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Indicating atmospheric sulfur by means of S-isotope in leaves of the plane, osmanthus and camphor trees

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ABSTRACT

Foliar δ^{34}S values of three soil-growing plant species (*Platanus Orientalis* L., *Osmanthus fragrans* L. and *Cinnamomum camphora*) have been analyzed to indicate atmospheric sulfur. The foliar δ^{34}S values of the three plant species averaged -3.11 ± 1.94‰, similar to those of both soil sulfur (-3.73 ± 1.04‰) and rainwater sulfate (-3.07 ± 2.74‰). This may indicate that little isotopic fractionation had taken place in the process of sulfur uptake by root or leaves. The δ^{34}S values changed little in the transition from mature leaves to old/senescing leaves for both the plane tree and the osmanthus tree, suggestive of little isotope effect during sulfur redistribution in plant tissues. Significantly linear correlation between δ^{34}S values of leaves and rainwater sulfate for the plane and osmanthus trees allowed the tracing of temporal variations of atmospheric sulfur by means of foliar sulfur isotope, while foliage δ^{34}S values of the camphor is not an effective indicator of atmospheric sulfur.

1. Introduction

Atmospheric sulfur deposition has increased in some Chinese areas during recent decades (e.g. Lü and Tian, 2007), and there is increasing concern that atmospheric sulfur deposition is damaging the ecosystem. Combustion of sulfur-containing fossil fuels and certain industrial processes involving sulfur compounds represent the main anthropogenic sources of primary SO_2 present in the atmosphere.

Sulfur isotope ratios (δ^{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 potential sources and, consequently, to assess the relative contribution and impacts of the different sources (Novák et al., 2001; Xiao and Liu, 2002; Pruett et al., 2004; Gislason and Torssander, 2006; Liu et al., 2009). The δ^{34}S values of anthropogenic emissions in industrial and consumer processes vary greatly, depending on the nature of the source (coal, oil, natural gas): petroleum natural gas, −20 to +30‰; oil, −8 to +23‰; coal, −35 to +30‰ (Neilson, 1974; Nielsen, 1978). The δ^{34}S values of Chinese coals in different localities also show wide variations, while specific individual coal deposits are relatively uniform in isotopic contents (Hong and Zhang, 1992).

Mosses, being sensitive to atmospheric sulfur deposition, have been shown to be outstanding bio-indicators in a wide range of air pollution studies and isotopic ratios in mosses can be used to discriminate atmospheric sulfur sources (Nriagu and Glooschenko, 1992; Xiao et al., 2008, 2009), possibly because little isotopic fractionation accompanies S assimilation (Mektiyeva et al., 1976; Trust and Fry, 1992). Mosses differ from soil-growing plants in that the former acquire sulfur only from the atmosphere, while the latter obtain sulfur from soils and atmosphere. Accordingly, soil-growing plants tend to have δ^{34}S values intermediate to those of the air and soils from the same sites (Krouse, 1977). Some previous studies, however, have suggested that sulfur isotope in leaves is useful to elucidate uptake of atmospheric sulfur. For instance, Gebauer et al. (1994) found that needles from the declining site were always more enriched in ^{34}S than needles of the same age from the healthy site because SO_2 at the declining site was more ^{34}S-enriched relative to that at the healthy site. There was some evidence that plant tissues systematically preferred the light isotope ^{32}S, on average by 2‰ (Trust and Fry, 1992; Novák et al., 2001). But the study conducted by Monaghan et al. (1999) showed that the isotope ratios of the whole wheat shoots, which had been supplied with only one S source, were very close to the δ^{34}S values of the sources, with a maximum deviation of ±0·6‰.

In this study, we aim to assess the potential of using foliar δ^{34}S values of three different soil-growing plants to indicate sulfur derived from the atmosphere. Specific questions addressed are (1)

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to understand the influences of canopies and foliar developmental stages on foliar sulfur contents and $\delta^{34}S$ values; (2) and to show whether foliar sulfur contents and $\delta^{34}S$ values are linearly correlated with those of atmospheric sulfur for the three plant species; (3) identify the main sources of atmospheric sulfur deposition through foliar $\delta^{34}S$ values.

