

The oxygen and sulfur isotopic compositions of soluble sulfate in the needles of *Pinus massoniana* Lamb.: Source discrimination and contribution estimation

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ABSTRACT

In order to identify the sources of sulfate in plant leaves, needles of *Pinus massoniana* Lamb. were collected from Guiyang (an area seriously affected by acid rain) and Yunnan areas (where acid rain barely occurred) in southwestern China to measure the isotopic compositions of the water-soluble sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$) and leaf water ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$). Compared to atmospheric sulfate, all needle samples were quite depleted in ^{18}O , indicating that sulfate in needles was rarely derived from atmospheric sulfate. The $\delta^{18}\text{O}_{\text{SO}_4}$ values in the needles (-5.3%) were similar to those in the soil (-5.2%) in the uncontaminated mountain area of Jinning, suggesting that sulfate in needles originated mainly from soil sulfate in barely SO_2 pollution areas. However, the $\delta^{18}\text{O}_{\text{SO}_4}$ values in the needles were significantly more negative than that of soil in most areas with relatively severe SO_2 pollution, and the $\delta^{18}\text{O}_{\text{SO}_4}$ values in the needles were positively correlated with the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of leaf water, indicating that a substantial part of the sulfate in the needles might be derived from atmospheric SO_2 oxidation in polluted areas. The estimated contributions of atmospheric SO_2 oxidation to the sulfate in the needles increased significantly with increasing atmospheric SO_2 and needle sulfate concentration. When the atmospheric SO_2 concentrations were $> 30 \mu\text{g m}^{-3}$, the contributions of SO_2 to needle sulfate were $> 50\%$. The $\delta^{18}\text{O}_{\text{SO}_4}$ values in needles decreased obviously with the increase of the distance from both the Steel Plant and the Power Plant, implying that part of needle sulfate likely to be derived from primary sulfate which generated in the industrial plant flues and secondary sulfate which generated in atmosphere.

1. Introduction

The sulfur in plants can be divided into organic sulfur and inorganic sulfur. Most inorganic sulfur is in the form of sulfate (SO_4^{2-}) accumulation in the cells, the content changes of which dramatically with the sulfur supply level (Thomas and Hexdbtcks, 1944). Generally, the sulfate taken up by the roots from soil is the main source for plants, the process is the active absorption of against a concentration gradient (Maruyama-Nakashita et al., 2004; Takahashi et al., 1997). But beyond that, atmospheric sulfur from SO_2 and particulates can also be used as sulfur nutrients if the sulfate supply to the roots from the soil is limited, especially when SO_2 concentrations are high due to air pollution (Cicek and Kopal, 2004). Atmospheric SO_2 can be taken up by plant leaves through the stomata. Oxidation appears to be the main pathway of SO_2 detoxification in conifers (Hüve et al., 1995) and leads to the

production of sulfuric acid, which burdens cells with protons and sulfate. The latter is phytotoxic by influencing the dark reaction of photosynthesis (Asada et al., 1968) and is actively sequestered into vacuoles (Kaiser et al., 1989). In addition to SO_2 , atmospheric sulfate (in particulates and precipitation) can be adsorbed in the leaves surface, thus infiltrating into leaf tissues (Bao et al., 2009).

Up to present, the research of sulfate sources and formation in plant tissues is rare. It is widely believed that most of sulfate in plant tissues comes from soil sulfate. For example, Cowling et al. (1973) found that absorbing SO_2 and particulates from the atmosphere accounts for about 10% to 20% of total sulfur demand for plants. And this absorption only partially alleviates the need for sulfur, plants cannot fully meet the requirements of the growth and development. However, with the development of the industrial economy, a large amount of anthropogenic sulfur has been input into the atmospheric system and has caused high

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atmospheric sulfur deposition (Galloway et al., 1987; Yang et al., 1999). More and more studies have found a dramatic increase of sulfate content in plant leaves in areas with high SO₂ concentrations (Bao et al., 2009; Lau and Luk, 2001; Sharma and Tripathi, 2009). So we're justified in believing the contribution of SO₂ oxidation to sulfate in plant leaves may be considerable. Unfortunately, no studies have been conducted to assess the contribution rate of various sources of sulfate in plant tissue. The process of SO₂ oxidation to sulfate is a hot research topic nowadays, especially in the process of haze, and has many controversies (Guo et al., 2017; Wang et al., 2016).

The use of plant tissues has long been shown to be an effective indicator of atmospheric pollution. Many studies have shown that the sulfur isotopic compositions of sulfate in plant leaves can be used to discriminate sulfur sources in the atmosphere (Guan et al., 2015; Liu et al., 2009; Xiao et al., 2008, 2009). However, the δ³⁴S of soil sulfate is largely affected by atmospheric deposition (Xiao et al., 2015). For instance, the δ³⁴S value of sulfate in rain (−4.9‰) was very similar to the soil sulfate (−5.5‰) in Guiyang city. It was caused by coal-derived atmospheric sulfur deposition (Guan et al., 2015; Xiao and Liu, 2011; Xiao et al., 2011). Hence, the δ³⁴S of sulfate is not distinct enough to determine sulfate sources (soil sulfate, atmospheric sulfate or SO₂ oxidation) in plant leaves. The analysis of oxygen isotopic compositions of sulfate in plant leaves may solve this problem. This is because SO₂ oxidation causes only small fractionations in sulfur isotopes, but it causes large fractionations in the oxygen isotopic values (Jamieson and Wadleigh, 1999). The oxygen isotopic composition is determined by the particular pathway utilized and involved oxidants (O₃, O₂, OH, metal) (Bao, 2015; Holt et al., 1981, 1982; Seinfeld and Pandis, 2012). Once formed, the sulfate retains the oxygen isotopic compositions of its formation mechanism since sulfate is very stable and undergoes little or no isotopic exchange under normal atmospheric conditions (pH = 4–8; Temperatures = −40–40 °C) (Chiba and Sakai, 1985; Jamieson and Wadleigh, 1999; Lloyd, 1968). More than that, little sulfur and oxygen isotopic fractionation of soil sulfate occurs during either the uptake by the roots or the transfer to the leaves (Forstel and Hutzen, 1983; Guan et al., 2015; White et al., 1985).

In this study, we investigated the sulfate isotopic compositions (δ³⁴S and δ¹⁸O) in the needles of *P. massoniana* collected from Guiyang and Yunnan in southwestern China. The aims of this work were to determine whether the isotopic compositions in the needles of *P. massoniana* can be used to assess the contributions of various sources of sulfate in plant tissues. Further, we expect to calculate the contribution rates of various sources of sulfate in the needles by δ¹⁸O of sulfate in the needles.

2. Materials and methods

2.1. Study area

Needles and soil samples were collected from two areas, Yunnan (including Jinning, Kunming and Qujing Districts) and Guiyang (Fig. 1a). The latter area was severely polluted by SO₂ and frequent acid rain, the average pH (4.43) of precipitation water from 2005 to 2010 was much lower than the pH standard of acid rain (5.6) (Luo et al., 2013). But acid rain was rarely observed in the former area, where the average pH of precipitation was 6.43 from 2000 to 2010 (Yunnan Environmental Protection Bureau, 2011). The atmospheric SO₂ concentrations were higher in Guiyang than in Yunnan in 2011 (Table 1).

2.2. Sample collection and treatment

Samples were collected in April 2012. The *P. massoniana* was selected because it meets many of the requirements of a good bioindicator plant. This easily identifiable species is widely distributed in China and has been used in previous bioindication studies (Legge et al., 1988). Soils and Pinus needles were sampled in three sites in Yunnan (Jinning,

Kunming and Qujing), and three sites in the Guiyang. All the sampling sites were in the suburbs, away from the main road, and away from point pollution sources. Trees of similar ages (approximately 20 years) and sizes (approximately 10–15 m in height) were selected to reduce the influence of canopy height and soil depth of the roots between sampling trees. Only green, healthy samples were taken, avoiding yellow or dark needles. Leaves were collected from the outer branches in the east, south, north, and west directions (approximately 12 m above the ground). For each type of needle, we collected five to eight representative samples from one to three selected trees at each site. Sampling was performed under the weather conditions of no rain. Two to three soil samples (approximately 100 g) were collected from the topmost 10 cm soil (soil below plant) layer with a high density of roots after sampling the leaves at each site, and the roots and needle litter were removed immediately. In addition, needle and soil samples were taken with different distances from two point polluted areas (the Kunming Steel Plant and Qujing Power Plant), and all the sampling sites were downwind from the industrial plants (Fig. 1b). The two point polluted areas were > 20 km away from the other sampling areas.

All fresh samples were put into plastic bags, labeled and stored immediately in an insulated, chilled box. In the laboratory, all washed plant samples were freeze-dried, and all soil samples were dried at 80 °C for 24 h. Finally, all samples were pulverized for homogenization. The plant powder samples were stored in liquid nitrogen before use. The soil samples were preserved in a desiccator.

2.3. Determination of concentrations and isotopic compositions of sulfate

For concentrations determination and isotopic analysis of the soluble sulfate in needles and soils, 5 g of air-dried powdered samples were weighed and put into an agate mortar and ground with quartz sand. Then, the sample was transferred into a 125 ml extraction vessel and extracted in 30 ml of boiling Milli-Q water on a reciprocating shaker for 12 h. The extract was filtered twice through a Whatman No. 42 filter paper, and the residue on the filter was carefully rinsed with enough boiling Milli-Q water to transfer all water-soluble sulfate into the filtrate. This water extraction method is a modification of the boiling acid extraction method developed by Kelly and Lambert (1972) and Richter and Johnson (1983). Boiling acid was not used because appreciable amounts of hydrolyzable organic sulfates are present in the extract obtained using boiling HCl. A 10 ml aliquot of filtrate was stored for determination of the water-soluble sulfate content by ion chromatography (Dionex ICS-1100, USA). The limit of detection was 0.01 mg l^{−1} SO₄^{2−}. Another aliquot of filtrate was transferred into a 500 ml beaker; 10 ml of 1 mol l^{−1} hot HCl was added, and the solution was heated to boiling to remove CO₃^{2−}. Then, 10 ml of 2 mol l^{−1} BaCl₂ was added, and boiling continued for 2 h. After precipitating for 24 h, the mixture was filtered through a dense ashless quantitative filter paper. The precipitate (BaSO₄) on the filters was carefully rinsed with enough Milli-Q water to remove Cl (silver nitrate was used to monitor), then transferred into crucibles with the filters and combusted at 850 °C for 1 h in air. No any other phase in the white powder in the crucible was detected by XRD. The BaSO₄ was weighed into tin capsules for δ³⁴S measured and weighed into silver capsules for δ¹⁸O measured, respectively.

