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Physiological and isotopic signals in epilithic mosses for indicating anthropogenic sulfur on the urban–rural scale

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ABSTRACT

The strength and source of anthropogenic sulfur (S) deposition is an important area of research in both environmental and ecological disciplines. Here S concentration, stable isotope ($\delta^{34}S$) and photosynthetic pigments analyses were performed on epilithic mosses at Guiyang area (SW China) for investigating the distribution, origin and effect of urban-derived S at the urban–rural scale. Based on the variation of moss S, anthropogenic S was estimated to account for about 52% of total S in urban mosses and 35% in rural mosses within 30 km. The deposition of urban-derived S was biologically determined within 57 km from the urban center, but only 22% (about 24.4×10^6 kg-S annually) reached over 30 km, with 78% (about 85.9×10^6 kg-S) deposited within 30 km. $\delta^{34}S_{moss}$ signatures suggested the major source of anthropogenic S was still from coal combustion, and comparable $\delta^{34}S_{moss}$ values along the urban–rural transect suggested the inputs of urban-derived S into rural ecosystems. Unexpectedly, moss photosynthetic pigments did not show a decrease with S deposition, but express higher concentrations in the urban than in the rural. In contrast, correlations between moss photosynthetic pigments, and tissue nitrogen (N) and $\delta^{15}N$ demonstrated a fertilizing effect of elevated N deposition on moss photosynthesis, which might buffer or offset the negative effect of S deposition on urban mosses. Collective evidences suggest that S% and $\delta^{34}S$ in epilithic mosses provided useful information for determining anthropogenic S deposition on the urban–rural scale, but moss photosynthetic pigments may not be applicable for reflecting S loading under high N deposition.

1. Introduction

Anthropogenic S has greatly exceeded the average natural S release into the atmosphere, which is responsible for elevated S deposition, ecosystem acidification as well as many other environmental consequences (Brimblecombe et al., 1989; Lefohn et al., 1999). Now even some high-elevation ecosystems have been found being influenced by elevated S deposition chiefly of anthropogenic sources (Pruett et al., 2004). As a major contributor of elevated S deposition, anthropogenic S in city areas have attracted many concerns, especially on the dispersion of urban-derived S pollutants and subsequent influences on natural ecosystems in surrounding rural areas (Brimblecombe et al., 1989; Krouse and Grinenko, 1991; Vingiani et al., 2004). It is therefore important to understand the source, distribution and effect of anthropogenic S on ecosystems at urban–rural scale. Such understandings can provide polluting information for policy makers to manage urban sprawling, resource use and ecosystem health, and to optimize their benefits.

Because of a high degree of spatial heterogeneity of city ecosystems, as well as the complexity of multiple S compounds in gaseous, particulate and wet deposition forms, more and more studies are exploring records in plants for integrating site-specific S deposition with an advantage of examining the effects of S pollution on natural vegetation (Trust and Fry, 1992; Legge and Krupa, 2002; Puig et al., 2008). The applicability of mosses as atmospheric monitoring organisms has become a world-wide accepted technique because they mainly acquire pollutants from atmosphere and their rhizines and rhizoils serve mainly for attachment (Thompson and Bottrell, 1998; Vingiani et al., 2004; Adamo et al., 2008). In parallel, the stable S isotope ($\delta^{34}S$) has been known as an important tool holding source-specific information that can serve as a fingerprint to identify S sources ranging from localized to regional scales (e.g. Nriagu et al., 1991; Zhao et al., 2003; Kawamura et al., 2006). Thus, moss S and $\delta^{34}S$ analyses were suggested to stress on the assessment of long-term and integrated S loading and source in atmospheric deposition (Nriagu and Glooschenko, 1992; Novák et al., 2001).

Characterized by insulation from substratum and effective traps of pollutants, tissue S concentration and $\delta^{34}S$ of epilithic mosses were recently recognized as sensitive parameters for indicating atmospheric S, which were comparable to that of precipitation sulfate and ambient SO_2 (Liu et al., 2009b). So far, these works were

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largely based on comparing mosses from scattered locations to get a general impression on the contribution of city human activities to elevated S deposition. One of the uncertainties remains on whether the parade route S concentration and δ^{34}S legacy in epilithic mosses can quantify the amount and source of anthropogenic S dispersed from the urban to neighboring areas. Moreover, the positive and negative effects of S deposition on moss species have not been fully recognized or measured in the field. Although we know mosses can serve as sensitive indicators among plant communities, insights into the physiological mechanisms of mosses in response to S deposition are rather limited due to diverse habitats as well as multiple effects from different other components in deposition.

