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The δ^{15}N values of epilithic mosses indicating the changes of nitrogen sources in Guiyang (SW China) from 2006 to 2016–2017

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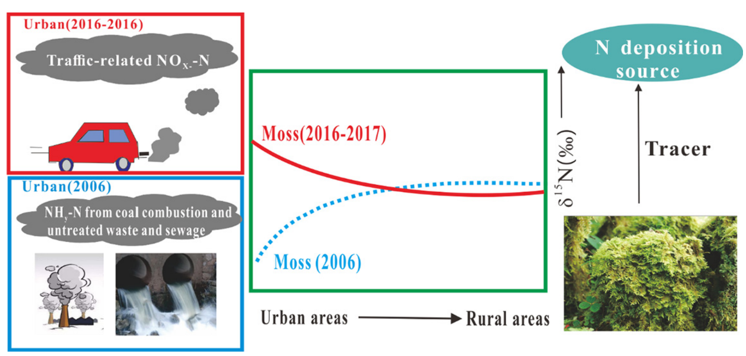
HIGHLIGHTS

- The nitrogen content and δ^{15}N values of mosses decrease from urban to rural area.
- Nitrogen deposition in Guiyang urban area is dominated by traffic-related NOx.
- Agricultural NHy-N was the main atmospheric nitrogen source in the rural area.
- Urban regional atmospheric nitrogen sources changed from NHy-N to NOx-N.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to trace changes in atmospheric nitrogen sources in Guiyang (SW China) from 2006 to 2016–2017, tissue nitrogen content and bulk stable isotope (δ^{15}N) values of epilithic moss (*Haplocladium microphyllum*), collected monthly between April 2016 and March 2017 along an urban-rural gradient (urban center, semi-urban, suburban, and rural) in Guiyang, Guizhou (SW China), were determined. These were then compared with previous surveys in 2006. The nitrogen concentrations (1.4 to 3.7%) and δ^{15}N values (−8.3 to −2.7‰) of the mosses (sampled in 2016–2017) showed an obvious downward trend from the urban center to the rural area, suggesting that ^{15}N enrichment in urban areas is associated with traffic-related NO_x—N. On the contrary, ^{15}N-depleted mosses collected in the rural area were primarily affected by atmospheric NH_y-N from agricultural activities. Our results showed an opposite trend for δ^{15}N variation in 2016/2017 compared to that in 2006, this may reflect a historical change in atmospheric nitrogen sources. A Bayesian isotope mixing model was then applied to estimate the contributions of atmospheric nitrogen sources. The results indicated that the dominant atmospheric nitrogen compounds and sources in the urban area had switched from NH_y-N (emissions from coal combustion and untreated waste and sewage) in 2006 to NO_x-N (from traffic emissions) in 2016/2017. These findings are critical for assessing the air quality of cities and for controlling atmospheric nitrogen pollution.

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1. Introduction

Since the 19th century, there has been a continual and substantial increase in the emission of anthropogenic reactive nitrogen(N), especially in densely populated urban areas, due to urbanization, industrialization, and increases in the number of vehicles and agricultural activities (Bustamante et al., 2006; Zhang et al., 2017). The most abundant anthropogenic reactive nitrogen species in the atmosphere are reduced nitrogen (NH_y—N) and oxidized nitrogen (NO_x—N). Both nitrogen compounds can be deposited into terrestrial and aquatic ecosystems by dry and wet deposition. It is generally accepted that NH_y-N is primarily derived from agricultural nitrogen applications, such as animal husbandry, as well as from the production and application of N-fertilizers (Asman et al., 1998). Emitted NH_y-N can quickly settle near the source due to its high holding capacity with water and acid components in the atmosphere and its weak transmission capacity (Chang and Choi, 2000). Meanwhile, the primary anthropogenic sources of NO_x-N are industry, transportation, and energy production (Zhang et al., 2012). NO_x-N can be retained in the atmosphere for a long period of time and easily undergoes chemical reactions with other substances, meaning that it can reside after long-distance transportation (Zhang, 2010).