The sulfur and oxygen isotope measurements (δ³⁴S and δ¹⁸O) were performed at the Institute of Geochemistry, Chinese Academy of Sciences, using a combustion elemental analysis with on-line continuous-flow isotope ratio mass spectrometry (EA-C-CF-IRMS, EA IsoPrime, Euro3000, GV instruments, UK). The δ³⁴S values are expressed in the standard delta notation relative to the Vienna Canyon Diablo Troilite standard (VCDT) and the δ³⁴S measurements were calibrated against the reference materials NBS127 (δ³⁴S = 21.7 ± 0.12‰, n = 10), the reproducibility of the measurements was better than ± 0.2‰. The δ¹⁸O values are reported in the standard delta notation against the Vienna Standard Mean Ocean Water

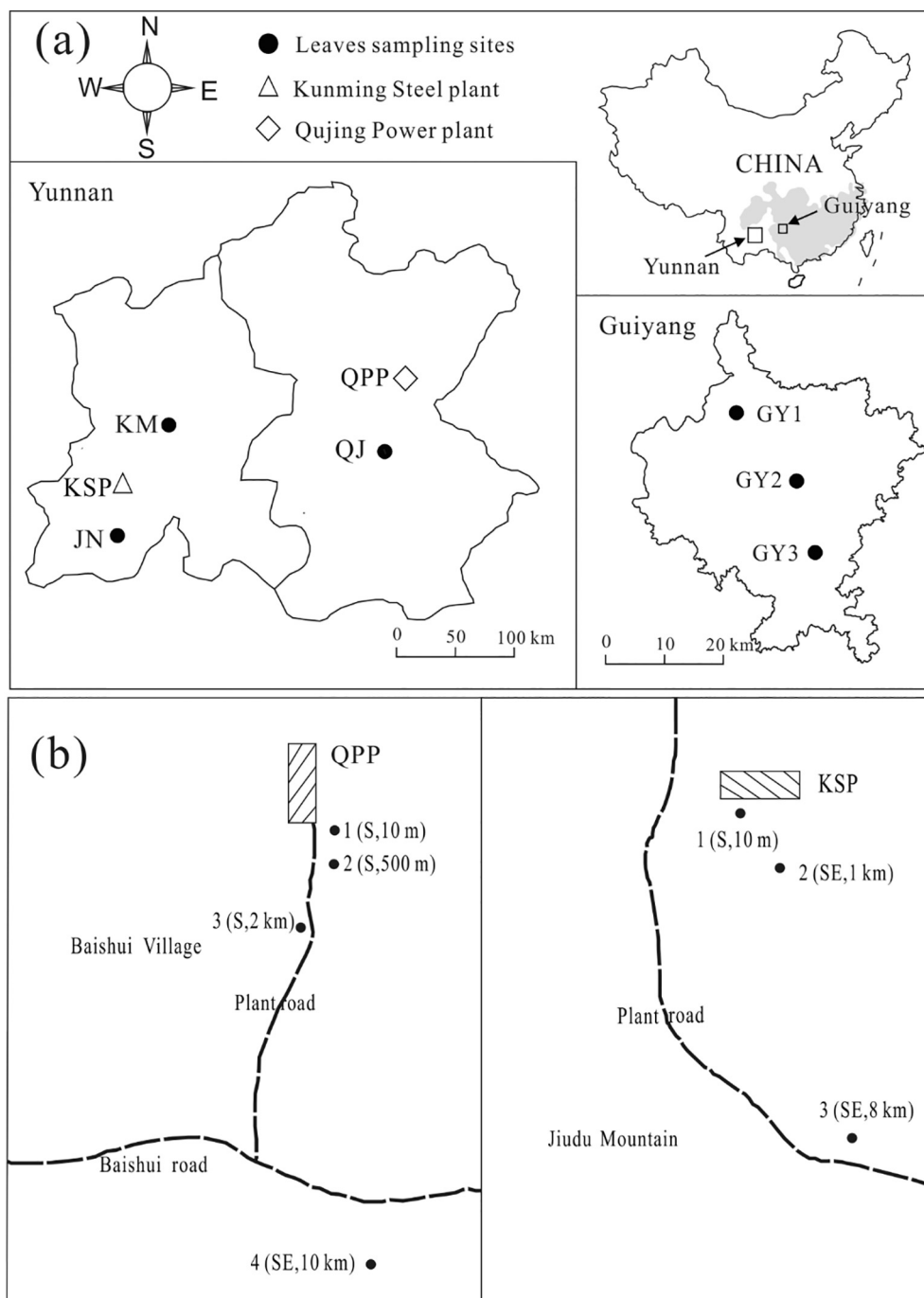


Fig. 1. Skeleton map showing the sampling sites. The shaded regions represent areas where acid rain was measured ($\text{pH} < 5$) (revised from the [Guiyang Environmental Protection Bureau, 2006](#)). JN, Jinning; KM, Kunming; QJ, Qujing; GY1-3, Guiyang; KSP, Kunming Steel Plant; and QPP, Qujing Power Plant.

(VSMOW) and the calibration of $\delta^{18}\text{O}$ measurements was performed using the reference material NBS127 ($\delta^{18}\text{O} = 8.59 \pm 0.25\text{‰}$, $n = 10$), the reproducibility of the measurements was better than $\pm 0.3\text{‰}$.

2.4. Analysis of oxygen isotopic compositions of leaf-water

Water was extracted from leaves by cryogenic vacuum distillation ([Martín-Gómez et al., 2015](#); [West et al., 2006](#)). The process of cryogenic vacuum distillation extracts all the water from a sample and freezes it into a collection tube. During this process, all volatile compounds are co-distilled with the water under the sample-tube conditions (vacuum and high temperature). The analyses were performed on a liquid water isotope analyzer (DLT-100) from Los Gatos Research (Mountain View,

CA, USA). Microliter quantities of water were injected into a vaporization chamber and then passed into an infrared absorbance cavity. The isotope ratios ($\delta^{18}\text{O}$) are calculated from the spectral absorbance at specific wavelengths using off-axis integrated cavity output spectroscopy (OA-ICOS) ([Lis et al., 2008](#)). The estimated precision for the DLT-100, based on the repeated analysis of four reference water samples, was 0.1‰ for $\delta^{18}\text{O}$. In order to remove the existence of interference problems in the water isotopic analyses with the laser methodology related to the salinity and the organic matter content, the post-processing correction of isotope values method was used to correct the measured $\delta^{18}\text{O}$ values of leaf-water ([Martín-Gómez et al., 2015](#)).

Table 1The average sulfate concentrations in needles, and soils and the average $\delta^{18}\text{O}$ values of leaf water in different sampling sites.

Areas	Sampling sites	SO ₂ conc. ($\mu\text{g m}^{-3}$)	Needles sulfate conc. (g/kg)	Soil sulfate conc. (g/kg)	Leaf water $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)
Guiyang	Guiyang	80 ^a	1.10 ± 0.50	0.40 ± 0.03	-7.2 ± 2.3
Yunnan	Qujing	63 ^a	0.40 ± 0.30	0.50 ± 0.10	-15.7 ± 3.1
	Kunming	37 ^a	0.40 ± 0.20	0.30 ± 0.09	-11.6 ± 2.4
	Jinning	10 ^a	0.20 ± 0.20	0.10 ± 0.06	-7.9 ± 2.3
KSP	KSP (10 m)	-	1.60	0.23	-11.5
	KSP (1000 m)	-	0.20	0.20	-10.7
	KSP (8000 m)	-	0.02	0.17	-12.2
QPP	QPP (10 m)	-	0.42	0.23	-15.8
	QPP (500 m)	-	0.19	0.25	-15.1
	QPP (2000 m)	-	0.16	0.18	-14.6
	QPP (10,000 m)	-	0.06	0.34	-15.2

- No data; KSP: Kunming Steel Plant; QPP: Qujing Power Plant.

^a From the [Guiyang Environmental Protection Bureau \(2012\)](#) and [Yunnan Environmental Protection Bureau \(2012\)](#).