2. Experimental section

2.1. Sample collection and treatment

We selected three plant species, plane tree (*Platanus Orientalis* L.), osmanthus (*Osmanthus fragrans* L.) and camphor (*Cinnamomum camphora*), in the Institute of geochemistry, CAS, for leaf sampling. The three plants are distributed within an area of 1 hm^2. The osmanthus tree and the camphor tree chosen for leaf sampling are about 10 years old and 4 m in height whereas the plane tree is about 40 years old and 10 m high. All the plant trees are not influenced by obvious sulfur sources.

For all the three selected plant trees, about 10 g of young leaves (yellow), mature leaves (green) and old/senescing leaves (dark green) were collected in 2009 from both the upper and lower canopies. Only the current year leaves (marked with a nylon line when they are young) were taken from the selected trees. We did not find enough current year leaves in lower canopies of the camphor trees, thus did not collect them. Leaf materials were gently rinsed with 1.5 mol L^{-1} HCl solution, then sonicated and washed with deionized water for several times until no SO_4^{2-} was detected in the washed water (spectrophotometry, the limit of detection was <0.01 mg L^{-1}). The main purpose of this washing procedure was to remove adsorbed pollutants. Then they were ground into a very fine powder (<100 mesh) using a mortar and pestle prior to chemical analyses. Just when plant leaves were collected, rhizospheric soil was sampled at each site by taking about 100 g from the topsoil layer (above 10 cm). Leaf litters and roots were removed from the soil samples. Soil samples were dried for 24 h at 80 °C and homogenized using a mortar and pestle.

Rainwater samples were collected on the roof of a two-storey building in 2009. In order to collect enough water samples for isotope analysis, a sampler with a large polyethylene sheet (1.5 m × 2 m) served as the collection device. Prior to use, the polyethylene sheet was cleaned with 2 N HCl solution and rinsed with Milli-Q water, and dried. Then a hole of 2 cm in diameter was punched in the center of the sheet. The polyethylene sheet was fastened 1.5 m upon the floor by a stainless bracket. Between each rain, the polyethylene sheet was closed to avoid dry deposition and other contaminations. After collection, the samples were immediately filtered to exclude material greater than 0.45 μm using acetate membrane filters. A small aliquot of these filtered samples were stored in brown clean plastic bottles for chemical determination, while other aliquots were frozen at 4 °C and stored for isotopic analysis after poisoned by $HgCl_2$(s).

2.2. Chemical and isotopic analyses

Measurements of ion concentrations in rainwater samples and soil washings were conducted on ion chromatography (Dionex, ICS-90) with a detection limit of 0.01 mg/L. All rainwater samples and soil washings were acidified at $pH < 2$ with 2 mol/L HCl solution, then sulfate was recovered by precipitating as $BaSO_4$ with enough 2 mol/L $BaCl_2$ solution. After precipitated for 24 h, the mixture was filtered through 0.22 μm acetate membrane filters.

Foliage sulfur contents were measured by an elemental analyzer (Model PE-2400 II, USA) with an analytical precision of 1%. Calibration of the instrument with cystine standard (N141-0324, provided by Perkin Elmer) was carried out. Accuracy and recovery of sulfur contents were checked by analyzing a sample of this standard material after each set of eight leaf analyses.

Plant samples were oxidized in a Parr bomb to convert all forms of sulfur present to sulfate. To assure complete conversion, hydrogen peroxide was added to all washings. Sulfate was recovered from plant 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 0.22 μm acetate membrane filter.

The precipitates ($BaSO_4$) on the filters collecting from rainwater, soils or plants were carefully rinsed with enough Milli-Q water to remove Cl^-, and then transferred into crucibles with the filters and combusted at 800 °C for 40 min in the air. In order to determine the composition of white powder in the crucible, it was analyzed with X-ray diffractometry. The results showed there is >99% $BaSO_4$ in the powder. Thermal decomposition of $BaSO_4$ (Yanagisawa and Sakai, 1983) was conducted to prepare SO_2 for sulfur isotopic analysis in a Finnigan MAT-252 mass spectrometer. The $\delta^{34}S$ analysis of NBS127 (barium sulfate, provided by the International Atomic Energy Agency, Vienna) gave a mean (±SD) value of $21.3 \pm 0.2‰$ ($n = 5$). Three to five replicate measurements per sample were carried out, and values were presented as the average of these measurements. The analytical precision (±SD) for $\delta^{34}S$ was ±0.2‰.