The sources of nitrogen deposition, and the potential environmental effects of this nitrogen deposition in areas of substantial reactive-N input, particularly urban areas, have become the focus of scientific research and garnered significant government attention (Felix et al., 2012). Until now, it has generally been accepted that urban sewage discharge (with 20% sewage treatment level) and enhanced agricultural activities are the cause of high atmospheric ammonia deposition and a low NO_x-N/NH_y-N ratio in Guizhou Province (Guiyang Environmental Protection Bureau, 2007–2017). However, continuing development of the regional economy and changes in the energy structure have led to quite complex nitrogen pollution in Guizhou Province (Xie et al., 2005; Gu et al., 2011). For example, dramatic increases in SO_2 and NO_x emissions have occurred in recent years due to rapid industrialization (Tian et al., 2013). Moreover, sewage treatment has been concentrated and the treatment rate is estimated to exceed 90% (Guiyang Environmental Protection Bureau, 2007–2017). In 2010, the total emission of NO_x in Guiyang was 36.6 kg N ha^{-1} a^{-1}, and almost half of that was attributed to vehicular emission (20.2 kt a^{-1}) (Tian et al., 2013; Xu et al., 2017). Additionally, the total emission of NO_x was approximately 12 times higher than that of NH_3 in 2010 over Guizhou province (MEP, 2011). The strengthening of agricultural activities has also led to a large increase in NH_3 emissions (Xiao et al., 2010a, 2012). Therefore, it is of great significance to better understand the current situation and distribution of atmospheric nitrogen pollution, and the sources of this pollution.

Moss is widely considered to be sensitive to environmental change, pollution, nutrient conditions, and ecosystem health (Turetsky and Merritt, 2003; Liu et al., 2008b, 2008c). Due to the physiological properties of moss, i.e., the lack of a cuticle and a large absorbing surface, moss is usually effective in absorbing nitrogen nutrients from ambient air and precipitation, with little subsequent loss (Gerdol et al., 2002; Liu et al., 2007). Nitrogen content and nitrogen isotopes in epilithic mosses are good indicators of nitrogen deposition (Pearson et al., 2010). Previous studies have shown that the nitrogen concentration of moss positively correlates with atmospheric nitrogen deposition (Bragazza and Gerdol, 2005; H.Y. Xiao et al., 2010b). H.Y. Xiao et al. (2010b) developed a quantitative equation describing the relationship between moss tissue nitrogen concentration and nitrogen deposition based on previous studies (Pitcairn et al., 2002; Bragazza and Gerdol, 2005; Solga et al., 2005). Moss $\delta^{15}N$ is considered an ideal tool for identifying nitrogen emission sources because the uptake of nitrogen into moss tissue does not introduce significant ^{15}N fractionation (Evans, 2001; Bragazza et al., 2010; Liu et al., 2012; Hobbie and Högberg, 2012). The different $\delta^{15}N$ values of reactive-N emissions from different sources (e.g., Table 1) also support the validity of moss $\delta^{15}N$ as a reliable means to distinguish nitrogen emission sources. For instance, the $\delta^{15}N$ of anthropogenic emissions of NO_x was reported to primarily be in the range of −5 to +5‰, while ammonia from animal manure was primarily ^{15}N-depleted in the range of −15 to −4‰ (Heaton, 1986; Pearson et al., 2000; Liu et al., 2008a; Xiao and Liu, 2011). A previous study showed that the $\delta^{15}N$ values of moss in London and Northern Italy were higher in urban areas than in rural areas (Pearson et al., 2000). The authors attributed the relatively higher moss $\delta^{15}N$ values in urban areas to NO_x emissions from traffic. Liu et al. (2008c) suggested that the more negative $\delta^{15}N$ values (−8.87 ± 1.65‰) of urban mosses were attributed to NH_3 released from excretory wastes and sewage, while the less negative $\delta^{15}N$ values (−2.48 ± 0.95‰) of rural mosses were attributed to the influence of agricultural NH_3. A negative correlation between moss $\delta^{15}N$ values and the NH_y-N/NO_x-N ratio in atmospheric nitrogen deposition has been established in earlier studies (Solga et al., 2005; Bragazza et al., 2010). Therefore, characterization of the annual level and main sources of nitrogen deposition based on tissue nitrogen and $\delta^{15}N$ of epilithic mosses is more reliable and easier to achieve than physical monitoring.