2.5. Estimate of the contribution of SO₂ oxidation to the sulfate in needles

The process of SO₂ oxidation into sulfate in needles can be represented according to previous research as ([Hüve et al., 1995](#); [Pfanzen et al., 1987](#); [Trust and Fry, 1992](#)):



The oxygen isotopic compositions of portion of needles sulfate which derived from SO₂ oxidation ($\delta^{18}\text{O}_{\text{SO}_2\text{-derived}}$) can be described as follows ([Böttcher et al., 2001](#); [McCarthy et al., 1998](#)):

$$\delta^{18}\text{O}_{\text{SO}_2\text{-derived}} = m (\delta^{18}\text{O}_{\text{H}_2\text{O}} + \epsilon_{\text{H}_2\text{O}}) + (1 - m) (\delta^{18}\text{O}_{\text{O}_2} + \epsilon_{\text{O}_2}) \quad (5)$$

where m is the fraction of oxygen contributed by H₂O. In this oxidation process, rapid equilibration occurs between SO₂ (g) and leaf-water (Eq. (1)) meaning the SO₂ (g) retains none of its initial oxygen isotopic compositions ([Jamieson and Wadleigh, 1999](#)). The $\delta^{18}\text{O}$ value of the SO₄²⁻ derived from the oxidation of SO₂ is dependent on the $\delta^{18}\text{O}$ value of the leaf-water ([Jamieson and Wadleigh, 1999](#); [Novák et al., 2007](#)). Furthermore, [Holt et al. \(1979\)](#) found that the water contributed (indirectly or directly) about 75% of the SO₄²⁻ (aq) oxygen. The ϵ in Eq. (5) is the kinetic or equilibrium isotope enrichment factor for each oxygen source, and the enrichment factors for this oxidation processes have been determined experimentally ($\epsilon_{\text{O}_2} = -9.7$ and $\epsilon_{\text{H}_2\text{O}} = 0$) ([Holt et al., 1981](#); [Van Stempvoort and Krouse, 1994](#)). In this oxidation process, because of occurring inside the chloroplast, and only with the light conditions ([Hüve et al., 1995](#); [Pfanzen et al., 1987](#); [Trust and Fry, 1992](#)), almost all the dissolved O₂ that participated in reaction (4) was produced by photosynthesis, and [Vinogradov et al. \(1959\)](#) concluded that photosynthesis produces O₂ with similar $\delta^{18}\text{O}$ to that of the associated water. This view was substantiated by later experiments ([Guy et al., 1993](#); [Helman et al., 2005](#); [Luz and Barkan, 2005](#)).

Normally, the water-soluble sulfate in needles is mainly derived from soil sulfate and atmospheric SO₂ oxidation (see [Section 4.1](#)). Therefore, according to isotopic mass conservation, the balance of the oxygen isotopes of sulfate between the needles and sources (soils and SO₂ oxidation) can be represented as follows:

$$\delta^{18}\text{O}_{\text{needles}} = x \cdot \delta^{18}\text{O}_{\text{SO}_2\text{-derived}} + (1 - x) \cdot \delta^{18}\text{O}_{\text{soil}} \quad (6)$$

where x is the contribution of SO₂ oxidation, $1 - x$ is the contribution from the soil, $\delta^{18}\text{O}_{\text{soil}}$ is the $\delta^{18}\text{O}$ of sulfate in the soil, and $\delta^{18}\text{O}_{\text{needles}}$ is the $\delta^{18}\text{O}$ of sulfate in the needles.

In certain areas, such as the two point sources (Kunming Steel Plant and Qujing Power Plant), the water-soluble sulfate in needles can be represented as follows:

$$\delta^{18}\text{O}_{\text{needles}} = x \cdot \delta^{18}\text{O}_{\text{SO}_2\text{-derived}} + y \cdot \delta^{18}\text{O}_{\text{soil}} + z \cdot \delta^{18}\text{O}_{\text{P}} \quad (7)$$

$$x + y + z = 1 \quad (8)$$

where x is the contribution from SO₂, y is the contribution from the soil, z is the contribution from primary sulfate (generated in the flues at very high temperature), $\delta^{18}\text{O}_{\text{soil}}$ is the $\delta^{18}\text{O}$ of sulfate in the soil, $\delta^{18}\text{O}_{\text{needles}}$ is the $\delta^{18}\text{O}$ of sulfate in the needles, and $\delta^{18}\text{O}_{\text{P}}$ is the $\delta^{18}\text{O}$ of primary sulfate.

3. Results

3.1. Soluble sulfate concentrations in needles and soils

Soluble sulfate concentrations in the needles under different areas varied from 0.01 g/kg to 2.40 g/kg ([Table 1](#)). The average needle sulfate concentrations in Guiyang (1.10 g/kg) area polluted the most by acid rain were significantly higher than that in three Yunnan areas (0.40 g/kg) ([Table 1](#)). The mean needle sulfate concentrations in Jinning (0.20 g/kg) where could be considered pristine were the lowest in all sampling sites, and this pattern of sulfate concentrations can be clearly related to the SO₂ level in the atmosphere. The sulfate concentrations in soils ranged between 0.10 g/kg and 0.50 g/kg ([Table 1](#)) with a mean of 0.30 g/kg. The soil sulfate concentrations from different areas did not show significant differences ($P > 0.05$).

A trend of dramatically decreasing in the needle sulfate concentrations with increasing distance from the point polluted areas (Kunming Steel Plant and Qujing Power Plant) was found, with the highest mean determined for the site closest to the two industrial plants ([Table 1](#)). The sulfate concentrations in soils ranged from 0.17 g/kg to 0.34 g/kg around the two industrial plants. Unlike the needles sulfate, the soil sulfate concentrations did not change significantly with the distance to the industrial plants ($P > 0.05$).

3.2. The $\delta^{34}\text{S}$ values of sulfate in the needles and soil

The $\delta^{34}\text{S}$ of sulfate in the needles under different areas varied widely from -14.5‰ to +7.3‰ ([Table S1](#)). The mean $\delta^{34}\text{S}$ values in Guiyang sites (-7.2‰) was significantly lower than that in Yunnan areas (+2.3‰). The same trend also was found in the soils, the $\delta^{34}\text{S}$ values of sulfate in soils averaged -5.8‰ in Guiyang areas, significantly lower than that in Yunnan areas (+1.2‰). In Yunnan areas, the mean soil sulfate $\delta^{34}\text{S}$ values varied widely from -4.3‰ to +5.2‰, with the lowest at Qujing and the highest at Jinning sites. The $\delta^{34}\text{S}$ values of sulfate in the needles were not significant different than the soils. Furthermore, the former was found to be significantly correlated with the latter ($y = 1.17x + 0.24$, $R^2 = 0.88$, $P < 0.05$) ([Fig. 2a](#)).

Around the two industrial plants, the $\delta^{34}\text{S}$ of sulfate in the needles varied from -3.5‰ to +5.0‰ ([Table S1](#)). At Kunming Steel Plant sites, the needle $\delta^{34}\text{S}$ values of sulfate showed a slight gradient with

increasing distance from the industrial plant, with the more positive $\delta^{34}\text{S}$ values close to the Plant and the more negative $\delta^{34}\text{S}$ values in the most distant site, clearly indicating that this may be caused by S deposition with a high $\delta^{34}\text{S}$. Whereas at Qujing Power Plant sites, the needle $\delta^{34}\text{S}$ values of sulfate strongly increased with distance from the power plant and significantly more negative than those at Kunming Steel Plant. The soil sulfate $\delta^{34}\text{S}$ values ranged between -6‰ and $+8.1\text{‰}$ at two industrial plants sites. The $\delta^{34}\text{S}$ values of sulfate in the needles were also found to be significantly correlated with that in the soils ($y = 0.56x - 0.14$, $R^2 = 0.96$, $P < 0.05$) (Fig. 2c).

3.3. The $\delta^{18}\text{O}$ values of sulfate in the needles and soil

The $\delta^{18}\text{O}$ values of sulfate in the needles from different areas varied from -12.5‰ to $+5.4\text{‰}$ (Table S1). Different with the $\delta^{34}\text{S}$ values, almost all of the $\delta^{18}\text{O}$ values of sulfate in the needles were negative (Fig. 3a). The $\delta^{18}\text{O}$ values in Guiyang (-3.4‰) were higher than those in Yunnan (-7.6‰). The sulfate in needles at Qujing had the lowest $\delta^{18}\text{O}$ value (-10.3‰) and Guiyang had the highest value (-3.8‰). Unlike the needles, most the $\delta^{18}\text{O}$ of sulfate in the soil were positive values and no much change except Jinning sites (Fig. 3a). Therefore, there is no correlation between the $\delta^{18}\text{O}$ values of sulfate in the needles and that in the soils ($y = 0.55x - 3.67$, $R^2 = 0.21$, $P = 0.13$) (Fig. 2b).

The $\delta^{18}\text{O}$ values of sulfate in the needles at the more distant sites decreased markedly around the two industrial plants. For instance, at the Kunming Steel Plant, the needle $\delta^{18}\text{O}_{\text{SO}_4}$ value was $+2.7\text{‰}$ at 10 m from the industrial plant, which was higher than that at 1000 m (-6.7‰) and 8000 m (-7.4‰) distance (Fig. 3b). In contrast, all the $\delta^{18}\text{O}$ values in the soil were positive and also changed little with the distance from the industrial plants (Fig. 3b). Hence, the difference between the $\delta^{18}\text{O}$ values of the soils and needles should increase with increasing distance from the industrial plants. Also no correlation was found between the $\delta^{18}\text{O}$ values of sulfate in the needles and that in the soils ($y = 0.13x - 3.82$, $R^2 = 0.008$, $P = 0.7$) (Fig. 2d).

3.4. The $\delta^{18}\text{O}$ values of leaf-water in the needles

The mean $\delta^{18}\text{O}$ values of leaf-water in Guiyang (-7.2‰) was higher than that in Yunnan (-11.7‰) (Table 1). The most negative $\delta^{18}\text{O}$ values were found at Qujing (averaging -15.7‰), followed by Kunming (averaging -11.6‰). The needles collected at Jinning had a mean $\delta^{18}\text{O}$ value (-7.9‰) that was similar to that at Guiyang (-7.2‰). Similar to the $\delta^{18}\text{O}$ values of sulfate, all the $\delta^{18}\text{O}$ values of leaf-water were negative. Additionally, the $\delta^{18}\text{O}$ values of sulfate were significantly correlated with the $\delta^{18}\text{O}$ values of leaf-water ($y = 0.71x + 0.86$, $R^2 = 0.98$, $P = 0.01$) (Fig. 4). At the two point sources, however, the $\delta^{18}\text{O}$ values of leaf-water were nearly invariant with the distance from the two industrial plants, and the mean $\delta^{18}\text{O}$ value of leaf-water at the Kunming Steel Plant and Qujing Power Plant sites were -11.5‰ and -15.2‰ , respectively, which were close to the $\delta^{18}\text{O}$ values of leaf-water in Qujing and Kunming (Table 1).