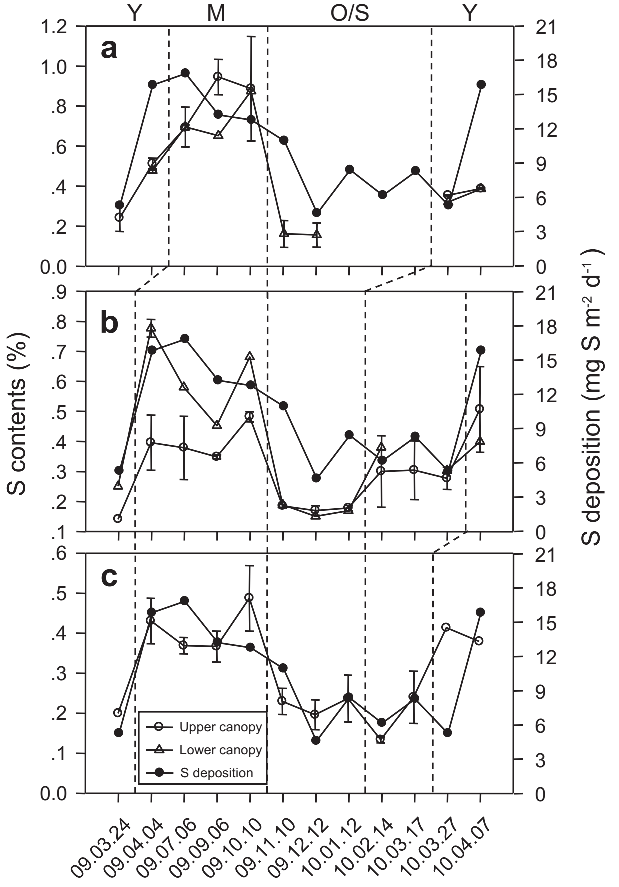

Fig. 1. Temporal variations of wet sulfur deposition and foliar sulfur contents in the plane tree (a), the osmanthus tree (b) and the camphor tree (c). Y – young leaves; M – mature leaves; O/S – old or senescing leaves.

2.3. Statistical analysis

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

3. Results

3.1. The $\delta^{34}S$ values in rhizospheric soils

All the rhizospheric soils of three trees showed negative $\delta^{34}S$ values, varying from $-4.73 \pm 1.26‰$ to $-2.66 \pm 0.46‰$, with the average of $-3.73 \pm 1.04‰$. The $\delta^{34}S$ values of the rhizospheric soils are not significantly different between the three sites ($p > 0.05$).

3.2. Wet sulfur deposition and $\delta^{34}S$ values in rainwater

Sulfate concentrations in rainwater have a wide range, with an average of 13.2 mg/L in 2009. Rainwater sulfate concentrations in summer and autumn were significantly lower than those in winter and spring. Based on sulfate concentrations and precipitation, we estimated wet sulfur deposition between two sampling times, as shown in Fig. 1. The highest wet sulfur deposition occurred between April 4, 2009 and July 6, 2009, being 16.8 mg S m^{-2} d^{-1}.