Regional analyses of the variation in $\delta^{15}N$ values of mosses allow assessment of the main sources of nitrogen inputs and mapping of the impact of nitrogen deposition on urban ecosystems (Stewart et al., 2002). Understanding of the origin and composition of anthropogenic reactive-N deposition will allow policymakers to assess political measures to control air quality.

Here, to explore the changes in anthropogenic reactive-N sources in the past decade, the nitrogen content and $\delta^{15}N$ values in the tissue of epilithic mosses collected monthly between April 2016 and March 2017 from the urban center of Guiyang to the rural area were assessed. Then, moss $\delta^{15}N$ values in the same region in 2006 (Liu et al., 2008c) were compared with those in 2016–2017. The percentages of the contribution of different nitrogen sources to moss nitrogen were determined from the $\delta^{15}N$ values of moss samples using a Bayesian isotope mixing model (SIAR; Stable Isotope Analysis in R) (Parnell and Jackson, 2008). The purpose of this study was to investigate the spatial and temporal variation in atmospheric nitrogen deposition, and its sources, in the Guiyang area.

2. Materials and methods

2.1. Study area

Sampling sites were distributed around Guiyang City and Puding County, Guizhou (SW China). Guiyang is the capital city and political, cultural, and economic center of Guizhou Province, with a population of about 4.6 million. Puding County, located in the midwestern region of Guizhou Province, is characterized by intensive agricultural activity and limited local road traffic. The study area is at an elevation of 1000–1500 m a.s.l. and is characterized by a typical subtropical monsoon climate, with a distinct seasonal pattern. Mean annual rainfall reaches 1174 mm. The annual average relative humidity is approximately 84%, and the annual average temperature is 16.2 °C. Vehicle ownership (4.4-fold increase between 2006 and 2016) (Fig. 1a) and coal-based energy consumption structure (1.5-fold increase between 2006 and 2016) have caused the annual average concentration of NO_2 in Guiyang to increase significantly from about 18 to 29 μg.m^{-3} between 2006 and 2016 (Guiyang Environmental Protection Bureau, 2007–2017) (Fig. 1a). In addition, the emissions and percentages of different ammonia sources in Guiyang in 2016 were estimated according to data from the Guiyang Statistical Yearbook (2017) and the ammonia emission factors from H.W. Xiao et al. (2010) (refer to Fig. 1b, for analytical results, and Supporting Information [SI], for methodological details). Of the total ammonia emissions, the anthropogenic ammonia emission was account for 99.4%, and the natural ammonia emission for 0.6%. Compared with the total ammonia emissions in Guiyang estimated in 2006 (H.W. Xiao et al., 2010), there was a higher level of ammonia emissions in 2016 (an increase of 52%), and a higher level of agricultural

Table 1
Compiled $\delta^{15}N$ values (mean ± SD) of major NO_x and NH_3 emissions from various sources.