High S pollution and deposition potentially cause toxicity and adverse impacts on plant physiology, with large amounts of H^+, $SO_3{}^{2-}$ or $SO_4{}^{2-}$ accumulation in plant body due to the ionization and oxidization of SO_2 (Legge and Krupa, 2002; Swanepoel et al., 2007). Such a decrease of pH value would cause the degradation of Chl because of a nonreversible exchange between intracellular H^+ and Mg^{2+} of Chl a ($2H^+$ + Chl a → phaeophytin a + Mg^{2+}). With single or few layers of parenchymaa cells and also due to the lack of a cuticular barrier, the chloroplast and photosynthetic pigments of mosses are potentially more sensitive than those of vascular leaves in response to atmospheric pollutants.

In view of the above points, we have been focusing on the urban-derived pollutants in Guiyang area (SW China) by using multiple isotopes in moss species. Such explorations directly contribute to the development of mosses as more accurate environmental indicators of pollution sources in deposition. Moreover, the elemental concentration and physiological parameters in mosses are straightforward to describe the status and impacts of ground-level deposition on terrestrial habitats, which can shed light on the quantification of deposition into ecosystem and further provide important insights into ecophysiological processes. By measuring photosynthetic pigments (Chl-a, Chl-b and Caro), tissue S concentration and δ^{34}S ratio in epilithic mosses along two urban–rural transects, the objectives of the present study are: (1) to quantify the distribution of anthropogenic S on urban–rural scale based on the variation of moss S; (2) to reexamine the major S source and test the utility of $\delta^{34}S_{moss}$ for tracing the dispersion of urban-derived S; (3) to further interpret the pattern and ecophysiological implications of moss photosynthetic pigments along the deposition gradient.

2. Materials and methods

2.1. Study area

The city of Guiyang, the capital of Guizhou province, is located in the Karst region of SW China with average altitude of 1250 m above mean sea level. It has a subtropical monsoon climate with an annual average temperature of 15.3 °C, annual rainfall of 1174 mm and the relative humidity of about 86%. With abundant epilithic mosses resources, Guiyang is an ideal city to carry out biomonitoring of atmospheric pollution in city ecosystem

With pillar industries including electric power, ferric, steel, phosphorus and rubber, Guiyang was once one of the most serious acid deposition cities of China. The ground SO_2 concentration reached 400–500 $\mu g\,m^{-3}$ during 1981–1990, which was three times higher than the average concentration of 10 major cities in North America, even the average SO_2 level in 1996 (300 $\mu g\,m^{-3}$) was about six times above the WHO annual guideline (50 $\mu g\,m^{-3}$) (Huang et al., 1995). In 1997, most of small-sized mills and mines as well as workshops with heavy pollution were forced to shut down and some heavy polluting industries were relocated. However, the total amount of anthropogenic SO_2 emission was still as high as 220.3×10^6 kg in 2005 (Guiyang Environmental Protection and Bureau, 2006).