3.5. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of sulfate in precipitation water

To better examine the needle sulfate sources, the $\delta^{18}\text{O}$ values of sulfate in atmospheric precipitation water over Guiyang from October 2008 to September 2009 were measured. The $\delta^{34}\text{S}$ of sulfate in precipitation water varied widely from -12.0‰ to $+9.4\text{‰}$, average for -2.8‰ . Unlike the large range of $\delta^{34}\text{S}$ values in precipitation water, the $\delta^{18}\text{O}$ values were ranged from $+12.1\text{‰}$ to $+16.0\text{‰}$ and also exhibited a relatively weak variation with high values in winter and low values in summer. Therefore, the $\delta^{18}\text{O}$ values of sulfate in precipitation water were higher than the $\delta^{18}\text{O}$ values of sulfate in needles.

3.6. The $\delta^{18}\text{O}_{\text{SO}_2\text{-derived}}$ values and the contribution of atmospheric SO_2 oxidation to sulfate in needles

The Eqs. (5) and (6) in Section 2.5 were used to calculate the $\delta^{18}\text{O}_{\text{SO}_2\text{-derived}}$ values and the contribution of atmospheric SO_2

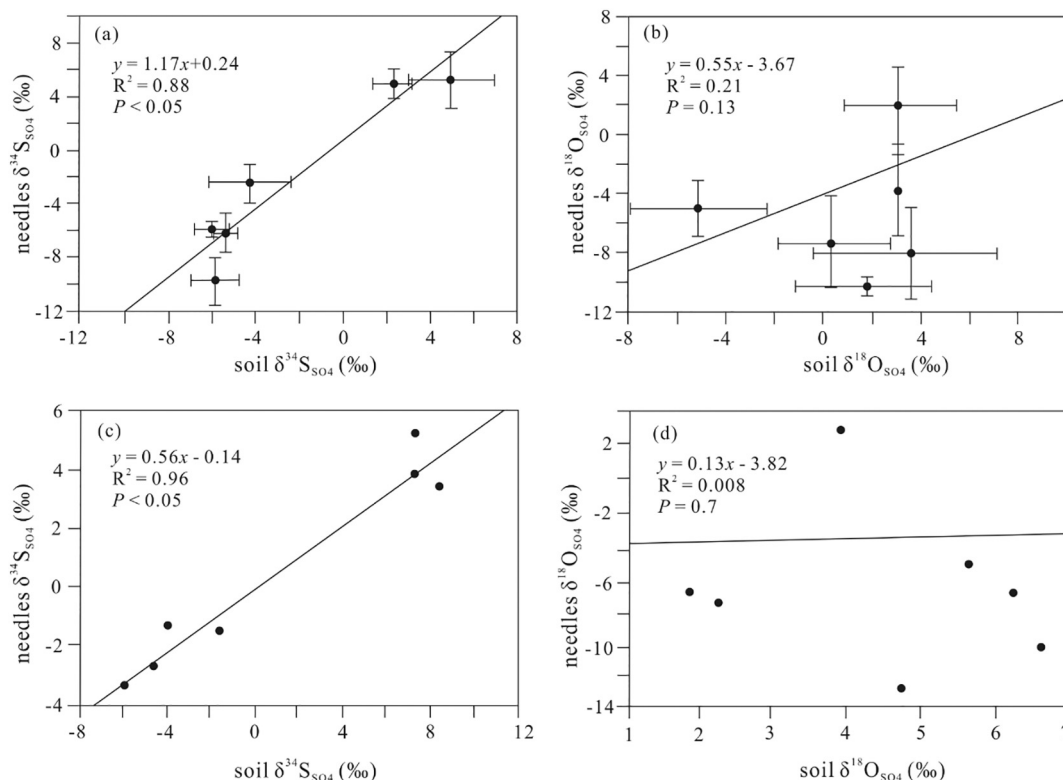


Fig. 2. Relationship between $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in needles and soil sulfate, respectively for a) $\delta^{34}\text{S}$ in different areas, b) $\delta^{18}\text{O}$ in different areas, c) $\delta^{34}\text{S}$ in two point polluted sites, d) $\delta^{18}\text{O}$ in two point polluted sites. The vertical lines represent standard deviations.

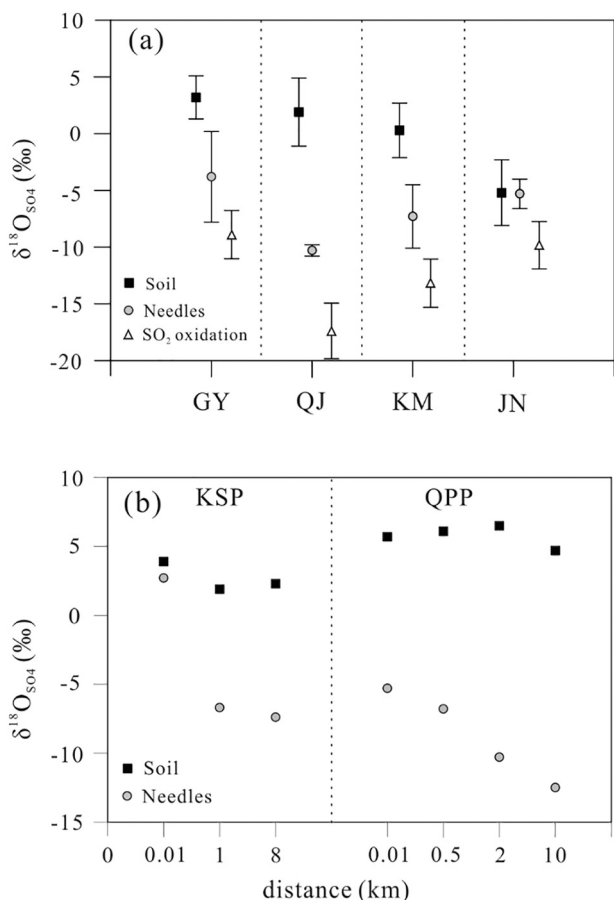


Fig. 3. Variation in $\delta^{18}\text{O}$ in the needles, soil and the calculated SO_2 oxidation sulfate. Sampling sites in a) are arranged such that the atmospheric SO_2 concentrations increases from left to right. Sampling sites in b) are arranged such that the distance from the industrial plants increases from left to right. The letters refer to the same locations as in Fig. 1.

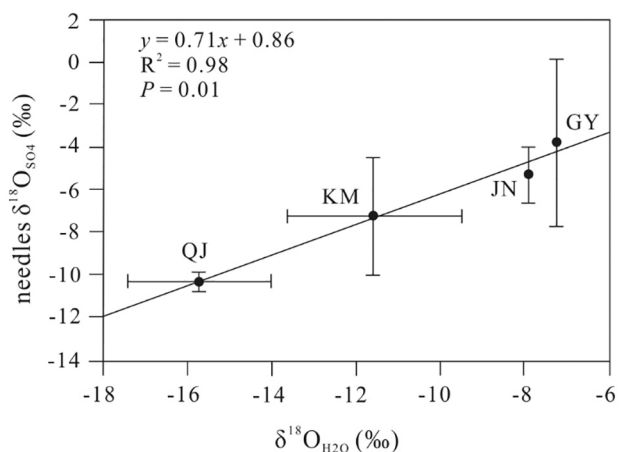


Fig. 4. Relationships between the $\delta^{18}\text{O}$ of leaf water and the $\delta^{18}\text{O}$ of water-soluble sulfate in the needles. The vertical lines represent standard deviations. The letters refer to the same locations as in Fig. 1.

oxidation to needle sulfate, respectively. According to the discussions in Section 2.5, the fraction (m) was approximately equal to 0.75, the kinetic or equilibrium isotope enrichment factors (ϵ_{O_2} and $\epsilon_{\text{H}_2\text{O}}$) for this oxidation processes were equal to -9.7 and 0 , respectively. The dissolved O_2 that participated in this oxidation processes was produced by photosynthesis in chloroplast, the $\delta^{18}\text{O}_{\text{O}_2}$ equal to $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. Thus only one variable ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) in Eq. (5) and the $\delta^{18}\text{O}_{\text{SO}_2\text{-derived}}$ values were

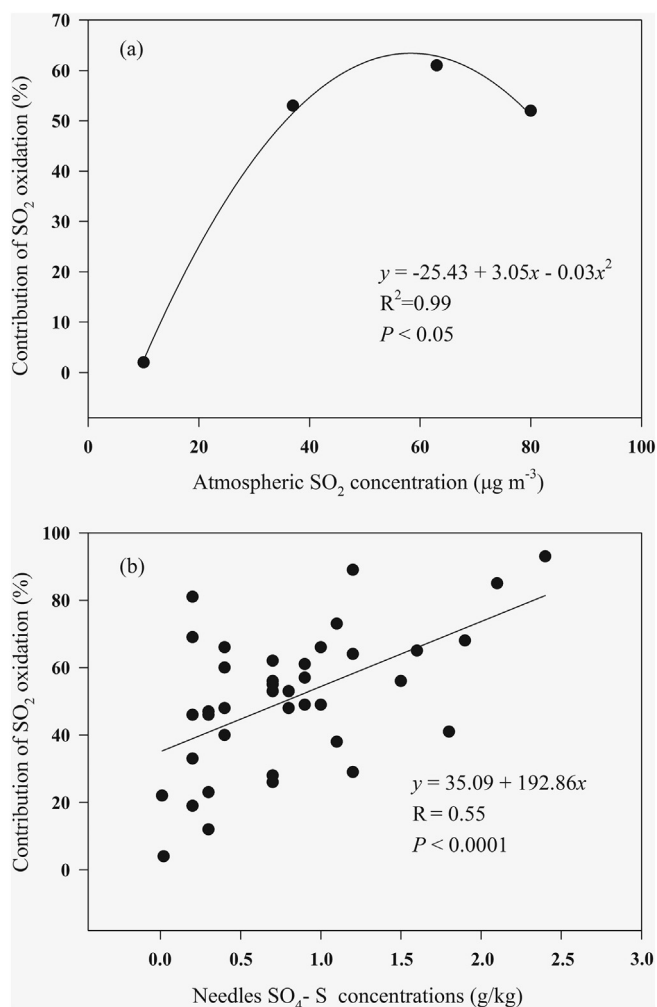


Fig. 5. Variation in the contribution of SO_2 to water-soluble sulfate in the needles with a) the atmospheric SO_2 concentration at four sampling areas, b) the needles water-soluble sulfate concentrations.

calculated by measured $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values. The calculated $\delta^{18}\text{O}_{\text{SO}_2\text{-derived}}$ values ranged from -20.4‰ to -4.0‰ (Table S1), which were more negative than the $\delta^{18}\text{O}_{\text{SO}_4}$ values of the needles and the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of leaf water (Fig. 3a).

