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ORIGINAL ARTICLE

Sulfur isotopic signatures of water-soluble sulfate in needles of *Pinus Massoniana Lamb* in two Chinese areas

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Abstract This study analyzed the water-soluble sulfate (S_{SO4}) and total sulfur (S_T) concentrations and their isotopic signatures ($\delta^{34}S_{SO4}$ and $\delta^{34}S_T$) in needles of *Pinus massoniana Lamb* collected from Guiyang (seriously affected by acid rain) and Yunnan areas (acid rain did not occur), China SW. The results indicated that the S_{SO4} concentrations in needles of *Pinus massoniana Lamb* collected from several Chinese areas were found to be significantly correlated to ambient sulfur dioxide ($R^2 = 0.9176, p = 0.01$), showing that S_{SO4} concentrations in needles were more reliable to indicate atmospheric sulfur. The average $\delta^{34}S_{SO4}$ (−7.2 ‰) and $\delta^{34}S_{TS}$ (−5.1 ‰) in needles in Guiyang areas were significantly lower than those in Yunnan areas (+3.9 and +5.7 ‰, respectively), which were in accordance with the lower $\delta^{34}S$ of coals in Guiyang areas than in Yunnan areas. The $\delta^{34}S_{SO4}$ and $\delta^{34}S_{TS}$ in needles became less positive with a distance from a plant combusted ^{34}S-enriched coals while for another plant combusted ^{34}S-depleted coals, more positive was observed. These results indicated that $\delta^{34}S_{SO4}$ in needles was also a good indicator of atmospheric sulfur sources. A very small difference between δ^{34} S_T and δ^{34} S_{SO4} for most needle samples suggested that little isotopic fractionation accompanies sulfur assimilation processes.

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Keywords *Pinus massoniana Lamb* · Needles · Water-soluble sulfate · Total sulfur · $\delta^{34}S$ · Source discrimination

Introduction

With the development of the industrial economy, a large amount of anthropogenic sulfur has been input into the atmospheric system and has caused high atmospheric sulfur deposition. This has become one of the major global environmental problems (Yang et al. 1999).

The use of plant tissues has long been shown to be an effective indicator of atmospheric pollution. In the 1970s, scientists found that sulfur concentration in plant tissue could be an indicator of pollution levels (Martinez et al. 1971; Yeaple 1972). Various kinds of plants have been studied to find if they are effective alternatives to the more usual monitoring methods, including mosses (Berg et al. 1995; Xiao et al. 2009), lichens (Sloof 1995), tree bark (Turkan et al. 1995; Fatoki and Ayodele 1991) and tree needles (Al-Shayeb et al. 1995; Lau and Luk 2001). However, most of these works have been done to analyze isotopic signatures of total sulfur ($\delta^{34}S_T$) in plant needles. For example, Zhao et al. (1998) determined soil and grass samples collected since 1856 and found that sulfur concentrations and isotopic ratios of monitoring samples showed SO_2 pollution on terrestrial ecosystem. Sulfate-S was believed to be superior to TS as an indicator of S status in plants because of large differences in SO_4-S levels between S-deficient and S-nondeficient plant tissues (Freney and Spencer 1967). However, few works have been done on the isotopic signatures of water-soluble sulfate ($\delta^{34}S_{SO4}$). Up to now, the possibility of using $\delta^{34}S_{SO4}$ as an indicator of atmospheric sulfur sources was still unknown.

In this study, the inorganic sulfur (S_{SO4}) and total sulfur (S_T) concentrations and their isotopic signatures ($\delta^{34}S_{SO4}$