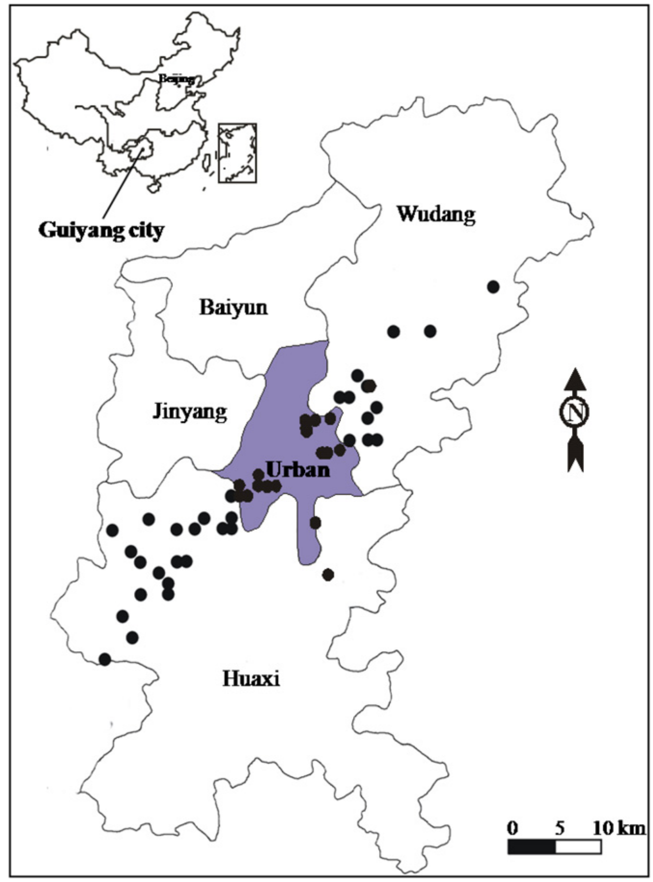

Fig. 1. Map showing the location of Guiyang city and the sampling sites of epilithic mosses.

In addition, reactive N deposition in Guiyang city has been elevated by ammonia (NH_3) releases from sewage discharge, which constructed a pressing environmental problem because of the high NH_3 content but a low level of wastewater treatment (17.2% in 2004 and 20% in 2005, Guiyang Environmental Protection Bureau, 2006). The level of N deposition in 2003 was about 37 kg-N $ha^{-1}\,yr^{-1}$ in the urban and 14.3 kg-N $ha^{-1}\,yr^{-1}$ in the rural area, with 76% of the total N deposition as NH_4-N in the urban area (Liu et al., 2009a).

2.2. Sample collection and analyses

Sampling was conducted in April 2006 at 57 sites along the NE–SW transect through Guiyang urban (Fig. 1). Moss samples at each sampling site were composed of four epilithic species (*Haplocladium microphyllum*, *Haplocladium angustifolium*, *Brachythecium salebrosum* and *Eurohypnum leptothallum*). We measured the mixed sample at each site because the amount of single species was not sufficient for all analyses of the present study. Eligible samples should be growing on natural naked rocks without soil, in open field without canopies or overhanging vegetation. Sampling was performed only at sites above ground level to avoid surface water splashes, and sites undisturbed by animals or pets d. At each site, 5–10 subsamples were combined into one representative sample, and a subjective assessment of sample health and age (the green leafy shoot) was made to keep them uniform. Sampling sites away from the urban area were located at least 500 m from main roads and at least 100 m from other roads or houses.

Moss S content (%, DW) was determined with an elemental analyzer (PE2400 II, USA). For δ^{34}S analysis, all forms of S in the body of clean moss samples were converted to sulfate based on Eschka method (ASTM, 1971; Mekhtiyeva et al., 1976), subsequently sulfate was recovered from washings by precipitating as $BaSO_4$ with enough 2 M $BaCl_2$ solution. δ^{34}S determination was conducted with an elemental analyzer combustion continuous flow isotope ratio mass spectroscopy (EA-C-CF-IRMS, EA-IsoPrime, Euro3000, GV Instruments, United Kingdom). The standard deviation for the δ^{34}S analysis of NBS127 (barium sulfate, δ^{34}S = +20.3‰) was better than 0.2‰ (n = 5). Detailed experimental description of δ^{34}S determination can be found in the work of Liu et al. (2009b).

The extraction of photosynthetic pigments was conducted on fresh mosses under poor light condition and low temperature soon after sampling (<30 h). The extracting solution was prepared through grounding with 95% ethanol solvent. After removing impurities, mosses (≈0.2 g) were cut into pieces (1–2 mm) and mixed evenly with proper quartz sands plus 2–3 mg of $CaCO_3$ powder. Then samples were ground into plasm with 2–3 ml 95% ethanol (analytical purity) in a glass mortar and further ground with 10 mL ethanol until all tissues became white. After standing for 3–5 min, the liquid was filtered into a brown bottle and rinsed with deionized water until there was no green liquid on the filter paper and residue, and finally added 95% ethanol to 25 ml for determination. The contents of pigments were measured with an ultraviolet visible spectrophotometer (Unico2000) by using 95% ethanol as black reference, and scanning under the spectrum of 665 nm, 649 nm and 470 nm for chlorophyll a (Chl-a), chlorophyll b (Chl-b) and carotenoid (Caro) respectively. The concentrations of photosynthetic pigments (mg g^{-1}, dry weight) were calculated using Arnon's calculations (Arnon, 1949):