In Eq. (6), the $\delta^{18}\text{O}_{\text{needles}}$ and $\delta^{18}\text{O}_{\text{soil}}$ values were determined, and the $\delta^{18}\text{O}_{\text{SO}_2\text{-derived}}$ values were calculated. Thus the contributions of SO_2 oxidation to needle sulfate (x) could be calculated. The contributions of atmospheric SO_2 to the sulfate in needles (Eq. (6)) collected from Guiyang and Yunnan averaged 52% and 38%, respectively. Among the three Yunnan sites, the highest mean contribution was found at Qujing (61%), and the lowest was observed at Jinning (2%). The mean contributions of atmospheric SO_2 oxidation to the sulfate in needles were parabolic with increased concentrations of atmospheric SO_2 (Fig. 5a). When SO_2 concentrations were $< 60 \mu\text{g m}^{-3}$, the contributions sharply increased with the increase of SO_2 concentrations, while the contributions slightly declined when SO_2 concentrations $> 60 \mu\text{g m}^{-3}$. Not only that, the contributions had significant positive correlation with sulfate concentrations in needles at all sampling sites (Fig. 5b).

4. Discussion

4.1. Using $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ to identify sulfur sources in needles

The potential sources of sulfate in needles are: soil sulfate, SO_2 oxidation and atmospheric sulfate (in particulates and precipitation

water) (Bao et al., 2009; Cicek and Koparal, 2004; Maruyama-Nakashita et al., 2004; Takahashi et al., 1997). Generally, in some of the remote areas with no serious SO₂ pollution, the sulfate taken up by the roots from soil is the main source for plants (Maruyama-Nakashita et al., 2004; Takahashi et al., 1997). For instance, Li et al. (2013) reported that the total sulfur concentration in mosses was as low as 0.20 g/kg in Gaoan, and the $\delta^{34}\text{S}$ value in mosses (+5.7‰) was similar to that in soil (+6.7‰). Thus they suggested that Gaoan was not affected by anthropogenic sulfur. Based on the research of Xiao et al. (2008), the very low measured sulfur concentration in mosses (0.20 g/kg) which located in Sichuan province at an altitude of 3276 m site could be used as the background value which not affected by anthropogenic sulfur. Similarly, in this study, we found that the sulfate concentration in needles was quite low as 0.20 g/kg at Jinning sites, and as expected, the $\delta^{34}\text{S}$ value in needles (+4.9‰) was very close to that in soil (+5.2‰). In most of cases, bedrock contributions are the most dominant to sulfate in soil. Karst areas in and around Yunnan-Guizhou Plateau in southwestern China are at the center of the Southeast Asian karst region, where the continuous outcrop area of carbonate rocks is the largest worldwide (Xu and Liu, 2007). The major soil types in the karst areas of southwest China are limestone soil and zonal yellow soil (following the Chinese soil classification), and the parent materials are carbonate rocks (Liu, 2009; Zhang et al., 2014). The $\delta^{34}\text{S}$ value in these carbonate rocks was fairly positive ($\approx +20.0\%$) and the same as the other common minerals in this soil like gypsum ($> +20.0\%$) (Liu et al., 2008). Therefore, the positive soil $\delta^{34}\text{S}$ values were mainly affected by bedrock at Jinning sites. Unlike Jinning, the negative soil $\delta^{34}\text{S}$ values (-5.8%) might be greatly affected by atmospheric wet and dry deposition in Guiyang areas (Liu et al., 2008; Zhang et al., 2014). More than that, the $\delta^{18}\text{O}$ value in needles (-5.3%) were also similar to soil (-5.2%) at Jinning. This was further evidence that the sulfate in needles mainly derived from soil in the remote areas is not affected by inputs of anthropogenic sulfur. Interestingly, soil at the Jinning sites was significantly depleted in ^{18}O relative to the $\delta^{18}\text{O}$ values observed at all other sites. Possibly, the Jinning sites located in forest, the soil sulfate may have been converted to carbon-bound S compounds. During the subsequent reoxidation of these organic S compounds, new oxygen atoms can be incorporated into the generated sulfate molecule, as sulfide oxidation (Mayer, 2005).

In contrast, in most urban areas, atmospheric sulfur from SO₂ and particulates can also be used as sulfur nutrients if the sulfate supply to the roots from the soil is limited, especially when SO₂ concentrations are high due to air pollution (Cicek and Koparal, 2004). In this study, whether at different levels of atmospheric sulfur deposition areas or around the two point pollution sources, the $\delta^{34}\text{S}$ values of sulfate in the needles were linearly correlated with that in the soils (Fig. 2a, c). However, the $\delta^{18}\text{O}$ values of sulfate in the needles were very much different than soil and there was no correlation between them (Fig. 2b, d). Similar results were found by Jędrysek et al. (2002), the $\delta^{34}\text{S}$ values of spruce needles show a very good correlation to the abundance of dust on needles. In their opinion, higher abundances of dust during dry conditions may limit foliar gas exchange and cause higher $\delta^{34}\text{S}$ values in needles, whereas lower abundances of dust during humid weather conditions cause lower $\delta^{34}\text{S}$ values characterize a higher gas exchange rate and more dynamic conditions for the sulfur system in needles. While the $\delta^{18}\text{O}$ values decreases with increased formation of needles sulfate from atmospheric SO₂ (Jędrysek et al., 2002). In this study, the weather condition of Guiyang is very humid and year-round rainy whereas Yunnan is dry and rainless (Guiyang Environmental Protection Bureau, 2012; Yunnan Environmental Protection Bureau, 2012). Additionally, the similarity between $\delta^{34}\text{S}$ values of needles and coals found in Guiyang and Yunnan areas, indicated that $\delta^{34}\text{S}$ in needles was a good indicator of coal-derived atmospheric sulfur deposition (Guan et al., 2015). The $\delta^{34}\text{S}$ in soil sulfate is more or less affected by atmospheric deposition (Li et al., 2013; Xiao and Liu, 2004; Xiao et al., 2015). Hence, the similar values of $\delta^{34}\text{S}$ between needles and soil sulfate are

mainly attributed to the weather conditions and the $\delta^{34}\text{S}$ of atmospheric sulfur source. While the obviously different $\delta^{18}\text{O}$ values between needles and soil was mainly affected by redox processes of needles sulfate from atmospheric SO₂. The significantly ^{18}O -depleted sulfate in needles and different $\delta^{18}\text{O}$ values between needles and soil indicated a significant portion of needles sulfate was generated by oxidation of atmospheric SO₂ in polluted areas.

In theory, atmospheric sulfate (in particulates and precipitation water) is a nonnegligible sulfate source in needles, but it is difficult to absorb through the needle stomatal pores. This is because the stomatal pores are continuations of the air-filled intercellular system of plant organs and normally function for gas exchange only. Furthermore, all external surface of conifer leaves are covered with a layer of lipoidal substances which form a cuticle. These lipoidal substances prevent wetting by hydrophilic solutions. Under normal conditions, watery liquid and particulates, are therefore difficult to absorb through stomatal pores (Franke, 1964; Slovik et al., 1995). Our study appears to confirm this. The measured $\delta^{18}\text{O}$ value of atmospheric precipitation water over Guiyang from October 2008 to September 2009 ranged between 12.1‰ to 16.0‰, which is within the typical $\delta^{18}\text{O}$ value of atmospheric precipitation water ranges between 7.0‰ to 18.0‰ (Mayer, 2005). Obviously, the ^{18}O -depleted sulfate source in the needles cannot be atmospheric sulfate and negligible amounts of sulfate in needles are derived from atmospheric sulfate. In conclusion, a substantial part of the sulfate in the needles could therefore be derived from atmospheric SO₂ oxidation in most sampling sites.