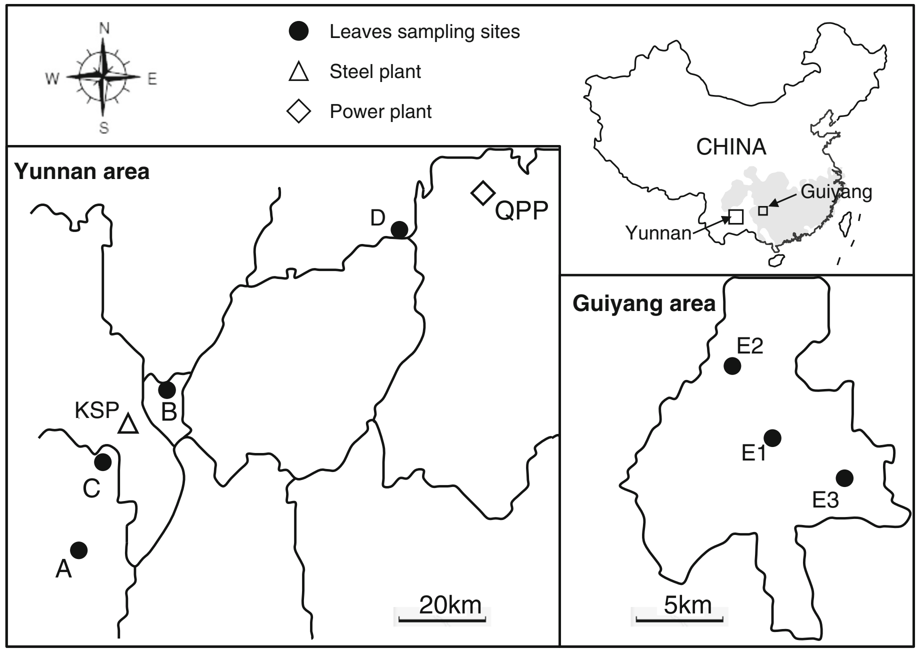

Fig. 1 Skeleton map showing location of different sampling regions and two point polluted areas. The shaded regions represent areas where acid rain was measured (pH < 5) (revised from Guiyang Environmental Protection Bureau 2006). *A* Jinning, *B* Kunming, *C* Anning, *D* Qujing, *E1–E3* Guiyang, *KSP* Kunming Steel Plant and *QPP* Qujing Power Plant

and $\delta^{34}S_T$) in needles of Pinus massoniana lamb collected from Guiyang and Yunnan areas, SW China were investigated. The Chinese red pine (Pinus massoniana lamb) was selected because it met many of the requirements of a good bioindicator plant. This species was widely distributed in China, easily identified, and had already been used in bioindication studies by some researchers (Hüve et al. 1995; Legge et al. 1988). The aims of this work were firstly, to know if sulfur isotopic signatures of water-soluble sulfate in needles of Pinus Massoniana Lamb can be a new indicator of atmospheric sulfur and secondly, to find if sulfur isotopes of S_{SO4} in needles can be used to discriminate sulfur sources in the atmosphere.

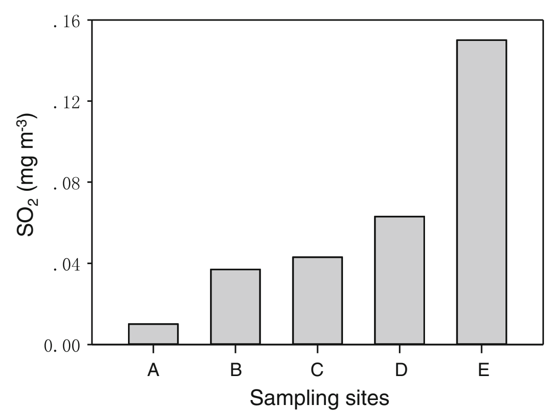

Fig. 2 Concentrations spatial change of ambient SO_2 from Yunnan (A–D) to Guiyang areas (E) of 2011. The data was cited from Guiyang Environmental Protection Bureau (2012) and Yunan Environmental Protection Bureau (2012). *A* Jinning, *B* Kunming, *C* Anning, *D* Qujing, *E* Guiyang

Materials and methods

Study area description

This study was carried out in Guiyang and Yunnan areas, SW China. The former was seriously polluted by SO_2 and acid rain, while acid rain was not found in the latter area (Fig. 1). The SO_2 concentrations in the atmosphere were obviously higher in Guiyang area than in Yunnan area in 2011 (Fig. 2). The main air pollution source in Guiyang area is coal combustion, which accounts for over 90 % of energy consumption of the whole city. It was once one of the most serious acid deposition cities in SW China (Galloway et al. 1987). Air quality in Guiyang improved from 1996 to 2005 (Guiyang Environmental Protection Bureau 2006; Xiao and Liu 2002, 2004) because coal had been replaced by natural gas. Similarly, major air pollutants in Yunnan areas were also from coal combustion, but the qualities of coals in these two places were different. Coals combusted in Yunnan areas were ^{34}S-enriched (averaging +13.8 ‰) while those used in Guiyang areas were ^{34}S-depleted (averaging −7.5 ‰; Xiao unpublished data). In addition, coals combusted contained higher content of sulfur (0.86 %; Ni, 1997) in Guiyang than that of Yunnan (0.5 %; Xiao unpublished data).

Four sites in the Yunnan area including Jinning, Anning, Kunming and Qujing and three sites in the Guiyang city were chosen for needles and soil collection (Fig. 1). Two point polluted areas (the Kunming Steel and the Qujing Power Plant) were also chosen for needle and soil sampling. The two point polluted areas were >20 km away from the other sampling area. ^{34}S-enriched coals were combusted in the Kunming Steel (averaging +13.8 ‰; Xiao unpublished data) and those in the Qujing Power Plant were ^{34}S-depleted (averaging −7.5 ‰; Xiao unpublished data).