Sources	N species	$\delta^{15}N$/%	References
Vehicle exhausts	NO_x	−2.5 ± 1.5	(Walters et al., 2015)
Vehicle exhausts	NH_3	−3.4 ± 1.7	(Felix et al., 2013)
Coal combustion (with catalyst)	NO_x	+19.8 ± 5.2	(Felix et al., 2012)
Coal combustion (with catalyst)	NH_3	−8.9 ± 4.1	(Felix et al., 2013)
Biomass burning	NO_x	+12.5 ± 3.1	(Hastings et al., 2009; Felix et al., 2012)
Biomass burning	NH_3	+12.0	(Kawashima and Kurahashi, 2011)
Microbial N cycle	NO_x	−30.3 ± 9.4	(Li and Wang, 2008; Felix et al., 2013)
Animal wastes	NH_3	−19.0 ± 14.1	(Freyer, 1978; Heaton, 1987; Felix et al., 2014; Felix et al., 2013)
N-fertilizers	NH_3	−1.55 ± 0.82	(Heaton, 1987; Freyer, 1978)

ammonia (fertilizer use and emissions, livestock, and poultry) in 2016 (an increase from 40.4 in 2006 to 57.7 kt in 2016). The amount of ammonia emissions from fertilizers was 9.1 in 2006 and 28.6 kt in 2016. The total ammonia emissions from livestock in 2016 (16.6 kt) was significantly lower than that in 2006 (27.8 kt).

2.2. Moss sampling

Moss samples were collected along a northwestern urban center (U; distance from urban center: 0–6 km, $n = 84$) - semi-urban (SU; 6–12 km, $n = 96$) - suburban (S; 12–18 km, $n = 60$) transect in Guiyang, and from a rural region (R; <100 km, $n = 24$) in Puding (Fig. 2, Table S1); All samples were collected from bare rock during the middle of each month (12th to 16th) between April 2016 and March 2017. Because of the variations in nitrogen uptake traits between different moss species, the nitrogen content in different moss species may differ, even at the same level of nitrogen deposition (Solga et al., 2006); for example, *Dicranum* needs to receive more nitrogen deposition than *Leurozium* and *Hylocomium*, to maximize nitrogen content in moss tissues (Salemaa et al., 2008). To avoid the effect of inter-species variation in moss nitrogen concentration in response to atmospheric nitrogen deposition, we focused on a single species: *Haplocladium microphyllum*. The epilithic mosses *Haplocladium microphyllum* in open field has long been used as a biomonitor of nitrogen deposition, the utility of which has been widely demonstrated in our previous studies (Liu et al., 2007, 2008b; H.Y. Xiao et al., 2010b). A total of eight plots (each containing 2–5 subplots) were set up to study the urban to rural pattern of nitrogen deposition (Fig. 2). All plots were located at least 100 m away from the road. In addition, we also set up five plots on one side of a major road in August 2016 (one-off sampling), which were at different distances away the road, ranging from near to far: 10 m, 60 m, 100 m, 550 m and 980 m, respectively, and each plot comprised six sub-plots. All of the sub-plots were carefully selected to avoid the influence of domestic animals and surface water, as much as possible.

All samples were collected from a dense cover of healthy moss, and excluded other co-living plants. The living parts of the moss were collected; mosses with soil substrates were avoided. Moss samples were washed with deionized water to thoroughly remove surface adsorbed pollutants. The washed moss samples were then dried in a freeze dryer connected with a vacuum pump at −50 to −40 °C. These freeze-dried samples were finely ground in a high-speed crusher mill, and then passed through a 200-mesh screen to ensure homogeneity of the sample.

2.3. Analytical method

All experimental analyses were performed in the Key Laboratory of the Causes and Control of Atmospheric Pollution, East China University of Technology. Moss nitrogen concentrations (%, dry weight) and bulk $\delta^{15}N$ (‰) values were determined by an Element Analyzer-Isotope Ratio Mass Spectrometer (EA-IRMS, Flash 2000 analyzer and MAT253 Plus, Thermo Fisher Scientific Inc., Massachusetts, USA). The analytical precision for the nitrogen concentration and bulk nitrogen isotope values was always better than 0.02%. IAEA-EA-600 (−27.77‰), USGS41a (+37.626‰), and IAEA-N-2 (+20.3‰) standards were used for calibration of the nitrogen isotope. Sorghum flour (+1.58 ± 0.15%) and urea (−0.32 ± 0.2%) were used as the working standards (standard reference material) to ensure accuracy within 5% of the known total N. The average standard deviation of repeated analysis of $\delta^{15}N$ values for an individual sample was ±0.2‰. The nitrogen isotope is expressed as $\delta^{15}N$. The value is expressed in units of per mil (‰), and is calculated