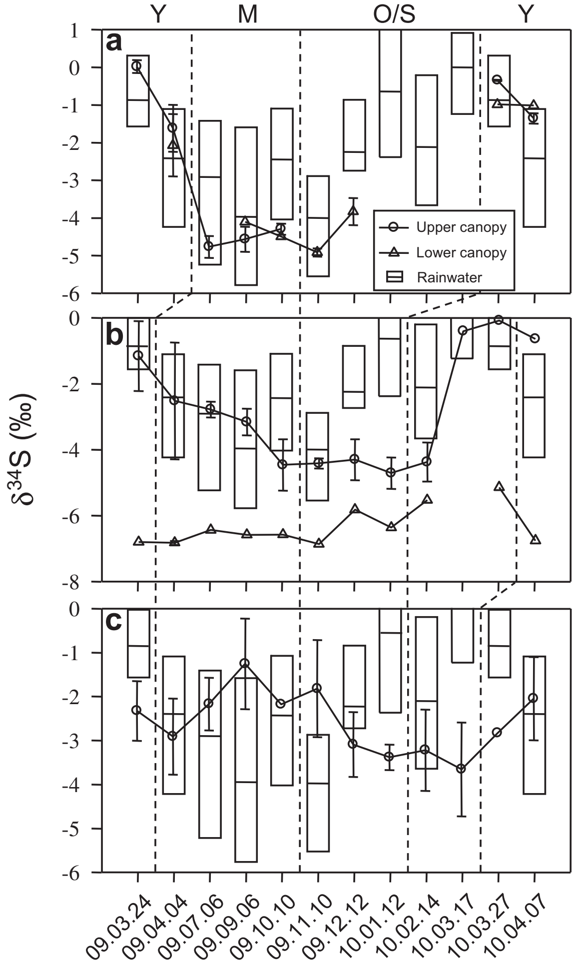

Fig. 2. Temporal variations of the δ^{34}S values of rainwater sulfate and foliar δ^{34}S values of the plane tree (a), the osmanthus tree (b) and the camphor tree (c). Box plots display the 10th, 25th, 50th, 75th, and 90th percentiles as solid lines. Y – young leaves; M – mature leaves; O/S – old or senescing leaves.

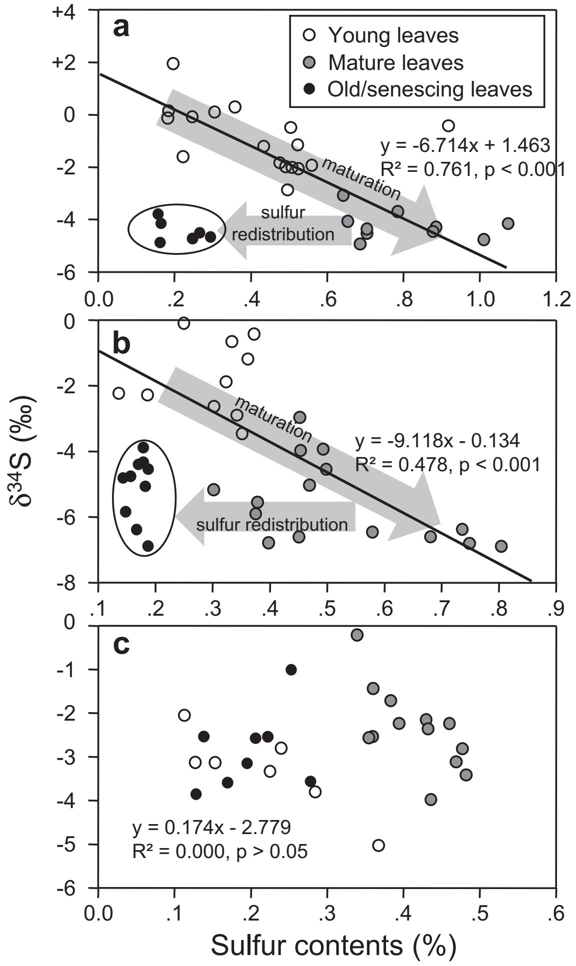

Fig. 3. Changes of the foliar δ^{34}S values with sulfur contents of the plane tree (a), the osmanthus tree (b) and the camphor tree (c).

Between Nov. 10, 2009 and Dec. 10, 2009, the lowest wet sulfur deposition (4.6 mg S m^{-2} d^{-1}) was found.

The average δ^{34}S values of rainwater sulfate in summer and autumn was about −3.26‰, significantly more negative ($p < 0.05$) than those in winter and spring (−1.13‰) (Fig. 2). In rainwater having higher sulfate concentrations, the relatively less negative δ^{34}S values were found. The δ^{34}S values of rainwater sulfate averaged −3.07 ± 2.74‰ in the whole year of 2009.