Sample collection and treatment

From March to April 2012, 56 *Pinus massoniana Lamb* needle samples and 23 rhizosphere soil samples were collected. All trees sampled were about 5–10 years old and only those 1.5 and 2 m high were selected. Only green, healthy samples were taken, avoiding yellow or dark samples. Fresh needles were stored in cleaned plastic bags before being transported to the laboratory.

For total sulfur (not adsorbed), all needles samples were gently rinsed in 1.5 mol L^{-1} HCl solution, then sonicated and washed with deionized water (Milli-Q). The main purpose of this washing procedure was to remove pollutants adsorbed on needles tissues thoroughly. Samples were finally dried in a vacuum oven at 70̊ and re-dried after being ground separately in liquid N into fine powders. Soil samples were taken at depths of 50–100 cm and dried for 24 h at 105̊, then passed through 100-mesh sieve.

Sample analytical methods

All needles and soils were air dried and ground to pass through a 100-mesh screen in order to ensure adequate homogeneity. Total sulfur contents of needles and soils (%, dry weight) were determined with an elemental analyzer (PE2400II, USA) with an analytical precision of ±0.1 %.

For determinations of water-soluble sulfate concentrations and $\delta^{34}S_{SO4}$, five grams air-dried sample powder was weighed into an agate mortar and grinded with quartz sands. Then, it was transferred into a 125-ml extraction vessel and extracted in 30 ml boiling Milli-Q water by placing on a reciprocating shaker for 12 h. The extract was filtered two times through a Whatman No. 42 filter paper; the material on the filter was carefully rinsed with enough boiling Milli-Q water to remove all the water-soluble sulfate into the filtrate. The water extract method was a modification of the boiling acid extraction method developed by Richter and Johnson (1983) and Kelly and Lambert (1972). Boiling acid was not used because appreciable amounts of hydrolysable organic sulfates are present in the extract from the boiling HCl method. Ten milliliter aliquot of filtrate was stored for water-soluble sulfate content determination and analyzed with ion chromatography (DIONEX ICS-1100, America). The limit of detection was 0.01 mg l^{-1} for SO_4^{2-}. The other aliquot of filtrate was transferred into a 500-ml beaker, added 10 ml of 1 mol l^{-1} hot HCl and heated to boiling. Then 10 ml of 2 mol l^{-1} $BaCl_2$ was added and kept boiling for 2 h. After precipitating for 24 h, the mixture was filtered through a dense ashless quantitative filter paper. The precipitate ($BaSO_4$) on the filters was carefully rinsed with enough Milli-Q water to remove Cl (silver nitrate was used to check), then transferred into crucibles with the filters and combusted at 850̊ for 1 h in air. The results of X-ray diffractometry showed >99 % $BaSO_4$ in the white powder in the crucible. The $BaSO_4$ was weighed into tin capsule and $\delta^{34}S$ determination was conducted with an elemental analyzer combustion continuous flow isotope ratio mass spectroscopy (EA-C-CF-IRMS, EAIsoPrime, Euro 3000, GV instruments, United Kingdom). The standard deviation for the $\delta^{34}S$ analysis of NBS127 (barium sulfate, $\delta^{34}S = +20.3$ ‰) was better than ±0.2 ‰ ($n = 5$).

For $\delta^{34}S_T$ analysis of needles, all forms of sulfur in leaves tissues were converted to sulfate based on the Eschka method (Mott et al. 1955). Sulfate was recovered from washings by precipitating as $BaSO_4$ with enough 2 mol L^{-1} $BaCl_2$ solutions. The subsequent procedure was the same as water-soluble $\delta^{34}S_{SO4}$ (see above).

Results

Total sulfur and water-soluble sulfate in needles at two areas

Water-soluble sulfate concentrations in *Pinus massoniana Lamb* needles under different areas ranged from 0.001 to 0.24 % and total sulfur ranged from 0.10 to 0.28 %. The average concentrations of sulfate and total sulfur in Yunnan areas were 0.04 and 0.16 %, respectively, significantly lower than that in Guiyang areas (averaging 0.11 and 0.20 %, respectively) (Fig. 3). Water-soluble sulfate concentrations account for more than 50 % of the total sulfur in Guiyang sites, significantly higher than the ratios in Yunnan sites. However, the soil sulfur concentrations from different sites changed little.

The concentration of water-soluble sulfate in the needles was found to be significantly correlated with ambient sulfur dioxide ($R^2 = 0.9176$, $P < 0.05$), but no correlation was seen between total sulfur concentration and ambient sulfur dioxide (Fig. 4).

The $\delta^{34}S_{SO4}$ and $\delta^{34}S_T$ value of *Pinus massoniana Lamb* needles in different areas varied widely from −14.5 to +7.3 ‰ and −10.6 to +10.8 ‰, respectively. The mean $\delta^{34}S_{SO4}$ and $\delta^{34}S_T$ values in Guiyang areas were about −7.2 and −5.1 ‰, respectively, significantly more negative than those in the Yunnan areas (+3.9 and +5.7 ‰) (Fig. 5).