$$\rho_{\text{Chl-a}} = 13.95A_{665\,\text{nm}} - 6.88A_{649\,\text{nm}}$$

$$\rho_{\text{Chl-b}} = 24.96A_{649\,\text{nm}} - 7.32A_{665\,\text{nm}}$$

$$\rho_{\text{Caro}} = \frac{1000A_{470\,\text{nm}} - 2.05\rho_{\text{Chl-a}} - 114.8\rho_{\text{Chl-b}}}{245}$$

$$\text{Pigment content (mg g}^{-1}) = \rho \times V \times \frac{N}{m} \times 1000$$

In which 'ρ' represents pigment content (mg l^{-1}), 'V' is the volume of extracting solvent (ml), 'N' stands for the multiple of dilution and 'm' is weight of moss sample (g).

3. Results and discussion

3.1. The level and distribution of anthropogenic S

Moss S concentration in this study ranged between 0.27% and 0.49%, the lowest concentration was similar to the highest mean value (0.29 ± 0.03%) observed at mountain sites (Mt. Fanjing, 250 km from Guiyang city) (Xiao et al., 2008). Urban mosses showed significant higher S concentration (0.42 ± 0.04% at 0–5 km) than rural mosses (0.31 ± 0.04% at 25–30 km) (P < 0.05) (Fig. 2a), which reflected the decline of atmospheric S from the urban to rural area. Previously, higher moss S accumulations under elevated S deposition have also been reported on different species (Novák et al., 2001; Vingiani et al., 2004).

Prior to this study, we observed that the moss S at Mt. Gongga (a background site in SW China with an altitude of 3276 m) was low as 0.20 ± 0.04%, which represents the normal amount of moss S with no influence from anthropogenic S (Xiao et al., 2008). The differences (ΔS_{moss}) between moss S in this study and the threshold (0.20 ± 0.04%, Xiao et al., 2008) demonstrate