The sulfur and oxygen isotopic compositions relevant to environment studies were illustrated in Fig. 6 (Holt et al., 1982; Lee et al., 2002; Mayer, 2005; Mayer et al., 2010). The oxygen isotopic compositions of atmospheric sulfate is dependent on the oxidation conditions in the atmosphere and the $\delta^{18}\text{O}$ value of the moisture involved in the oxidation of precursors compounds such as SO₂. The oxygen isotopic compositions of sulfate generated by sulfur compound oxidation are often lower than those of sulfate from evaporitic or atmospheric sources and sulfate derived from oxidation of sulfur compound often has distinct isotopic compositions with comparatively low $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values (Mayer, 2005). During the oxidation of SO₂ to SO₄²⁻, rapid equilibration occurs between SO₂ (g) and associated water, that made the SO₂ (g) retains none of its initial oxygen isotopic compositions (Jamieson and Wadleigh, 1999). Then four oxygen atoms are incorporated into the newly formed sulfate, which are either derived from H₂O or O₂. The proportion of water and atmospheric oxygen incorporated into the sulfate molecule is dependent on whether the reaction occurs abiologically or biologically under reducing or oxidizing

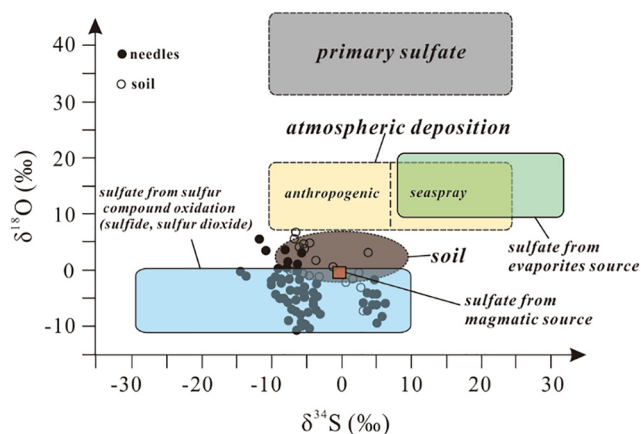


Fig. 6. Typical ranges for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of sulfate from a) evaporites, b) atmospheric deposition, c) soil solutions, d) sulfide and sulfur dioxide, e) magmatic sources and f) primary sulfate (Holt et al., 1982; Lee et al., 2002; Mayer, 2005; Mayer et al., 2010). The solid circles represent the water-soluble sulfate in needles and the empty circles represent the soil sulfate in this study.

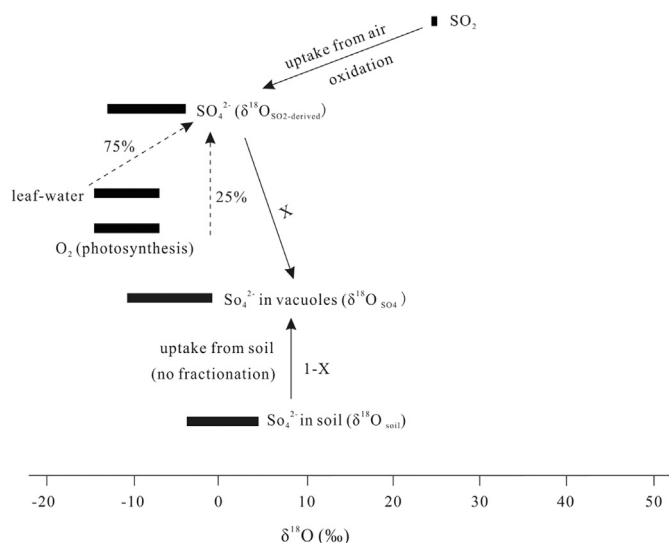


Fig. 7. Variations in $\delta^{18}\text{O}$ of the water-soluble sulfate from different sources in needles collected at the four sampling areas. x represents the contribution of SO_2 to water-soluble sulfate in the needles. Leaf water and O_2 produced by photosynthesis contributed to 75% and 25% of the sulfate that was oxidized by SO_2 ($\delta^{18}\text{O}_{\text{SO}_2\text{-derived}}$), respectively.

conditions (e.g. Taylor and Wheeler, 1994; Taylor et al., 1984). In this study, the $\delta^{18}\text{O}$ values of sulfate in needles were significantly correlated with the $\delta^{18}\text{O}$ values of leaf-water, and as noted in Fig. 6, most of needles sulfate has lower $\delta^{34}\text{S}$, particularly lower $\delta^{18}\text{O}$ values than the atmospheric sulfate and soil, which is fully consistent with previous studies. All the results indicate that the oxidation of SO_2 is a very important source of sulfate in needles.

4.2. Using $\delta^{18}\text{O}$ for contribution estimations

During the oxidation of atmospheric SO_2 into sulfate in needles, both SO_2 (g) and HSO_3^- (aq) equilibrate rapidly with water, meaning that the products retain none of the initial oxygen isotopic compositions (Jamieson and Wadleigh, 1999). Sulfate formed in this manner should exhibit a positive correlation between $\delta^{18}\text{O}_{\text{SO}_4}$ and the associated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (Longinelli and Bartelloni, 1978), which was also found in this study (Fig. 4). This indicated that the considerable $\delta^{18}\text{O}$ values of sulfate may be related to a variation in the $\delta^{18}\text{O}$ values of leaf-water. The variations in $\delta^{18}\text{O}$ from different sulfate sources to the needles from different areas are shown in Fig. 7. Consequently, the contribution of atmospheric SO_2 oxidation to the sulfate in the needles can theoretically be determined.

As we expected, the contributions of atmospheric SO_2 oxidation to the sulfate in the needles were consistent with the discussion in Section 4.1. At remote areas like Jinning, the SO_2 concentration was quite low so as the sulfate concentration in needles, the contribution of SO_2 oxidation to the needles sulfates close to 0%. In contrast, the SO_2 concentration was very high so as the sulfate concentration in needles at urban areas like Guiyang, the contribution of SO_2 oxidation to the needles sulfate reached about 50%. As previously shown, the sulfate concentration in needles is a reliable indication of ambient SO_2 pollution level (Guan et al., 2015). Hence, the result demonstrated that the higher SO_2 pollution level, the greater contributions of SO_2 oxidation to the needle sulfate. In other words, sulfate in needle is mainly derived from soil in the remote areas with low SO_2 pollution levels and partly derived from SO_2 oxidation in industrial cities with high SO_2 pollution levels. It was worth noting that the contributions of SO_2 oxidation slightly declined when SO_2 concentrations $> 60 \mu\text{g m}^{-3}$ (Fig. 5a). The stomatal diffusion resistance of plant leaves increased with the increase of SO_2 concentration. The higher the SO_2 concentration was, the greater

the stomatal diffusion resistance increased in a short time, thus the high SO_2 concentration would make leaves stomata close (Ashenden, 1979; Majernik and Mansfield, 1971). When the SO_2 concentration $> 60 \mu\text{g m}^{-3}$, partially needles stomata closed, thus the contributions of SO_2 oxidation declined. These corroborate that the estimation method of the contributions of SO_2 oxidation to the sulfate in needles was reasonable. The mean contribution of Guiyang was calculated to be 52% based on the oxygen isotope method (Fig. 5a), which was similar to that (82%) calculated based on the sulfur isotope balance method, assuming -7.5‰ for the $\delta^{34}\text{S}$ of both coal and SO_2 (Mukai et al., 2001). However, in Yunnan, the contributions estimated using the oxygen and sulfur methods greatly differed if the $\delta^{34}\text{S}$ values of coal in the area was assumed to be $+13.8\text{‰}$ (Xiao et al., 2011) potentially because coals combusted in this area originate from either local or other sources.

4.3. Oxygen isotopic signatures of water-soluble sulfate in needles near the point sources

The $\delta^{18}\text{O}$ values of sulfate in the needles at the more distant sites decreased markedly around all the two industrial plants, but almost all the $\delta^{18}\text{O}$ values in the soil were positive and also changed little with the distance from the industrial plants (Fig. 3b). This result was unexpected. Hence, the contributions of SO_2 oxidation to the sulfate in the needles also decreased with increasing distance from the two industrial plants. If the needle sulfate were only derived from soil sulfate and SO_2 oxidation, since the $\delta^{18}\text{O}$ values of leaf-water were very negative and nearly invariable with the distance from the two industrial plants, the $\delta^{18}\text{O}$ values of sulfate in the needles should increase with increasing distance from the two industrial plants. But it was actually quite the opposite. Therefore, around the two industrial plants, in addition to soil sulfate and SO_2 oxidation, the sulfate in the needles had other sources with positive $\delta^{18}\text{O}$ values.

The oxidation of SO_2 to SO_4^{2-} may occur within a combustion stack at high temperatures ($\approx 450^\circ\text{C}$) or at lower temperatures after emission of SO_2 to the atmosphere. The former is termed 'primary' sulfate, and the latter is termed 'secondary' sulfate. The primary sulfate (formed at high temperatures in combustion sources, e.g., power plants and smelters) is substantially enriched ^{18}O ($\delta^{18}\text{O} = +40.0\text{‰}$ to $+45.0\text{‰}$) as a result of the reactions that occur between atmospheric oxygen, water vapor, and SO_3 (g) at high temperatures (Holt et al., 1982; Lee et al., 2002), while the $\delta^{18}\text{O}$ values of secondary sulfate (formed in the atmosphere at lower temperatures by the heterogeneous and homogeneous oxidation of SO_2) range widely (-15.0‰ ~ $+30.0\text{‰}$) (Jamieson and Wadleigh, 1999). In this research, the measured $\delta^{18}\text{O}$ values of sulfate in precipitation water ($+12.1\text{‰}$ ~ $+16.0\text{‰}$) were able to represent the $\delta^{18}\text{O}$ values of secondary sulfate. Therefore, in addition to soil sulfate and SO_2 oxidation, the primary sulfate from discharged flue gases and secondary sulfate formed in the atmosphere might be the other sources of needle sulfate. However, almost all the $\delta^{18}\text{O}$ values of sulfate in the needles were negative. It suggested that the contribution of SO_2 oxidation was still dominant, but the changing trend of the sulfate $\delta^{18}\text{O}$ values in the needles might be caused by primary sulfate and secondary sulfate. The closer to the industrial plants, the primary sulfate and secondary sulfate concentrations were relative higher, the effect on the $\delta^{18}\text{O}$ values of needle sulfate was relatively greater. On the other hand, as shown in Fig. 8, whether the steel plant (Fig. 8a) or the power plant (Fig. 8b), the shorter the distance was to the industrial plants, the similar the $\delta^{34}\text{S}$ values of needle sulfate were to coal. Since the $\delta^{34}\text{S}$ of both primary sulfate and secondary sulfate depended on the $\delta^{34}\text{S}$ of the source (coal) (Jamieson and Wadleigh, 1999; Mayer, 2005), the variation $\delta^{34}\text{S}$ of needles sulfate further demonstrated that the needle sulfate around the industrial plants was affected by primary sulfate and secondary sulfate.