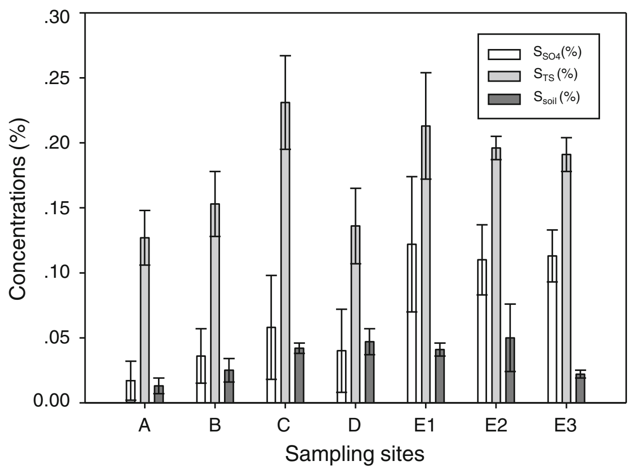

Fig. 3 Between-site comparisons of sulfur concentration of water-soluble sulfate (S_{SO4}-S), total sulfur (S_{TS}) and soil total sulfur (S_{soil}) in Yunnan (A–D) and Guiyang (E1–E3) areas. The error bars represent 1 sigma. *A* Jinning, *B* Kunming, *C* Anning, *D* Qujing, *E1–E3* Guiyang

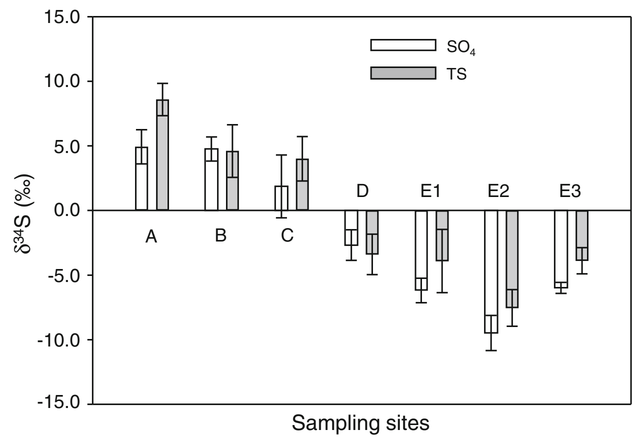

Fig. 5 Comparisons of the $\delta^{34}S$ values of water-soluble sulfate ($\delta^{34}S_{SO4}$) and the $\delta^{34}S$ values of total sulfur ($\delta^{34}S_{TS}$) in needles in Yunnan (A–D) and Guiyang (E1–E3) areas. The error bars represent 1 sigma. *A* Jinning, *B* Kunming, *C* Anning, *D* Qujing, *E1–E3* Guiyang

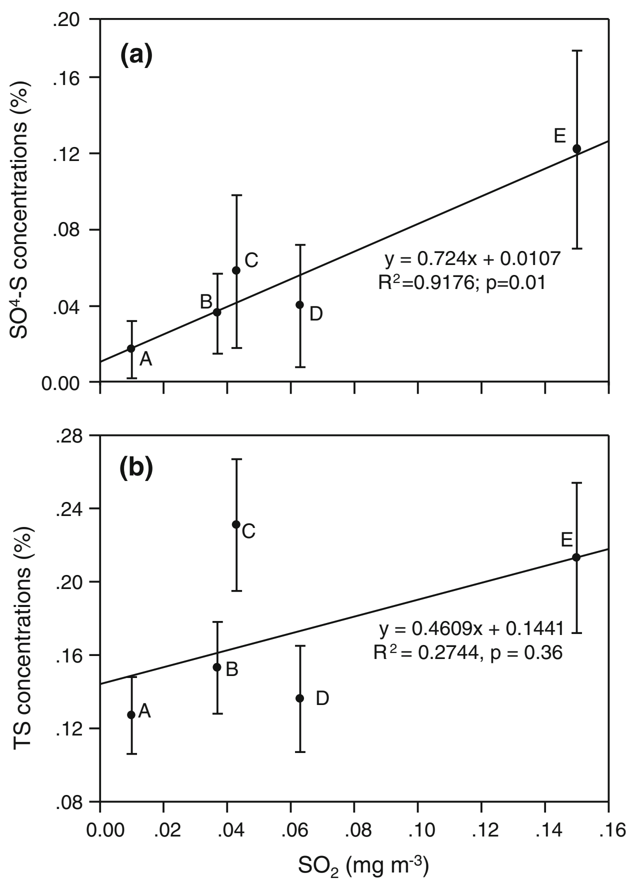

Fig. 4 **a** Relationship between SO_2 concentration and water-soluble sulfate S (S_{SO4}-S) concentrations in needles in Yunnan and Guiyang areas. **b** Relationship between SO_2 concentration and total sulfur (S_{TS}) concentrations in needles in Yunnan and Guiyang areas. *A* Jinning, *B* Kunming, *C* Anning, *D* Qujing, *E* Guiyang