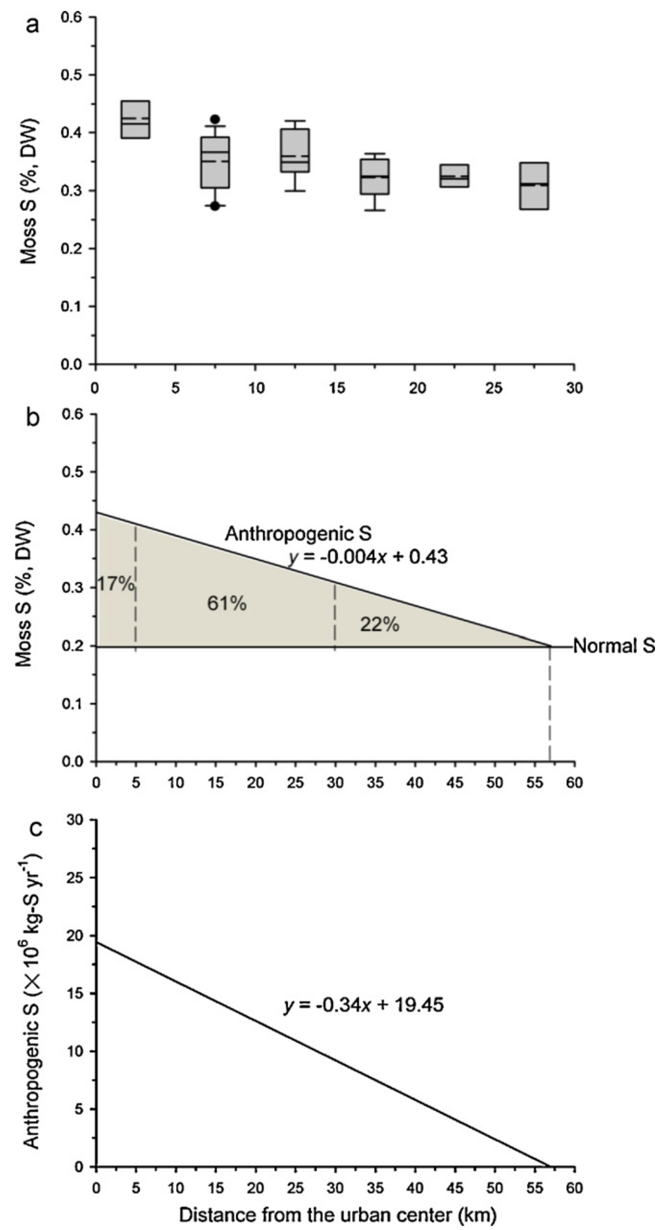

Fig. 2. (a) The variation of moss S from Guiyang urban to rural area (n = 7, 19, 14, 9, 5, 3 for each 5 km from 0 km to 30 km, respectively). The boundary of the box indicates the 25th and 75th percentile, the solid and dash lines within the box mark the mean and the median values, respectively. (b) The variations of anthropogenic S in mosses and in corresponding zones (calculated from the area of shadow triangle) at different distances from Guiyang urban center. The normal S in mosses (0.20%) was determined at background sites of SW China (Xiao et al., 2008); (c) The spatial distribution of annual anthropogenic S with distance from Guiyang urban to rural area.

that anthropogenic S has caused about 55–110% increase of S in deposition at Guiyang area, which accounted for about 52% (ΔS_{moss} = 0.22%) in urban mosses and 35% (ΔS_{moss} = 0.11%) in rural mosses within 30 km. The other evidence for this reduction of urban-derived S in mosses is the linear relationship between moss S and distance, which approached to 0.00% at the distance of 57 km (y = −0.004x + 0.43), thus it can be estimated that the deposition of urban-derived S mainly occurred within 57 km from the urban (Fig. 2b). Moreover, the distribution of urban-derived S should be proportional to the area of the profile (shadow triangle in Fig. 2b), accordingly it can be calculated that about 17% of anthropogenic S was distributed in the urban area (<5 km),

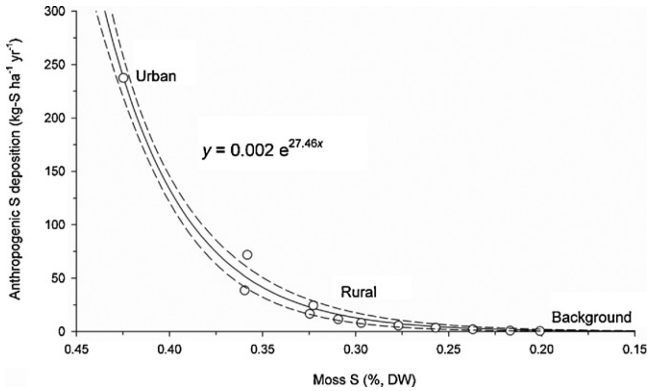

Fig. 3. The quantitative relation between moss S concentration and the level of anthropogenic S deposition at Guiyang area. The dashed lines represent 95% confidence bands.

with 78% within 30 km, and about 22% access to the zone of 30–60 km.

As the total emission of anthropogenic S (mainly from the urban) was 110.15×10^6 kg in Guiyang city in 2005 (Guiyang Environmental Protection Bureau, 2006), the amount of urban-derived S can be calculated according to the percentages obtained from Fig. 2b. Then the spatial variation of anthropogenic S emission with the distance can be modeled as $y = -0.34x + 19.45$ (Fig. 2c). Although this quantification is somewhat simplified and integrated in reflecting the real situation, such high-resolution dataset is rather difficult to get from direct sampling and analysis of deposition. Therefore, by using moss biomonitoring method, it is likely to evaluate site-based S deposition level and urban-derived S transportation over specific distance to sensitive prefectures such as natural conservation forests. Moreover, the relationship between moss S concentration and the level of anthropogenic S deposition from the urban to background can be established as $y = 0.002e^{27.46x}$ (Fig. 3), which can be taken as a matrix for evaluating anthropogenic S inputs to designated sites, especially for remote sites with scarce monitoring data.