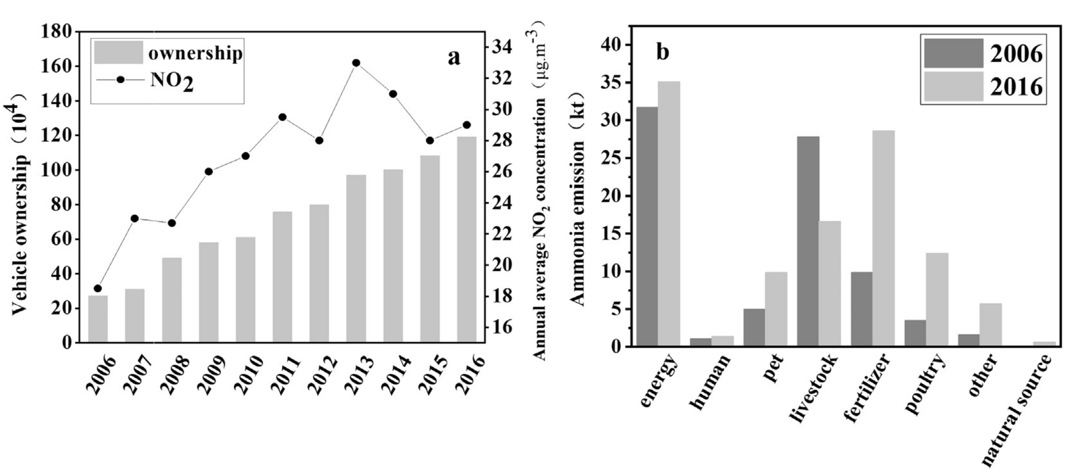

Fig. 1. (a) Annual variation of vehicle ownership and annual average NO_2 concentration in Guiyang from 2006 to 2016 and (b) Amount of ammonia emissions from the different sources in Guiyang in 2006 and 2016.

as follows:

$$\delta^{15}N\ (‰) = \left(R_{sample}/R_{standard} - 1\right) \times 1000 \quad (1)$$

where $R = {}^{15}N/{}^{14}N$ in samples and standards, the standard is N_2 in atmospheric air (AIR, ${}^{15}N/{}^{14}N = 0.00368$).

2.4. Statistical analysis and modeling

Statistical analysis was performed with SPSS 12.0 (SPSS Inc., Chicago). Charts were created using Origin 2018 (origin Lab, Chicago). Significant differences between the means were determined using multiple comparison tests (Tukey, HSD, LSD); statistically significant differences were set at $p < .05$ unless otherwise stated. The Spearman rank correlation coefficient (ρ) was used to determine the correlation between the tissue nitrogen concentration and $\delta^{15}N$.

We used the SIAR model to provide an approximate estimate of the fractional contribution (*F*, %) of potential nitrogen sources (Table 1) to the mixture (total nitrogen of moss tissue) (Dong et al., 2017; Wang et al., 2017). A Bayesian stable isotope mixing model (Parnell et al., 2010) has been implemented in the software package SIAR (stable isotope analysis in R). The model establishes a logical prior distribution using a Bayesian framework based on the Dirichlet distribution (Parnell et al., 2010; Evans et al., 2000). This method provides a reliable estimate of the fractional contribution of different nitrogen sources to moss bulk nitrogen because isotope fractionation is negligible during nitrogen uptake processes of mosses. Furthermore, SIAR offers a number of advantages, as it can incorporate sources of uncertainty, isotope fractionation and multiple nitrogen sources (Xue et al., 2012). In our estimations, uncertainties were evaluated for the $\delta^{15}N$ variabilities of major nitrogen sources (using the $\delta^{15}N$ values of each source, expressed as mean ± SD, as inputs).