Table 1 Contents of SO_4-S and total sulfur in needles and soil total sulfur around Kunming Steel Plant and Qujing Power Plant

Distance from the plants (m)	SO_4-S in needles (%, DW)	Total sulfur of needles (%, DW)	Soil total sulfur (%, DW)
Kunming Steel Plant			
10	0.160	0.330	0.023
100	0.020	0.150	0.020
8,000	0.002	0.100	0.017
Qujing Power Plant			
10	0.042	0.123	0.023
500	0.019	0.115	0.025
2,000	0.016	0.108	0.018
10,000	0.006	0.113	0.034

Total sulfur and water-soluble sulfate in needles around two plants

The sulfate and total sulfur concentrations in leaves around Kunming Steel Plant and Qujing Power Plant decreased with the distance from the factories. For instance, the sulfate and total sulfur concentrations were 0.16 and 0.33 %, respectively, at 10 m from Kunming Steel Plant, significantly higher than that at 8,000 m from Kunming Steel Plant (0.002 and 0.10 %, respectively) (Table 1). The sulfate to total sulfur ratios decreased with the distance from the factories. For instance, the sulfate accounted for 50 % of the total sulfur at 10 m from the Kunming Steel Plant while only 2 % at 8,000 m from the plant. The soil total sulfur concentrations did not change with the distance to the factories.

Table 2 The $\delta^{34}S$ values of water-soluble sulfate and total sulfur in needles around Kunming Steel Plant and Qujing Power Plant

Distance from the plants (m)	Water-soluble sulfate (‰, CDT)	Total sulfur (‰, CDT)
Kunming Steel Plant		
10	+4.9	+8.1
100	+3.4	+5.9
8,000	+3.8	+4.6
Qujing Power Plant		
10	−3.5	−1.5
500	−2.9	−1.1
2,000	−1.9	−1.3
10,000	−1.8	−0.3

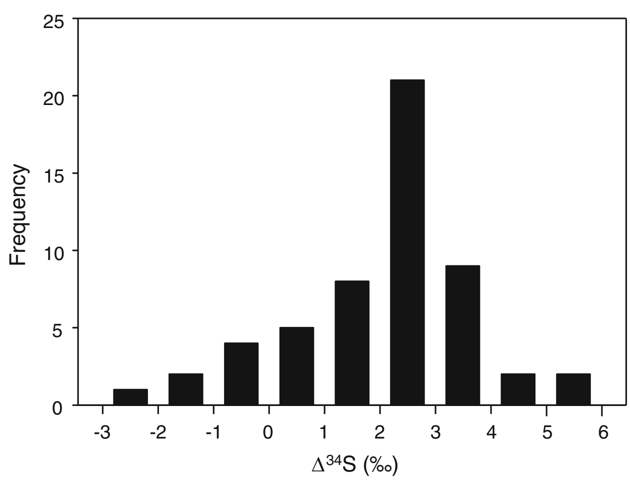

Fig. 6 Differences between $\delta^{34}S$ values of water-soluble sulfate and total sulfur in needles. $\Delta^{34}S = \delta^{34}S_T - \delta^{34}S_{SO4}$. X-coordinate represented the values of $\Delta^{34}S$, Y-coordinate represented the number of occurrences. The frequency of $\Delta^{34}S$ was in normal distribution

At Kunming Steel Plant sites, the $\delta^{34}S_{SO4}$ and $\delta^{34}S_T$ value of needles decreased with the distance from the factory (Table 2). For instance, the $\delta^{34}S_{SO4}$ and $\delta^{34}S_T$ value of needles were +5.0 and +8.1 ‰, respectively, at 10 m from the factory, higher than that at 8000 m (+3.8 and +4.6 ‰, respectively). However, contrary to that at Kunming Steel Plant sites, the $\delta^{34}S_{SO4}$ and $\delta^{34}S_T$ values of needles at Qujing Power Plant sites increased with distance from the factory and significantly more negative than those at Kunming Steel Plant.

Isotopic comparisons between total sulfur and water-soluble sulfate in needles

Compared with $\delta^{34}S_{SO4}$ values of the needle samples, the $\delta^{34}S_T$ values were slightly higher (Fig. 5; Table 2). As shown in Fig. 6, the frequency of $\Delta^{34}S$ (δ^{34} S_T- δ^{34} S_{SO4}) was in normal distribution. The $\Delta^{34}S$ values of most samples were focused within the range of +2 to +3 ‰.