3.2. The major source of anthropogenic S

Atmospheric δ^{34}S in city environment was strongly associated with those in fossil fuels used by industries and residents. In China, the regional difference in mean atmospheric δ^{34}S ratios was considered to correspond well to those of source coals (Maruyama et al., 2000; Mukai et al., 2001). δ^{34}S of rainwater in Guiyang city was characterized by ^{34}S-depletion and consistent with much more negative δ^{34}S of coals produced and consumed in Guizhou Province (−8.1‰ to 4.7‰) (Mukai et al., 2001; Xiao and Liu, 2002; Zhang et al., 2002). In present study, mosses δ^{34}S ratios varied widely between −8.1% and −1.5‰, but no significant difference was observed between the urban (−4.9 ± 1.0‰) and rural areas away from the urban (−5.3 ± 1.4‰ to −4.2 ± 1.4‰) ($P < 0.05$) (Fig. 4). Urban mosses assumed very similar δ^{34}S as the average value of atmospheric $\delta^{34}SO_2$ (−4.3‰, −7.8‰ to 2.7‰), even much closer to the $\delta^{34}SO_4{}^{2-}$ of rainwater (−4.9 ± 2.8‰) collected in the urban area in 2001 (Mukai et al., 2001; Xiao and Liu, 2002). The good correspondence of average $\delta^{34}S_{moss}$ to the values of source rainwater suggested a dominating contribution of coal combustion to the local S deposition.

Although the reduction of S was shown in deposition since the implementation of controlling policy of coal combustion from 1997 (Xiao and Liu, 2002; Liu et al., 2009b), it is actually difficult to evaluate the efficiency of such controlling policy and the complete banning of coal combustion in Guiyang city seems impossible. This study demonstrated the major S source was still from coal combustion, not ^{34}S-enriched traffic or oil emission (Maruyama et al., 2000; Mukai et al., 2001). Similar $\delta^{34}S_{moss}$ across the transect supported that areas within 30 km from the urban are currently receiving large amount of urban-derived S.

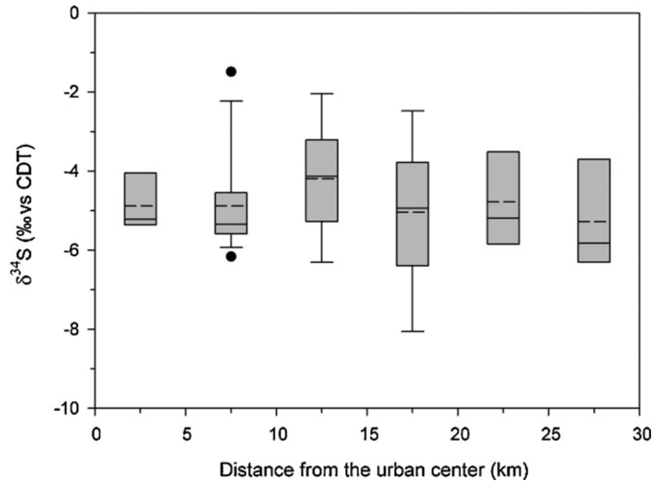

Fig. 4. The average δ^{34}S signatures of epilithic mosses in every 5 km from Guiyang urban ($n = 7$, 19, 14, 9, 5, 3 for each 5 km from 0 km to 30 km, respectively). The boundary of the box indicates the 25th and 75th percentile, the solid and dash lines within the box mark the mean and the median values, respectively.