The mixing model (Parnell et al., 2010) can be expressed by defining a set of nitrogen mixture measurements for J isotope by K source contributors, as follows:

$$X_{ij} = \sum_{k=1}^{k} F_k \left(s_{jk} + c_{jk}\right) + \varepsilon_{ij} \quad (2)$$

$$s_{jk} \sim N\left(\mu_{jk}, \omega_{jk}{}^2\right)$$

$$c_{jk} \sim N\left(\lambda_{jk}, \tau_{jk}{}^2\right)$$

$$\varepsilon_{ij} \sim N\left(0, \sigma_j{}^2\right)$$

where all *F* values sum to 1 (unity); X_{ij} is the isotope value j of the mixture i, in which $i = 1, 2, 3, \ldots, N$ and $j = 1, 2, 3, \ldots, J$; S_{jk} is the source value k on isotope j ($k = 1, 2, 3, \ldots, K$), and is normally distributed with mean μ_{jk} and standard deviation ω_{jk}. F_k is the proportion of source k estimated by the SIAR model; c_{jk} is the fractionation factor for isotope j on source k, and is normally distributed with mean λ_{jk} and standard deviation τ_{jk}; ε_{jk} is the residual error representing the additional unquantified variation between individual mixtures; it is normally distributed with a mean of 0 and a standard deviation σ_j described, as is detailed elsewhere (Jackson et al., 2009; Moore and Semmens, 2010; Parnell et al., 2010). SIAR was applied to estimate the proportional contributions of potential nitrogen sources in different sampling sites (urban and rural) for different periods (2006 and 2016–2017) and for different seasons in 2016–2017. The $\delta^{15}N$ values of replicate moss samples (data of whole year) from each study site were analyzed as a group. Furthermore, the $\delta^{15}N$ values of mosses in urban and rural areas in Guiyang in 2006, taken from moss sampling in April, 2006 (according to Liu et al., 2008c), were also analyzed, using the SIAR model as a contrast. Isotopic measurements of each sampling site (urban and rural) in 2016–2017 were grouped into the four seasons, for SIAR analysis, since different contributions from seasonal sources were expected. Five potential nitrogen sources in the urban center (NO_x from vehicle exhausts, NO_x from coal combustion, NH_3 from coal combustion, NH_3 from vehicle exhausts, NH_3 from animal wastes) and five potential nitrogen sources in the rural area (NO_x from biomass burning, NO_x from microbial nitrogen cycle, NH_3 from biomass burning, NH_3 from N-fertilizers, NH_3 from animal wastes) were applied in this study (more details about major sources of nitrogen in moss has been shown in Supporting Information