Discussion

Tissue sulfate and total sulfur concentrations of needles indicating atmospheric SO_2

Generally, sulfate taken up by the root is the main source of sulfur for plant. However, atmospheric sulfur from SO_2 and particulate matter can also be used as the sulfur source if the sulfate supply to the roots from the soil is limited, in the case of high SO_2 concentration due to air pollution. Plant tissues can be used as an effective indicator because of large leaf areas and the physical properties of their surfaces, trapping and absorbing air pollutants (Bao et al., 2009). More and more researches have shown that some plant leaves have the capability of absorbing and accumulating sulfur dioxide. The amount of sulfur contained in plants may be closely related to the concentration of SO_2 in the air (Alfani et al. 2000; Cicek et al. 2004). This study found significantly high total sulfur and sulfate concentrations in Pinus massoniana Lamb needles in higher SO_2 areas (Guiyang) than in lower SO_2 areas (Yunnan) (Fig. 3). A similar study reported by Bao et al. (2009) also demonstrated that the long-term coal-burning pollution resulted in an enhanced concentration of the total sulfur and sulfate in the leaves. They found that the uptake of sulfur by leaves had exceeded the metabolic requirement of plants and the excess of sulfur was stored as SO_4^{2-}.

The concentration of water-soluble sulfate in the needles was found to be significantly correlated with ambient sulfur dioxide ($R^2 = 0.9176$, $P < 0.05$), but no correlation was seen between total sulfur concentration and ambient sulfur dioxide (Fig. 4), indicating that sulfate concentration in needles was more reliable to reflect ambient sulfur input relative than the total sulfur concentration. Some previous studies (Legge et al. 1988; Yang et al. 2006) have suggested that chronic SO_2 exposure tended to increase the levels of inorganic and total sulfur in plants, whereas the organic sulfur pool frequently remained less affected, since the foliar organic sulfur fraction reflected the process of assimilation of S by plant tissue while the sulfate fraction reflected the process of accumulation of S by the plant tissue.

Isotopic signatures of water-soluble sulfate and total sulfur in needles indicating atmospheric sulfur sources

The sulfur isotopic signatures in non-vascular plants have been proved to be a good tool to identify their long-term sulfur sources because: (1) most sulfur sources had distinct $\delta^{34}S$ signals; (2) there was very little isotopic discrimination during sulfate assimilation and reduction by plants (Ishii 1953; Xiao et al. 2009). Therefore, epiphytic lichens and many mosses have been found to have $\delta^{34}S$ values close to their major source of sulfur, which usually is atmospheric SO_2 (Krouse 1977; Case and Krouse 1980; Winner et al. 1978). However, for vascular plants, whether sulfur isotopic signatures can be used for source discrimination or not is still unclear.

Subsequent surveys of marine, freshwater and terrestrial plants (most vascular plants) have found that plants have $\delta^{34}S$ values that average about 1.5 ‰ less than that of environmental sulfate (Trust and Fry 1992). The total sulfur contained inorganic sulfur and organic sulfur. Inorganic sulfur was present in SO_4^{2-} form stored in vacuoles, the contents of which depended on the level of sulfur supply. Sulfate could enter the sulfur assimilatory pathway and was utilized for organic sulfur compound synthesis as sulfur nutrient. There was very little isotopic discrimination during sulfate assimilation and reduction by plants (Ishii 1953). In this study, the $\delta^{34}S_T$ values were slightly higher than $\delta^{34}S_{SO4}$ values of the needle samples, due to the little isotopic discrimination during sulfate assimilation process in *Pinus massoniana Lamb* needles. The difference between sulfate and total sulfur $\delta^{34}S$ values in Pinus *massoniana Lamb* needles was also small. As shown in Fig. 6, $\Delta^{34}S$ (δ^{34} S_T- δ^{34} S_{SO4}) for most needle samples was within range of +2 to +3 ‰, demonstrating that little isotopic fractionation accompanies occurred during sulfur assimilation process in *Pinus massoniana Lamb* needles.

