and a remote area, *Science*, 1987, **236**, 1559–1562.

- 18 F. Yanagisawa, S. Jia, H. Masuda, H. Yang, A. Ueda, A. Kawabata, N. Akata and R. Motoyama, Sulfur isotopic ratio of sulfate in the rain collected in November and December, *Journal of Chengdu University of Technology*, 2003, **30**(1), 96–98 (in Chinese).
- 19 Chinese Environmental Protection Bureau, *Bulletin of environmental conditions of 2004 in China*, 2005 (in Chinese).
- 20 State Bureau of Technical Supervision, *GB 481–93, Sampling method of coal sample for production*, Standardization Administration of the People's Republic of China, Beijing, 1993, <http://www.sac.gov.cn> (in Chinese).
- 21 X. Y. Liu, H. Y. Xiao, C. Q. Liu and Y. Y. Li, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of moss (*Haplocladium microphyllum* (Hedw.) Broth) for indicating environment variations and canopy retention on atmospheric nitrogen deposition, *Atmos. Environ.*, 2007, **41**, 4897–4907.
- 22 R. K. Siegfried, J. S. Wiberley and R. W. Moore, Determination of sulfur after combustion in a small oxygen bomb, *Anal. Chem.*, 1951, **23**, 1008–1011.
- 23 F. Yanagisawa and H. Sakai, Thermal decomposition of barium sulfate-vanadium pentoxide-silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements, *Anal. Chem.*, 1983, **55**, 985–987.
- 24 T. Maruyama, T. Ohizumi, Y. Taneoka, N. Minami, N. Fukuzaki, H. Mukai, K. Murano and M. Kusakabe, Sulfur isotope ratios of coals and oils used in China and Japan, *The Chemistry Society of Japan*, 2000, **1**, 45–51 (in Japanese).
- 25 N. Nakai and M. L. Jensen, Sources of atmospheric sulfur compounds, *Geochem. J.*, 1967, **1**, 199–210.
- 26 Y. T. Hong, H. B. Zhang and Y. X. Zhu, Sulfur isotopic characteristics of coal in China and sulfur isotopic fractionation during coal-burning process, *Chinese Journal of Geochemistry*, 1993, **12**(1), 51–59.
- 27 G. S. Liu, Geochemical characteristics of aerosols and their environmental significance in Guiyang area, Ph.D. Dissertation, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China (in Chinese), 1991.
- 28 H. Kawamura, N. Matsuoka, S. Tawaki and N. Mimoshima, Sulfur isotope variations in atmospheric sulfur oxides, particulate matter and deposits collected at Kyushu Island, Japan, *Water, Air, Soil Pollut.*, 2001, **130**, 1775–1780.
- 29 H. R. Krouse, L. N. Grinenko, V. A. Grinenko, J. Newman, J. Forrest, N. Nakai, Y. Tsuji, T. Yatsumimi, V. Takeuchi, B. W. Robinson, M. K. Stewart, A. Gunatilaka, L. A. Chambers, J. W. Smith, L. A. Plumb, F. Buzek, J. Cerny, J. Sramek, S. H. Menon, J. W. Iyer, V. S. Venkatasubramanian, B. E. C. Egboka, M. M. Irogbenachi and C. A. Eligwe, Case studies and potential applications, in *Stable Isotopes: Natural and Anthropogenic Sulfur in the Environment*, ed. H. R. Krouse and V. A. Grinenko, SCOPE 43, John Wiley and Sons, Chichester, 1991, pp. 307–422.
- 30 M. Novák, J. W. Kirchner, H. Groscheová, M. Havel, J. Černý, R. Krejčí and F. Buzek, Sulfur isotope dynamics in two Central European watersheds affected by high atmospheric deposition of SO₂, *Geochim. Cosmochim. Acta*, 2000, **64**, 367–383.
- 31 M. T. A. Kusakabe, J. D. Rafter, J. Stout and T. W. Collie, Isotopic ratios of sulfur extracted from some plants, soils and related materials, *New Zealand Journal of Science*, 1976, **19**, 433–440.
- 32 M. A. Wadleigh and D. M. Blake, Tracing sources of atmospheric sulfur using epiphytic lichens, *Environ. Pollut.*, 1999, **106**, 265–271.
- 33 D. R. Van Stempvoort, J. J. Wills and P. Fritz, Aboveground vegetation effects on the deposition and cycling of atmospheric sulfur: chemical and stable isotope evidence, *Water, Air, Soil Pollut.*, 1991, **60**, 55–82.
- 34 V. L. Mektiyeva, E. Y. Gavrilov and R. G. Pankina, Sulfur isotopic composition in land plants, *Geochem. Int.*, 1976, **13**, 85–88.
- 35 B. A. Trust and B. Fry, Stable sulfur isotopes in plants: a review, *Plant Cell Environ.*, 1992, **15**, 1105–1110.
- 36 L. Bragazza, J. Limpens, R. Gerdol, P. Grosvernier, M. Hájek, T. Hájek, P. Hajkova, I. Hansen, P. Iacumin, L. Kutnar, H. Rydin and T. Tahvanainen, Nitrogen concentration and $\delta^{15}\text{N}$ signature of ombrotrophic *Sphagnum* mosses at different N deposition levels in Europe, *Global Change Biol.*, 2005, **11**, 106–114.
- 37 W. E. Winner, C. L. Smith, G. W. Koch, H. A. Mooney, J. D. Bewley and H. R. Krouse, Rates of emission of H₂S from plants and patterns of stable sulphur isotope fractionation, *Nature*, 1981, **289**, 672–673.
- 38 H. R. Krouse, Sulfur isotope abundances elucidate uptake of atmospheric sulfur emissions by vegetation, *Nature*, 1977, **265**, 45–46.
- 39 H. R. Krouse and J. W. Case, Sulfur isotope ratios in water, air, soil and vegetation near Teepee Creek Gas Plant, Alberta, *Water, Air, Soil Pollut.*, 1981, **15**, 11–28.