3.3. *Sulfur contents and δ^{34}S values in plant leaves*

Foliar sulfur contents of the three plants varied very widely from 0.11% to 1.08%, with a mean of 0.39 ± 0.21%. The mean sulfur content of the plane tree was 0.46 ± 0.24%, significantly higher ($p < 0.05$) than that of the osmanthus tree (0.37 ± 0.20%) and the camphor tree (0.31 ± 0.13%). For all the three trees, the highest foliar sulfur contents occurred in July to October of 2009 whereas those in November of 2009 to January of 2010 were lowest (Fig. 1).

Most of the leaves showed negative δ^{34}S values except that of the plane sampled on Mar 24, 2009 (Fig. 2). Compared to those of the osmanthus tree (−4.22 ± 2.12‰), the plane tree (−2.37 ± 0.95‰) and the camphor tree (−2.66 ± 1.91‰) were significantly less ^{34}S-depleted ($p < 0.05$). The foliar δ^{34}S values of the plane tree and the osmanthus tree presented seasonal variation pattern whereas the foliar δ^{34}S values of the camphor tree were relatively stable.

For the plane tree, both the foliar sulfur contents and the foliar δ^{34}S values between upper and lower canopies were not significantly different ($p > 0.05$) (Figs. 1 and 2). But for the osmanthus tree, there was a significant difference ($p < 0.05$) in the foliar δ^{34}S values between upper (−2.94 ± 1.70‰) and lower canopies (−6.57 ± 0.43‰). The foliar sulfur contents in upper canopies of the osmanthus tree were significantly lower than those in lower canopies only between April 4, 2009 and Oct. 10, 2009 (Fig. 1). The foliar δ^{34}S values in lower canopies of the osmanthus tree were observed not changing with time (Fig. 2).

For the plane tree and the osmanthus tree, there was a significantly linear correlation between the δ^{34}S values and tissue sulfur contents of young and mature leaves (Fig. 3a, b). And from mature leaves to old/senescing leaves, the δ^{34}S values did not change significantly ($p > 0.05$) although sulfur contents decreased about five times. There was no significant difference in δ^{34}S values between young/mature, and old/senescing leaves (Fig. 3c).

The sulfur contents of young, mature and old/senescing leaves showed similar variation pattern for the three trees (Fig. 4). The highest and lowest sulfur contents were observed in mature and old/senescing leaves, respectively. For the plane tree (Fig. 4d), the δ^{34}S values in young leaves (−0.85 ± 0.83‰) were significantly less negative ($p < 0.05$) than those in mature and old/senescing leaves (−4.33 ± 0.53‰ and −4.54 ± 0.26‰, respectively). The δ^{34}S values

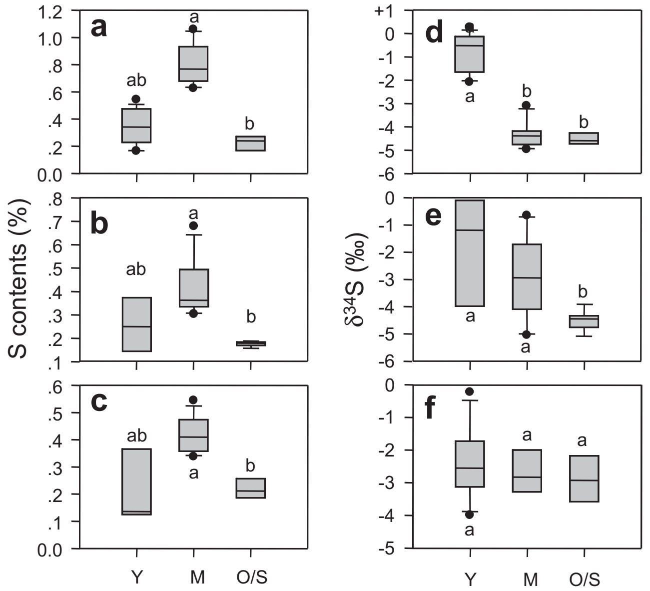

Fig. 4. Changes of sulfur contents and the foliar $\delta^{34}S$ values with foliar developmental stage of the plane tree (a, d), the osmanthus tree (b, e) and the camphor tree (c, f). Box plots display the 10th, 25th, 50th, 75th, and 90th percentiles as solid lines. Symbols indicate 5th and 95th percentiles. Data from different sampling sites that do not share a letter below the bars are significantly different at $p < 0.05$. Y – young leaves; M – mature leaves; O/S – old or senescing leaves.