Coals from different areas had various geological backgrounds; therefore, their $\delta^{34}S$ values were very different (Xiao and Liu 2011). The $\delta^{34}S_{SO4}$ in leaves at Guiyang sites (averaging −7.2 ‰) was significantly more negative than that at Yunnan sites (averaging +3.9 ‰) in this study (Fig. 5), indicating that their sulfur sources were different between these two areas. The $\delta^{34}S_{SO4}$ values in leaves at Guiyang sites (−7.2 ‰) were similar to the $\delta^{34}S_{SO4}$ of rainwater (−4.9 ± 2.8 ‰) which was collected in the same study area in 2001 (Xiao and Liu 2002), even much closer to the coal $\delta^{34}S$ value (−7.5 ‰) reported by Hong and Zhang (1992) for Guiyang city, suggesting that $\delta^{34}S_{SO4}$ in leaves at Guiyang sites is mainly affected by coal-derived atmospheric sulfur deposition. Although we did not find similar $\delta^{34}S_{SO4}$ values in leaves (+3.9 ‰) to coal $\delta^{34}S$ values (+13.8 ± 0.6 ‰; Xiao and Liu 2011) at Yunnan areas, they are both more positive than those in Guiyang area. This may be related to the influence of ^{34}S-depleted soil sulfur. According to the study by Mayer (2005), the typical range for $\delta^{34}S$ value of sulfate from soil solutions was −10 to +10 ‰ and more negative than that of atmospheric deposition. Just because of mixing of ^{34}S-depleted soil sulfur sources ($\delta^{34}S$ +7 to +12 ‰), the $\delta^{34}S$ values in leaves of *Picea glauea* and *Abiesbalsamea* (averaging +18 ‰) were more negative than those in mosses (averaging +24 ‰) near a gas smelter (Winner et al. 1978).

The $\delta^{34}S_{SO4}$ values of needles decreased with the distance from the Kunming Steel Plant while they increased with the distance from the Qujing Power Plant (Table 2). This may be due to the much different $\delta^{34}S$ values of coals combusted in the two plants (+13.8 and −7.5 ‰, respectively). With the increasing distance from plants, the contribution of coal-derived sulfur turned out to be less, and so the closer to the Kunming Steel Plant, $\delta^{34}S_{SO4}$ value was higher in the leaves while the closer to the Qujing Power Plant, lower $\delta^{34}S_{SO4}$ value was found in the leaves. This provides further evidence that $\delta^{34}S_{SO4}$ in leaves was a good indicator of atmospheric sulfur deposition.

Conclusions

The results of the study are summarized as follows:

(1) The concentrations of water-soluble sulfate in *Pinus massoniana Lamb* needles were found to be significantly correlated to ambient sulfur dioxide, and the concentrations of soil sulfur in these sampling sites were not significantly different. No correlations were seen between total sulfur concentrations of *Pinus massoniana Lamb* needles and ambient sulfur dioxide, implying that concentration of water-soluble sulfate in needles was more reliable to indicate ambient sulfur input relative to the total sulfur.

(2) In accordance with higher isotopic values of coals in Yunnan areas than in Guiyang areas, the S_{SO4} and S_{TS} values in *Pinus massoniana Lamb* needles collected in the former areas were more ^{34}S-enriched than those in the latter areas. And very similar $\delta^{34}S$ values between needles and coals were found in Guiyang areas. These indicated that $\delta^{34}S_{SO4}$ in needles was a new good indicator of coal-derived atmospheric sulfur deposition.

(3) In the point pollution areas, both the $\delta^{34}S_{SO4}$ and $\delta^{34}S_{TS}$ values in needles increased with the distance from the Kunming Steel Plant or decreased with the distance from the Qujing Power Plant and this was mainly controlled by the $\delta^{34}S$ values of coals used.

(4) The differences between δ^{34} S_T and δ^{34} S_{SO4} for most needle samples were within the range of +2 to +3 ‰, suggesting that little isotopic fractionation accompanies occurred during sulfur assimilation process in needles of *Pinus massoniana lamb.*

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References

Alfani A, Baldantoni D, Maisto G, Bartoli G, Virzo De Santo A (2000) Temporal and spatial variation in C, N, S and trace element contents in the leaves of Quercus ilex within the urban area of Naples. Environ Pollut 109:119–129

Al-Shayeb SM, Al-Rajhi MA, Seaward MRD (1995) The date palm (Phoenix dactylifera L) as a biomonitor of lead and other elements in arid environments. Sci Total Environ 168:1–10

Bao LM, Zhang GL, Zhang YX, Li Y, Lin J, Liu W, Cao QC, Zhao YD, Ma CY, Han Y (2009) Transfer characterization of sulfur from coal-burning emission to plant leaves by PIXE and XANES. Chinese Physics C 33:1010–1015

Berg T, Royset O, Steinnes E, Vadset E (1995) Atmospheric trace element deposition: principal component analysis of ICP-MS data from moss samples. Environ Pollut 88:67–77

Case JW, Krouse HR (1980) Variations in sulphur content and stable sulphur isotope composition of vegetation near a SO_2 source at Fox Creek, Alberta, Canada. Oecologia 44:248–257

Cicek A, Koparal AS (2004) Accumulation of sulfur and heavy metals in soil and tree leaves sampled from the surroundings of Tunçbilek Thermal Power Plant. Chemosphere 57:1031–1036