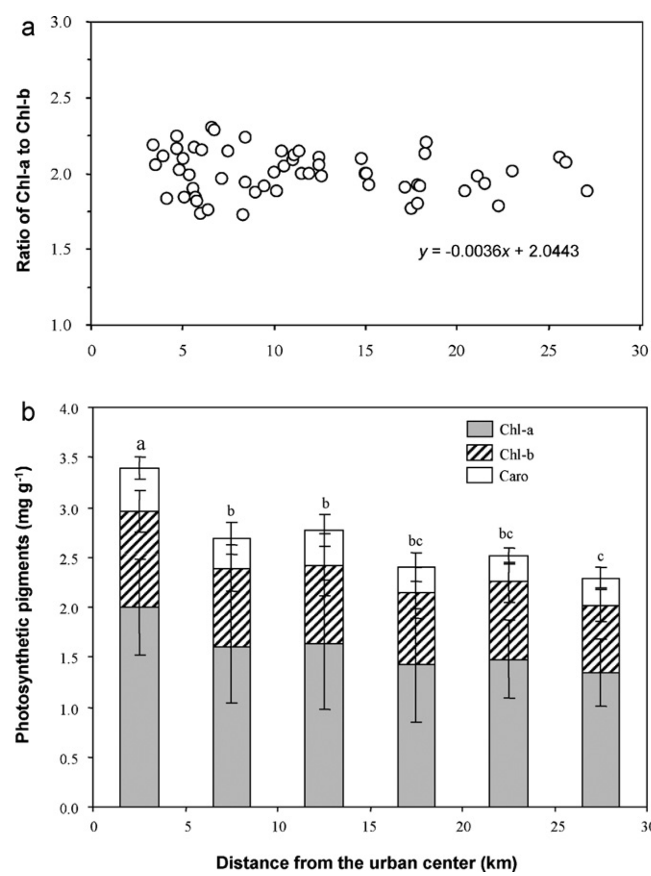

Fig. 5. (a) The variation of Chl-a/Chl-b ratio in epilithic mosses with distance from Guiyang urban. (b) The concentrations of moss photosynthetic pigments (Chl-a, Chl-b and Caro) at every 5 km from Guiyang urban. Different letters above the bars indicate a significant statistical difference at $P < 0.05$.

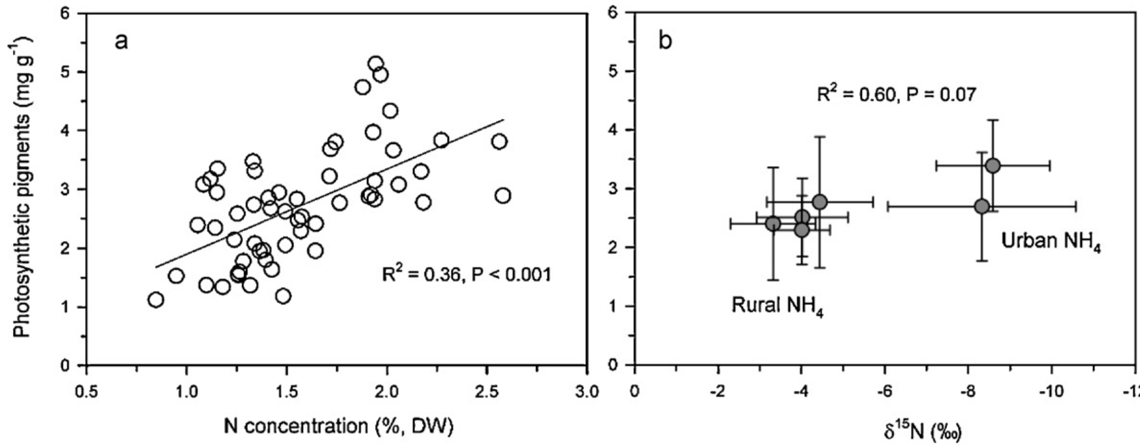

Fig. 6. Correlations between moss photosynthetic pigments and (a) tissue N, (b) mean δ^{15}N at Guiyang area.

3.3. Ecophysiolgical implications of photosynthetic pigments in epilithic mosses

Moss pigments are useful parameters to reflect environmental stresses and nutritional status (Proctor, 1982; Bonnett et al., 2010). The ratio of Chl-a/Chl-b is as a function of the ability to use light for carbon synthesis (Martin and Churchill, 1982; Barsig and Schneider, 1998). There is no substantial variation of Chl-a/Chl-b from the urban to rural area (≈2.00, Fig. 5a), suggesting similar photosynthetic features (e.g. efficiency of light capture) among species investigated in this study.

Total Chl (Chl-a and Chl-b) of epilithic mosses in this study was generally lower than those reported on terricolous mosses in SW China. For example, Bao and Leng (2005) reported that the concentration of total Chl was 4.85 ± 0.88 mg g^{-1} for *Rhodobryum Giganteum* and 3.58 ± 0.55 mg g^{-1} for *Mnium lycopodioides*, which are significantly higher than the maximum of epilithic mosses (2.96 ± 0.68 mg g^{-1}) in Guiyang area. Such lower Chl concentration in epilithic mosses was attributed to lower water availability on rock surfaces compared with terricolous mosses growing on soils or forest floors. As poikilohydric plants, mosses may regulate the normal metabolism and Chl synthesis to adapt the poor water condition in dry habitats (Glime, 2007). In contrast, the enhancement of water availability would improve moss photosynthesis, the optima water contents for *Plagiomnium acutum*, *Thuidium cymbifolium* and *Chrysocladium retrorsum* were found as 70–95% (Liu et al., 2001), which could not be satisfied for epilithic mosses on rock surfaces. Additionally, low Chl owing to poor water availability for epilithic mosses was supported by lower δ^{13}C fractionations, epilithic mosses in this study showed a similar δ^{13}C (−28.5 ± 0.9‰, unpublished data) with that collected in August 2006 (−28.2 ± 0.4‰), both were more positive than those of terricolous mosses (−30.0 ± 0.9‰) and under canopies (−30.8 ± 1.4‰) (Liu et al., 2007).