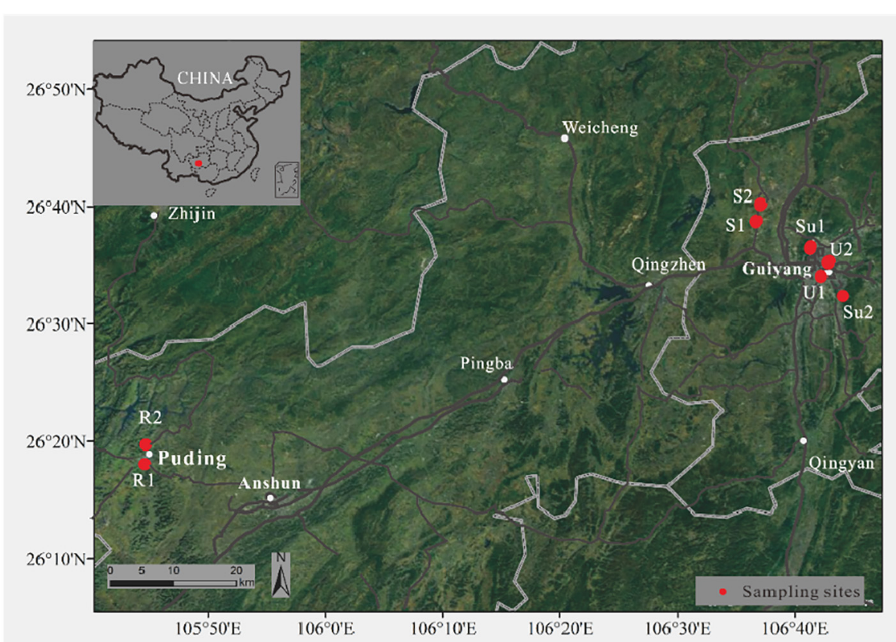

Fig. 2. Map showing the locations of Guiyang and Puding areas and sampling sites of natural mosses. U, SU, S and R represent urban, semi-urban, suburban, and rural, respectively.

(SI)). The $\delta^{15}N$ values of nitrogen sources were consistent with previous studies (Table 1). Since there is negligible isotope fractionation during the absorption of nitrogen by mosses (Liu et al., 2007; Liu et al., 2008c), we assume that there is no substantial difference between moss $\delta^{15}N$ values and different nitrogen sources, i.e., $c_{jk} = 0$ in Eq. (2).

3. Results

3.1. Spatial and seasonal variations in moss nitrogen concentrations and $\delta^{15}N$ signatures

The spatial and seasonal variation in nitrogen content and $\delta^{15}N$ values across four different areas (urban center, semi-urban, suburban, and rural) during the study period are shown in Fig. 3. The total nitrogen content ranged from 1.4 to 3.7%, with an average value of 2.4 ± 0.5%. The maximum nitrogen content was found in the urban center in autumn, while the minimum tissue nitrogen was observed in the rural area in spring. The average nitrogen content showed a significant downward trend from the urban center to the suburban area ($p<0.05$), regardless of the season. All the $\delta^{15}N$ values of epilithic mosses were negative, ranging between −8.2 to −2.7‰, with an average value of −4.9 ± 1.3‰ (Fig. 3). The mosses with the highest $\delta^{15}N$ values were located in the urban center in spring, while those with lowest $\delta^{15}N$ values appeared in the rural area in autumn. Spearman correlation analysis revealed a significant positive correlation between tissue nitrogen concentration and $\delta^{15}N$ (Rs = 0.36, $p<0.01$). The average $\delta^{15}N$ value across the whole year also exhibited a significant downward trend from the urban center to the rural area ($p < .05$) (Fig. 3), which is clearly parallel with the spatial variation tendency in moss nitrogen content. However, significant differences were found between suburban and rural areas in $\delta^{15}N$ values ($p < .05$), but not in tissue nitrogen concentrations ($p > .05$). The average $\delta^{15}N$ values in spring and winter showed a slight downward trend from the urban center to the suburban area ($p < .05$), the average $\delta^{15}N$ value in spring in the rural area was higher than that in the suburban. The average $\delta^{15}N$ value of epilithic mosses in summer and autumn significantly decreased from the urban center to the rural area ($p < .05$). The $\delta^{15}N$ values in the rural area in summer and autumn, particularly in autumn, indicated a much more negative nitrogen isotope relative to the three other areas ($p < .05$).