Fatoki OS, Ayodele ET (1991) Zinc and copper levels in tree barks as indicators of environmental pollution. Environ Int 17:455–460

Freney JR, Spencer K (1967) Diagnosis of sulphur deficiency in plants by soil and plant analysis. J Aust Inst Agric Sci 33:284–288

Galloway JN, Zhao DW, Xiong JL, Likens GE (1987) Acid rain: China, United States, and a remote area. Science 236:1559–1562

Guiyang Environmental Protection Bureau (2006) Bulletin of Environmental Conditions of 2005 in Guiyang (in Chinese)

Guiyang Environmental Protection Bureau (2012) Bulletin of Environmental Conditions of 2011 in Guiyang (in Chinese)

Hong YT, Zhang HB (1992) Sulfur isotope characteristic of coal in China and isotopic fractionation during coal burning. Sci China B 00B(8):868–873 (in Chinese)

Hüve K, Dittrich A, Kindermann G, Slovik S, Heber U (1995) Detoxification of SO_2 in conifers differing in SO_2-tolerance. Planta 195:578–585

Ishii MM (1953) A study of the fractionation of sulphur isotopes in the plant metabolism of sulphates. McMaster University, Canada

Kelly J, Lambert MJ (1972) The relationship between sulphur and nitrogen in the foliage of Pinus radiate. Plant Soil 37:395–407

Krouse HR (1977) Sulfur isotope abundances elucidate uptake of atmospheric sulfur emissions by vegetation. Nature 265:45–46

Lau OW, Luk SF (2001) Leaves of Bauhinia blakeana as indicators of atmospheric pollution in Hong Kong. Atmos Environ 35:3113–3120

Legge AH, Bogner JC, Krupa SV (1988) Foliar sulphur species in pine: a new indicator of a forest ecosystem under air pollution stress. Environ Pollut 55:15–27

Martinez JD, Dharmarajan V, Nathany M (1971) Spanish moss, a sensor for lead. Nature 233:564–565

Mayer B (2005) Assessing sources and transformations of sulphate and nitrate in the hydrosphere using isotope techniques. In: Radeep K, Gat J, Oel R, Froehlich K, Laus FO (eds) Aggarwal P. Isotopes in the Water Cycle Springer, Netherlands, pp 67–89

Mott RA, Ruell DA, Wilkinson HC (1955) Determination of total sulphur in coal and coke by the Eschka method I precipitation and recovery of soluble sulphates as barium sulphate. Fuel 34:78–94

Richter DD, Johnson DW (1983) Determination of inorganic sulfate in foliage with barium chloranilate. Soil Sci Soc Am J 47:522–524

Sloof JE (1995) Lichens as quantitative biomonitors for atmospheric trace element deposition, using transplants. Atmos Environ 29:11–20

Trust BA, Fry B (1992) Stable sulphur isotopes in plants: a review. Plant Cell Environ 15:1105–1110

Turkan I, Henden E, Celik U, Kivilcim S (1995) Composition of moss and bark samples as biomonitors of heavy metals in a highly industrialised area in Izmir, Turkey. Sci Total Environ 166:61–67

Winner WE, Bewley JD, Krouse HR, Brown HM (1978) Stable sulfur isotope analysis of SO_2 pollution impact on vegetation. Oecologia 36:351–361

Xiao HY, Liu CQ (2002) Sources of nitrogen and sulfur in wet deposition at Guiyang, Southwest China. Atmos Environ 36:5121–5130

Xiao HY, Liu CQ (2004) Chemical characteristics of water-soluble components in TSP over Guiyang, SW China, 2003. Atmos Environ 38:6297–6306

Xiao HY, Liu CQ (2011) The elemental and isotopic composition of sulfur and nitrogen in Chinese coals. Org Geochem 42:84–93

Xiao HY, Tang CG, Xiao HW, Liu XY, Liu CQ (2009) Identifying the change of atmospheric sulfur sources in China using isotopic ratios in mosses. J Geophys Res 114:D16304. doi:10.1029/2009JD012034

Yang XX, Gao QX, Qu JZ, Jiang ZY (1999) The exploration and initial assessment of total amount control method for SO_2 emission in China. Res Environ Sci 12:17–20 (in Chinese)

Yang LP, Stulen I, De Kok LJ (2006) Sulfur dioxide: Relevance of toxic and nutritional effects for Chinese cabbage. Environ Exp Bot 57:236–245

Yeaple DS (1972) Mercury in bryophytes (moss). Nature 235:229–230

Yunnan Environmental Protection Bureau (2012) Bulletin of Environmental Conditions of 2011 in Guiyang (in Chinese)

Zhao FJ, Spiro B, Poulton PR, McGrath SP (1998) Use of sulfur isotope ratios to determine anthropogenic sulfur signals in a grassland ecosystem. Environ Sci Technol 32:2288–2291