in young and mature leaves of the osmanthus tree (Fig. 4e) were not significantly different (-1.85 ± 1.92‰ and -2.94 ± 1.40‰, respectively), but both were significantly less negative ($p < 0.05$) than those in old/senescing leaves (-4.52 ± 0.34‰). The $\delta^{34}S$ values in young, mature and old/senescing leaves of the camphor tree were very similar (Fig. 4f).

3.4. Correlation between atmospheric sulfur and foliar sulfur

Using a one-way ANAVO analysis, we found that foliar sulfur contents of both the osmanthus tree and the camphor tree were significantly linearly correlated with wet sulfur deposition ($p < 0.01$) (Table 1). For the plane tree, there was no significant linear correlation between them, but the $\delta^{34}S$ values of leaves and rainwater sulfate were significantly linearly correlated ($p < 0.05$). The $\delta^{34}S$ values between leaves of the camphor and rainwater sulfate were negatively correlated ($p < 0.01$). If excluding the periods of old/senescing leaves between November and January, significant linear correlations between foliar sulfur contents and wet sulfur deposition were observed for the osmanthus tree and the camphor tree while not for the plane tree. Interestingly, when we combined all the three plants for correlation analysis, we also found a significantly linear correlation between foliar sulfur contents and wet sulfur deposition ($p < 0.05$) but there was no correlation between $\delta^{34}S$ values of leaves and rainwater sulfate ($p > 0.05$).

4. Discussion

4.1. The $\delta^{34}S$ values of main sulfur sources available for plants

The natural variation in stable sulfur isotope ratios in vegetation has been widely used to delineate sources of S in different ecosystems (Krouse, 1977; Nriagu et al., 1991; Stam et al., 1992). Since soil-growing plants usually have two main sulfur sources: sulfate as natural products of mineralization processes in soils and sulfur compounds (SO_4^{2-}, SO_2) in the atmosphere, they tend to acquire $\delta^{34}S$ values intermediate to that of the air and soil at the same sites (Krouse, 1977).

Many previous studies indicated that soil $\delta^{34}S$ values tend to change with depth (e.g. Giesemann et al., 1995). For instance, Gebauer et al. (1994) reported that the mean $\delta^{34}S$ values increased from +0.9‰ in the uppermost organic layer to about +4.5‰ in the mineral soil. Although deeper soil sulfur may be acquired by the plane tree (the highest tree among the three species), we did not observe obvious increase in foliar $\delta^{34}S$ values of plane tree relative to other two plant species (Fig. 2). Also significant differences in $\delta^{34}S$ values of soil sulfate were not observed between these sites, indicating that soil sulfur cannot result in the temporal variation as shown in Figs. 1 and 2.

Atmospheric sulfur includes natural sources such as biogenic emissions and anthropogenic sources mainly due to the combustion of fossil gas and fuels in the form of oil or coal, each of which has an inherent $\delta^{34}S$ value (Xiao et al., 2009). In the last decades sulfur isotopes have been widely used as an effective tool to distinguish sources of sulfur in atmospheric gases and precipitation (Gebauer et al., 1994; Xiao and Liu, 2002). In Guiyang city, Mukai et al. (2001) reported that the average $\delta^{34}S$ value of SO_2 was −4.1‰ in winter and −4.5‰ in summer whereas that of particulate sulfate was +1.2‰ and −1.3‰, respectively. In this study, rainwater sulfate in 2010 showed an average $\delta^{34}S$ value of -3.07 ± 2.74‰, slightly less negative than that of SO_2 reported by Mukai et al. (2001). Because the foliar $\delta^{34}S$ values were similar to those of rainwater sulfate and soil sulfur, we don't know which one is more important between the two sulfur sources.