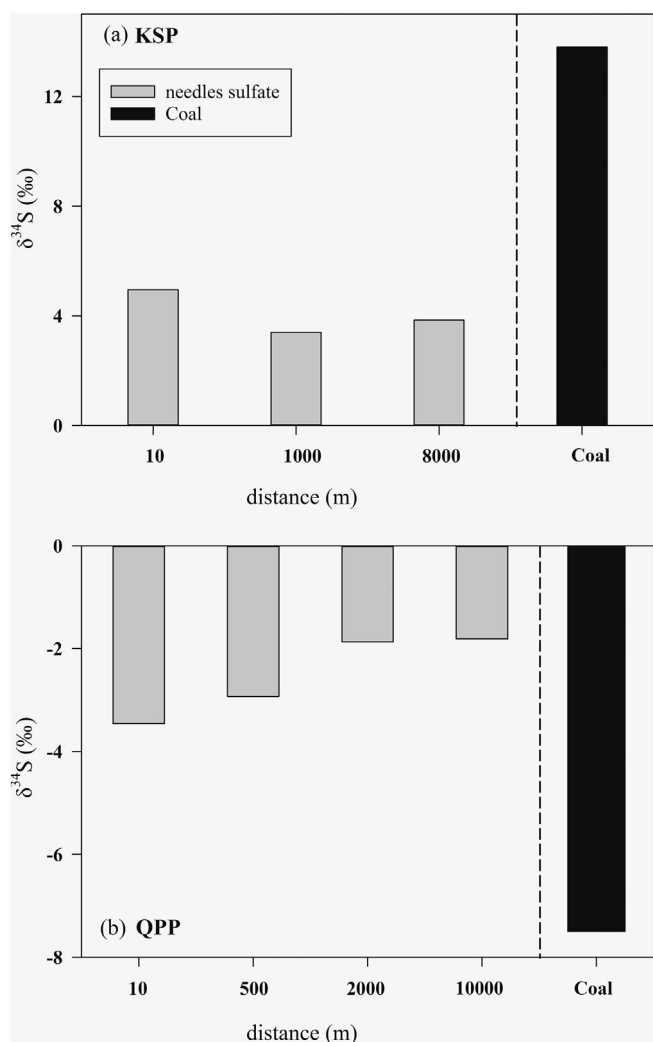


Fig. 8. The spatial variations in $\delta^{34}\text{S}$ of the water-soluble sulfate in needles versus the distance from two industrial plants. Sampling sites in a) and b) are arranged such that the distance from the industrial plants increases from left to right. The letters refer to the same locations as in Fig. 1. The gray bars represent the sulfate in needles and the black bars represent the coal source.

5. Conclusions

The needle sulfate was rarely derived from atmospheric sulfate. In Jinning sites with no serious SO_2 pollution, most of the sulfate in the needles was derived from soil. In contrast, the $\delta^{18}\text{O}_{\text{SO}_4}$ values in the needles varied and were significantly lower than that of soil in the areas with relatively severe SO_2 pollution. In this case, the oxygen isotopes of SO_2 equilibrated rapidly with those of water. A substantial part of the sulfate in the needles might be derived from atmospheric SO_2 oxidation in SO_2 pollution areas.

The contributions of atmospheric SO_2 based on the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values in needles and the $\delta^{18}\text{O}_{\text{SO}_4}$ values in soils could theoretically be estimated. The atmospheric SO_2 oxidation contributions to the sulfate in needles increased significantly with increased atmospheric SO_2 and needle sulfate concentration. When atmospheric SO_2 concentrations were $> 30 \mu\text{g m}^{-3}$, the contributions of SO_2 to needles sulfate were $> 50\%$ in the sampling areas.

At both the Kunming Steel Plant and Qujing Power Plant, the $\delta^{18}\text{O}$ values of sulfate in needles decreased with decreasing atmospheric SO_2 concentration. The sulfate in the needles had other sources with positive $\delta^{18}\text{O}$ values in addition to soil sulfate and SO_2 oxidation. The sources could well be primary sulfate which generated in the industrial

plant flues and secondary sulfate which generated in atmosphere.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gexplo.2019.106402>.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Asada, K., Deura, R., Kasai, Z., 1968. Effect of sulfate ions on photophosphorylation by spinach chloroplasts. *Plant Cell Physiol.* 9, 143–146.
- Ashenden, T.W., 1979. Effects of SO_2 and NO_2 pollution on transportation in *Phaseolus vulgaris* L. *Environ. Pollut.* 18, 143–146.
- Bao, H., 2015. Sulfate: a time capsule for earth's O_2 , O_3 , and H_2O . *Chem. Geol.* 395, 108–118.
- Bao, L.M., Zhang, G.L., Zhang, Y.X., Li, Y., Lin, J., Liu, W., Cao, Q.C., Zhao, Y.D., Ma, C.Y., Han, Y., 2009. Transfer characterization of sulfur from coal-burning emission to plant leaves by PIXE and XANES. *Chin. Phys. C* 33, 1010–1015.
- Böttcher, M.E., Thamdrup, B., Vennemann, T.W., 2001. Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur. *Geochim. Cosmochim. Acta* 65, 1601–1609.
- Chiba, H., Sakai, H., 1985. Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures. *Geochim. Cosmochim. Acta* 49, 993–1000.
- Cicek, A., Kopal, A.S., 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.
- Cowling, D.W., Jones, L.H.P., Lockyer, D.R., 1973. Increased yield through correction of sulfur deficiency in ryegrass exposed to sulfur dioxide. *Nature* 243, 479–480.
- Forstel, H., Hutzen, H., 1983. $^{18}\text{O}/^{16}\text{O}$ ratio of water in a local ecosystem as a basis of climate record. *Paleoclimates and paleowaters: a collection of environmental isotope studies.* Panel Proc. Ser. 1, 67–81.
- Franke, W., 1964. Role of guard cells in foliar absorption. *Nature* 202, 1236–1237.
- Galloway, J.N., Dianwu, Z., Jiling, X., Likens, G.E., 1987. Acid rain: China, United States, and a remote area. *Science* 236, 1559–1562.
- Guan, H., Xiao, H.Y., Liu, C.Q., 2015. Sulfur isotopic signatures of water-soluble sulfate in needles of *Pinus massoniana* Lamb in two Chinese areas. *Environ. Earth Sci.* 73, 1805–1811.
- 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).
- Guo, H., Weber, R.J., Nenes, A., 2017. High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production. *Sci. Rep.* 7, 12109.
- Guy, R.D., Fogel, M.L., Berry, J.A., 1993. Photosynthetic fractionation of the stable isotopes of oxygen and carbon. *Plant Physiol.* 101, 37–47.
- Helman, Y., Barkan, E., Eisenstadt, D., Luz, B., Kaplan, A., 2005. Fractionation of the three stable oxygen isotopes by oxygen-producing and oxygen-consuming reactions in photosynthetic organisms. *Plant Physiol.* 138, 2292–2298.
- Holt, B.D., Cunningham, P.T., Kumar, R., 1979. Seasonal variations of oxygen-18 in atmospheric sulfates. *Int. J. Environ. Anal. Chem.* 6, 43–53.
- Holt, B.D., Cunningham, P.T., Kumar, R., 1981. Oxygen isotopy of atmospheric sulfates. *Environ. Sci. Technol.* 15, 804–808.
- Holt, B.D., Kumar, R., Cunningham, P.T., 1982. Primary sulfates in atmospheric sulfates: estimation by oxygen isotope ratio measurements. *Science* 217, 51–53.
- Hüve, K., Ditttrich, A., Kindermann, G., Slovik, S., Heber, U., 1995. Detoxification of SO_2 in conifers differing in SO_2 -tolerance. *Planta* 195, 578–585.
- Jamieson, R.E., Wadleigh, M.A., 1999. A study of the oxygen isotopic composition of precipitation sulfate in Eastern Newfoundland. *Water Air Soil Pollut.* 110, 405–420.
- Jędrysek, M.O., Kaluźny, A., Hoefs, J., 2002. Sulphur and oxygen isotope ratios in spruce needles as a tracer of atmospheric pollution. *J. Geophys. Res. Atmos.* 107, 4353.
- Kaiser, G., Martinoia, E., Schroppel-Meier, G., Heber, U., 1989. Active transport of sulfate into the vacuole of plant cells provides halotolerance and can detoxify SO_2 . *J. Plant Physiol.* 133, 756–763.
- Kelly, J., Lambert, M.J., 1972. The relationship between sulfur and nitrogen in the foliage of *Pinus radiata*. *Plant Soil* 37, 395–407.