The most important characteristic of moss pigments was that urban mosses expressed higher photosynthetic pigments than those in rural area ($P < 0.05$) (Fig. 5b). This unexpected pattern cannot be interpreted with the detrimental effect of S pollution on plant photosynthesis, e.g. total Chl in lichen decreased with total S after transplanted from clean sites to polluted sites (Garty et al., 1993). It was therefore inferred that current S loading was actually not harmful to the photosynthesis of epilithic mosses in Guiyang city, which may partly reflect the reduced S pollution due to the banning policy of coal combustion since 1997 (Liu et al., 2009b).

The positive correlation between photosynthetic pigments and tissue N (Fig. 6a) showed a plausible regulation of photosynthetic pigments in mosses by N supply. As N is one of the most important components in both Chl-a ($C_{55}H_{72}O_5N_4Mg$) and Chl-b ($C_{55}H_{70}O_6N_4Mg$), the lack of N directly limits even prohibit Chl synthesis because the main unit of Chl molecules is the porphyrin ring that can only be formed with the existence of four N atoms. In practice, N content in mosses is sensitive to the variation of atmospheric N deposition (Bragazza et al., 2005; Zechmeister et al., 2008; Liu et al., 2009b). Accordingly, higher Chl and N in urban mosses were mainly caused by elevated urban N deposition (37 kg-N ha^{-1} yr^{-1}), which decreased to 14.3 kg-N ha^{-1} yr^{-1} in the rural (Liu et al., 2009a). Actually, Chl and net photosynthesis in lichens were also found to increase with atmospheric SO_2 (6–61 μg m^{-3}) from rural to urban area (Von Arb et al., 1990), the main reason is the fertilizing effect of atmospheric N on lichen photosynthesis and Chl synthesis, urban lichens expressed higher Chl (>4.00 mg g^{-1}) than those in suburb and rural areas, and the total Chl (1.94–6.42 mg g^{-1}) correlated positively with atmospheric NO_2 (5–69 μg m^{-3}). The fertilization of traffic NO_2 on moss photosynthesis was also found in different species, atmospheric N caused mosses N assimilation near roads 22% higher than those far away from motorway, meanwhile total Chl and Caro near the motorway were 11–75% higher than those 150 m away from motorway (Bignal et al., 2008). Based on higher photosynthetic pigmentation under higher N supply, *S. capillifolium* was recently found to tolerate high N deposition via morphophysiological mechanisms (Bonnett et al., 2010). Thus more works are necessary on the biodiversity and physiological responses of moss species to N availability altered by N deposition.

Moreover, N deposition in Guiyang area is typically dominated by NH_4-N, the fraction of NH_4-N in urban moss N was estimated bout 76% (Liu et al., 2008a,b). Higher photosynthetic pigments in urban mosses were virtually confronted with elevated NH_4-N deposition, which was well characterized by mosses N isotopic signatures (Fig. 6b). As a fact, sulfur pollution in several cities (including Guiyang) of Southern China that once experienced the most serious acid deposition since 1960s has been improved to some extents (Xiao and Liu, 2002), but the rapid increase of N deposition and high NH_4-N in deposition has become a more and more prominent environmental problem (Liu et al., 2008a,b; Wang, 1993).

4. Conclusions

Combined S concentration and isotopic analysis in epilithic mosses was shown to provide quantitative information on the source and distribution of anthropogenic S on the urban–rural scale. Compared with long-term instrumental monitoring methods, to get such integrated information in moss bioindicators showed an inexpensive and effective method, which has the potential to be extended to congeneric cities for more exceptional determinations or models. Moss photosynthetic pigments allowed us to understand both biotic and abiotic mechanisms employed by natural epilithic mosses in response to elevated deposition, but attention should be paid to the pitfall of the fertilizing effect of N deposition when the physiological consequences of atmospheric S loading on plant pigmentation was examined by photosynthetic pigments.

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