4.2. Foliar sulfur isotope indicating atmospheric sulfur sources

Previous work has shown that lichens (Krouse, 1977) and terrestrial mosses (Xiao et al., 2008, 2009) acquire $\delta^{34}S$ values similar to those found for atmospheric sulfur oxides. Although soil-growing plants obtain sulfur from both soils and the atmosphere, more and more studies have confirmed that sulfur isotope in their leaves is useful to elucidate sulfur derive from the atmosphere. For instance, Gebauer et al. (1994) found that mean annual $\delta^{34}S$ over the sampling period was +2.0‰ for SO_2 at the healthy site and +2.3‰ for SO_2 at the declining site. And hence needles from the declining site were always more enriched in ^{34}S than needles of the same age from the healthy site. However, using isotope in leaves of soil growing plants to indicate atmospheric sulfur, we should take isotope effects into account, which may occur during the uptake of atmospheric/soil sulfur, or during the process of sulfur redistribution within plant tissue.

The fate of sulfur absorbed by tree leaves includes translocation to roots, allocation from mature leaves to younger leaves and release to the atmosphere in the form of H_2S. Previous studies showed that some parts of sulfur in trees can be redistributed between organs to support new growth (Blake-Kalff et al., 1998; Anderson, 2005) while those that are incorporated into protein during early leaf development are relatively less mobile (Hawkesford and De Kok, 2006). Garten (1990) reported that translocation occurred principally in late summer, consistent with the decrease of sulfur contents from mature leaves to old/senescing leaves (Fig. 1). Studies on sulfur isotope fractionation associated with redistribution of sulfur in the plant tissue are very limited up to now. Although Fry and Smith (2002) observed that detrital leaves had higher sulfur isotopic compositions than yellow leaves, the $\delta^{34}S$ values changed little from mature leaves to old/senescing leaves for both the plane tree and the osmanthus tree in this study (Fig. 3a, b). For the camphor tree, the $\delta^{34}S$ values of mature leaves were also similar to those of old/senescing leaves (Fig. 4f). These suggested

Table 1
Linear aggression analyses between rainwater (y) and plants (x).

			Plane tree (*Platanus Orientalis L.*)	Osmanthus tree (*Osmanthus fragrans L.*)	Camphor tree (*Cinnamomum camphora*)	Three plant species
The whole year	Foliar S% and wet S deposition	Coefficients	9.954	24.960[b]	26.175[b]	20.334[b]
		R^2	0.298	0.614	0.547	0.528
	Foliar $\delta^{34}S$ and rainwater $\delta^{34}S$	Coefficients	0.457[a]	0.496	−1.366[b]	0.391
		R^2	0.550	0.318	0.627	0.102
Periods excluding Nov. to Jan.	Foliar S% and wet S deposition	Coefficients	8.931	33.422[b]	25.705[a]	24.075[a]
		R^2	0.200	0.727	0.560	0.554
	Foliar $\delta^{34}S$ and rainwater $\delta^{34}S$	Coefficients	0.506[a]	0.636[a]	−1.225[a]	0.653
		R^2	0.642	0.581	0.542	0.280

[a] $P < 0.05$.
[b] $P < 0.01$

that sulfur redistribution in the three plant species accompanied little isotope effect, probably related to passive accumulation and transport of sulfate in plant tissue. Gebauer et al. (1994) found that the continuous passive uptake of atmospheric sulfur compounds occurred (primarily in the form of inorganic sulfate) and not used for growth. Kaiser et al. (1993) concluded that only about 30% of total sulfur is incorporated into organic compounds, while the other 70% is stored in cell vacuoles or cell walls as sulfate. Köstner et al. (1998) also believed that the transport of organic sulfur was low (up to 3% of total sulfur) compared to the transport of sulfate. Generally, sulfate is a much larger pool than other sulfur compounds such as glutathione and *S*-methylmethionine methylmethionine.