- Lau, O.W., Luk, S.F., 2001. Leaves of *Bauhinia blakeana* as indicators of atmospheric pollution in Hong Kong. *Atmos. Environ.* 35, 3113–3120.
- Lee, C.C.W., Savarino, J., Cachier, H., Thiemens, M.H., 2002. Sulfur (^{32}S , ^{33}S , ^{34}S , ^{36}S) and oxygen (^{16}O , ^{17}O , ^{18}O) isotopic ratios of primary sulfate produced from combustion processes. *Tellus B Chem. Phys. Meteorol.* 54, 193–200.
- Legge, A.H., Bogner, J.C., Krupa, S.V., 1988. Foliar sulfur species in pine: a new indicator of a forest ecosystem under air pollution stress. *Environ. Pollut.* 55, 15–27.
- Li, N., Xiao, H.Y., Chen, Y.Z., Zhou, D., Luo, L., Wu, D.S., 2013. Comparisons of sulfur contents and isotopes between mosses and surface soils in Jiangxi Province. *Environ. Sci.* 34, 3782–3787 (in Chinese).
- Lis, G., Wassenaar, L.L., Hendry, M.J., 2008. High-precision laser spectroscopy D/H and $^{18}\text{O}/^{16}\text{O}$ measurements of microliter natural water samples. *Anal. Chem.* 80, 287–293.
- Liu, C.Q., 2009. Biogeochemical processes and cycling of nutrients in the earth's surface: Cycling of nutrients in soil-plant systems of karstic environments, southwest China. Science Press, Beijing. (in Chinese).
- Liu, C.Q., Jiang, Y.K., Tao, F.X., Lang, X.C., Li, S.L., 2008. Chemical weathering of carbonate rocks by sulfuric acid and the carbon cycling in Southwest China. *Geochimica* 37, 404–414. (in Chinese).
- Liu, X.Y., Xiao, H.Y., Liu, C.Q., Xiao, H.W., Wang, Y.L., 2009. Assessment of atmospheric sulfur with the epilithic moss *Haplocladium microphyllum*: evidences from tissue sulfur and $\delta^{34}\text{S}$ analysis. *Environ. Pollut.* 157, 2066–2071.
- Lloyd, R.M., 1968. Oxygen isotope behavior in the sulfate-water system. *J. Geophys. Res.* 73, 6099–6110.
- Longinelli, A., Bartelloni, M., 1978. Atmospheric pollution in Venice, Italy, as indicated by isotopic analyses. *Water Air Soil Pollut.* 10, 335–341.
- Luo, N.X., Zeng, L.P., Wu, Y.H., Lv, H., 2013. Characteristic analysis of acid rain in Guiyang (SW China) in recent years. *J. Guizhou Meteorol.* 37, 18–23 (in Chinese).
- Luz, B., Barkan, E., 2005. The isotopic ratios $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ in molecular oxygen and their significance in biogeochemistry. *Geochim. Cosmochim. Acta* 69, 1099–1110.
- Majerník, O., Mansfield, T.A., 1971. Effects of SO_2 pollution on stomatal movements in *Vicia faba*. *J. Phytopathol.* 71, 123–128.
- Martín-Gómez, P., Barbeta, A., Voltas, J., Peñuelas, J., Dennis, K., Palacio, S., Dawson, T.E., Ferrio, J.P., 2015. Isotope-ratio infrared spectroscopy: a reliable tool for the investigation of plant-water sources? *New Phytol.* 207, 914–927.
- Maruyama-Nakashita, A., Nakamura, Y., Watanabe-Takahashi, A., Yamaya, T., Takahashi, H., 2004. Induction of SULTR1; sulfate transporter in *Arabidopsis* roots involves protein phosphorylation/dephosphorylation circuit for transcriptional regulation. *Plant Cell. Physiol.* 45, 340–345.
- Mayer, B., 2005. Assessing sources and transformations of sulfate and nitrate in the hydrosphere using isotope techniques. In: *Isotopes in the Water Cycle*. Springer, Dordrecht, pp. 67–89.
- Mayer, B., Shanley, J.B., Bailey, S.W., Mitchell, M.J., 2010. Identifying sources of stream water sulfate after a summer drought in the Sleepers River watershed (Vermont, USA) using hydrological, chemical, and isotopic techniques. *Appl. Geochem.* 25, 747–754.
- McCarthy, M.D.B., Newton, R.J., Bottrell, S.H., 1998. Oxygen isotopic compositions of sulfate from coals: implications for primary sulfate sources and secondary weathering processes. *Fuel* 77, 677–682.
- Mukai, H., Tanaka, A., Fujii, T., Zeng, Y., Hong, Y., Tang, J., Guo, S., Xue, H., Sun, Z., Zhou, J., Xue, D., Zhao, J., Zhai, G., Gu, J., Zhai, P., 2001. Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. *Environ. Sci. Technol.* 35, 1064–1071.
- Novák, M., Mitchell, M.J., Jačková, I., Buzek, F., Schweigstillová, J., Erbanová, L., Přikryl, R., Fottová, D., 2007. Processes affecting oxygen isotope ratios of atmospheric and ecosystem sulfate in two contrasting forest catchments in Central Europe. *Environ. Sci. Technol.* 41, 703–709.
- Pfanz, H., Martinoa, E., Lange, O.L., Heber, U., 1987. Flux of SO_2 into leaf cells and cellular acidification by SO_2 . *Plant Physiol.* 85, 928–933.
- Richter, D.D., Johnson, D.W., 1983. Determination of inorganic sulfate in foliage with barium chloranilate 1. *Soil Sci. Soc. Am. J.* 47, 522–524.
- Seinfeld, J.H., Pandis, S.N., 2012. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. John Wiley & Sons.
- Sharma, A.P., Tripathi, B.D., 2009. Biochemical responses in tree foliage exposed to coal-fired power plant emission in seasonally dry tropical environment. *Environ. Monit. Assess.* 158, 197–212.
- Slovik, S., Siegmund, A., Kindermann, G., Riebeling, R., Balázs, Á., 1995. Stomatal SO_2 uptake and sulfate accumulation in needles of Norway spruce stands (*Picea abies*) in Central Europe. *Plant Soil* 168, 405–419.
- Takahashi, H., Yamazaki, M., Sasakura, N., Watanabe, A., Leustek, T., Engler, J.A., Engler, G., Montagu, M.V., Saito, K., 1997. Regulation of sulfur assimilation in higher plants: a sulfate transporter induced in sulfate-starved roots plays a central role in *Arabidopsis thaliana*. *Proc. Natl. Acad. Sci.* 94, 11102–11107.
- Taylor, B.E., Wheeler, M.C., 1994. Sulphur and oxygen isotope geochemistry of acid mine drainage in the Western United States: field and experimental studies revisited. In: Alpers, C.N., Blowes, D.W. (Eds.), *Environmental Geochemistry of Sulphide Oxidation*. ACS Symposium Series 550. American Chemical Society, pp. 481–514.
- Taylor, B.E., Wheeler, M.C., Nordstrom, D.K., 1984. Isotope composition of sulphate in acid mine drainage as measure of bacterial oxidation. *Nature* 308, 538–541.
- Thomas, M.D., Hexdeltck, R.H., 1944. The hydrolysis of cystine and the fractionation of sulfur in plant tissues. *J. Biol. Chem.* 153, 313–325.
- Trust, B.A., Fry, B., 1992. Stable sulfur isotopes in plants: a review. *Plant Cell Environ.* 15, 1105–1110.
- Van Stempvoort, D.R., Krouse, H.R., 1994. Controls of $\delta^{18}\text{O}$ in Sulfate: Review of Experimental Data and Application to Specific Environments. ACS Symposium Series 550. American Chemical Society, pp. 446.
- Vinogradov, A.P., Kuturyn, V.M., Zadorozhnyi, I.K., 1959. Isotope fractionation of atmospheric oxygen. *Geochemistry* 3, 241–253.
- Wang, G., Zhang, R., Gomez, M.E., et al., 2016. Persistent sulfate formation from London fog to Chinese haze. *Proc. Natl. Acad. Sci.* 113, 13630–13635.
- West, A.G., Patrickson, S.J., Ehleringer, J.R., 2006. Water extraction times for plant and soil materials used in stable isotope analysis. *Rapid Commun. Mass Spectrom.* 20, 1317–1321.
- White, J.W.C., Cook, E.R., Lawrence, J.R., 1985. The DH ratios of sap in trees: Implications for water sources and tree ring DH ratios. *Geochim. Cosmochim. Acta* 49, 237–246.
- Xiao, H.Y., Liu, C.Q., 2004. Chemical characteristics of water-soluble components in TSP over Guiyang, SW China, 2003. *Atmos. Environ.* 38, 6297–6306.
- Xiao, H.Y., Liu, C.Q., 2011. The elemental and isotopic composition of sulfur and nitrogen in Chinese coals. *Org. Geochem.* 42, 84–93.
- Xiao, H.Y., Tang, C.G., Liu, X.Y., Xiao, H.W., Liu, C.Q., 2008. Sulphur isotopic ratios in mosses indicating atmospheric sulphur sources in southern Chinese mountainous areas. *Geophys. Res. Lett.* 35, L19807.
- Xiao, H.Y., Tang, C.G., Xiao, H.W., Liu, X.Y., Liu, C.Q., 2009. Identifying the change in atmospheric sulfur sources in China using isotopic ratios in mosses. *J. Geophys. Res.* Atmos. 114, D16304.
- Xiao, H.Y., Tang, C.G., Zhu, R.G., Wang, Y.L., Liu, C.Q., 2011. Tracing sources of coal combustion using stable sulfur isotope ratios in epilithic mosses and coals from China. *J. Environ. Monit.* 13, 2243–2249.
- Xiao, H.Y., Li, N., Liu, C.Q., 2015. Source identification of sulfur in uncultivated surface soils from four Chinese provinces. *Pedosphere* 25, 140–149.
- Xu, Z., Liu, C.Q., 2007. Chemical weathering in the upper reaches of Xijiang River draining the Yunnan-Guizhou Plateau, Southwest China. *Chem. Geol.* 239, 83–95.
- Yang, X., Gao, Q., Qu, J., Jiang, Z.Y., 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).
- Yunnan Environmental Protection Bureau, 2011. *Bulletin of Environmental Conditions of 2010 in Yunnan*. (in Chinese).
- Yunnan Environmental Protection Bureau, 2012. *Bulletin of Environmental Conditions of 2011 in Yunnan*. (in Chinese).
- Zhang, W., Liu, C.Q., Wang, Z.L., Zhang, L.L., Luo, X.Q., 2014. Speciation and isotopic composition of sulfur in limestone soil and yellow soil in karst areas of Southwest China: implications of different responses to acid deposition. *J. Environ. Qual.* 43, 809–819.