Although there is some evidence that assimilation by some plants discriminates against ^{34}S, the isotope discrimination only leads to an average depletion of ^{34}S by 1–2‰ in the organic S, compared with the sulfate source (Trust and Fry, 1992; Novák et al., 2001). Monaghan et al. (1999) showed that the isotope ratios of the whole wheat shoots, which had been supplied with only one sulfur source, were very close to the $\delta^{34}S$ values of the sources, with a maximum deviation of ±0·6‰. In this study, we also found that both the average $\delta^{34}S$ value of the soil sulfur (−3.73 ± 1.04‰) and the rainwater sulfate (−3.07 ± 2.74‰) were similar to those of foliar sulfur of the three plant species (−3.11 ± 1.94‰). Additionally, the significantly linear correlation of the $\delta^{34}S$ values between plant species and rainwater sulfate was observed for the plane and osmanthus trees (Table 1). Although rainwater sulfate was negatively isotopically correlated with camphor leaves, the $\delta^{34}S$ values between them were similar (Fig. 2c). All suggested that little isotopic fractionation had taken place in the process of sulfur uptake by root or leaves.

It has been a long held view that the canopy had slightly decreased the $\delta^{34}S$ value of sulfate in throughfall on average by 1.1‰ relative to that in rainwater (Van Stempvoort et al., 1992; Zhang et al., 1998; Novák et al., 2001). Puig et al. (2008) believed that the net throughfall fluxes of sulfur were mostly due to the dry deposition of SO_2. This was supported by the relatively stable values with time for Osmanthus leaves in lower canopies (Fig. 2b) because the average $\delta^{34}S$ values of SO_2 in summer and winter were similar (Mukai et al., 2001), whereas that of rainwater sulfate showed obvious seasonal variation. Based on the $\delta^{34}S$ values of SO_2 (averaging −4.3‰) reported by Mukai et al. (2001) and that of rainwater sulfate (averaging −3.07‰) determined in this study, lower foliage $\delta^{34}S$ values may be expected in lower canopies than in upper canopies. This can be seen from Fig. 2b.

4.3. Developmental stage-related variations of foliage $\delta^{34}S$ values

It has been shown by Winner et al. (1978) that the $\delta^{34}S$ values of conifers vary in relation to age. Usually due to different isotopic composition of soil sulfur and atmospheric sulfur, the ^{34}S abundance in the vegetation would change with time of exposure to atmospheric sulfur deposition (i.e. age). If atmospheric deposition was the heavier end-member, an increasing ^{34}S ratio with the time of exposure to ambient air will be expected. This can be used to explain why the $\delta^{34}S$ in the needles increased continuously with needle age (Gebauer et al., 1994; Giesemann et al., 1995; Novák et al. 1996). For instance, Gebauer et al. (1994) estimated that the contribution of sulfur from atmospheric SO_2 (+2.0‰ at the healthy site and +2.3‰ at the declining site) increased from 19% (healthy stand) or 28% (declining stand) in current-year needles to 39% (healthy stand) or 57% (declining stand) in 3-year old needles. In Guiyang city, although both the average $\delta^{34}S$ value of the soil sulfur and the rainwater sulfate are similar to that of foliar sulfur, higher $\delta^{34}S$ value of rainwater sulfate in spring (−1.13‰) than in summer (−3.26‰) resulted in less ^{34}S-depleted young leaves than mature leaves of the plane tree (−0.85 ± 0.83‰ and −4.33 ± 0.53‰, respectively; Fig. 4d) and the osmanthus tree (−1.85 ± 1.92‰ and −2.94 ± 1.40‰, respectively; Fig. 4e). For the camphor tree, the smooth surface and thick waxy layer of the leaves stopped the uptake of rainwater sulfate due to short retention time of rainwater droplet and thus the foliar $\delta^{34}S$ values were influenced little by the seasonal variation of rainwater $\delta^{34}S$ values (Fig. 4f).

5. Conclusions

In this study, although the average $\delta^{34}S$ value of soil sulfur was similar to that of atmospheric sulfur, the latter showed a temporal variation, which was consistent with that of foliar sulfur of the osmanthus tree and the plane tree. We still don't know which one is more important between soil sulfur and atmospheric sulfur for plant growth. But the consistence of $\delta^{34}S$ temporal variations between foliar sulfur and atmospheric sulfur indicated that the foliage $\delta^{34}S$ values of the plane tree and the osmanthus tree are useful to trace temporal variations of atmospheric sulfur, while those of the camphor cannot effectively indicate atmospheric sulfur.

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