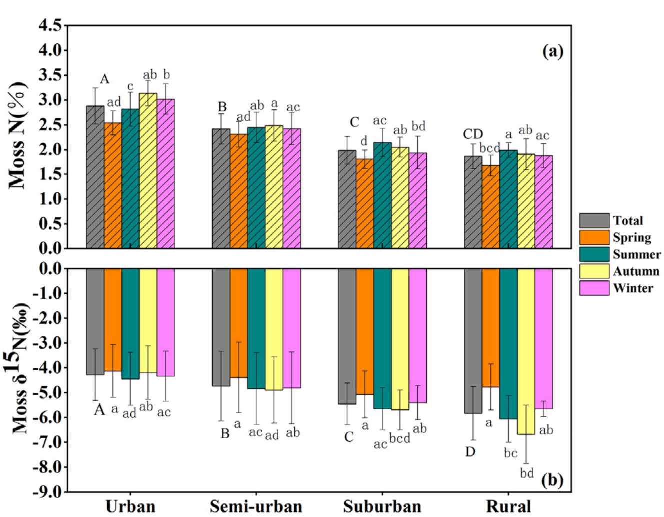

Fig. 3. Moss N concentration (a) and N isotopic signature (b) among seasons and at different areas. The boxes encompass the 25th to 75th, and the whiskers represent the SD values. Monthly data were seasonally averaged (Spring: March to May, Summer: June to August, Autumn: September to November, Winter: December to February). Significant and spatial differences in moss tissue nitrogen concentrations and $\delta^{15}N$ are marked with uppercase letters, significant and temporal differences in moss tissue nitrogen concentrations and $\delta^{15}N$ are marked with lowercase letters ($p < .05$).

3.2. Variations in moss $\delta^{15}N$ along a distance gradient from the road

The $\delta^{15}N$ value of moss showed a significant decreasing trend along a distance gradient from the road (<100 m) (Fig. 4). The highest $\delta^{15}N$ values (−2.1 ± 0.7‰) were observed 10 m away from the road. At a distance of >100 m from the road, the moss $\delta^{15}N$ values exhibited little or no fluctuation and showed a slight decreasing trend with increasing distance from the road (Fig. 4). The Pearson's coefficient indicates a strong correlation between moss $\delta^{15}N$(y) values and distance from the road (x) ($y = -0.9\ln(x) - 0.6$, $R^2 = 0.88$) ($p < .01$).

3.3. Using the SIAR model to partition the sources of moss bulk nitrogen

The mixture calculated by SIAR model primarily reflects the combined effect of the $\delta^{15}N$ values of the primary probable nitrogen sources on the moss bulk nitrogen concentration (Wang et al., 2017). Fractional contributions of NO_x (F_{NOx}) and NH_3 (F_{NH3}) from different sources to the bulk nitrogen concentrations of mosses in urban and rural areas in 2016–2017 and 2006 are shown in Fig. 5a and Table 2. The fractional contributions of NO_x (F_{NOx}) and NH_3 (F_{NH3}) from different sources (assuming that these sources did not differ in $\delta^{15}N$ values between different seasons) to the bulk nitrogen concentrations of mosses in urban and rural areas, in different seasons during 2016–2017, were also estimated by SIAR (Fig. 5b). Our estimation based on moss $\delta^{15}N$ values in 2016–2017 indicated that F_{NOx} in the urban area reached 43.9 ± 10.8%, which was much higher than F_{NOx} in the rural area (35.9 ± 10.3%) (Table 2). The mean ratio of F_{NH3} to F_{NOx} was about 1.28 and 1.78 in urban and rural areas, respectively (Table 2). On the other hand, the estimations by moss $\delta^{15}N$ values in 2006 ($\delta^{15}N$ data from Liu et al., 2008c), F_{NOx} comprised 24.8 ± 9.4% in the urban area, which was much lower than the F_{NOx} in the rural area (42.5 ± 13.3%) (Table 2). The mean ratio of F_{NH3} to F_{NOx} was about 3.04 and 1.35 for urban and rural areas, respectively (Table 2).

According to the estimations in 2016–2017, the bulk nitrogen of moss in the urban area was mainly derived from vehicle exhausts (75.1%), with the highest contribution (41%) from NO_x of vehicle exhausts. Traffic emissions showed higher contributions (75.1%) than coal combustion (20.3%). Fossil-derived NO_x contributed less to nitrogen concentrations (43.9%) than fossil-derived NH_3 (51.5%) (Table 2). In 2016–2017, the bulk nitrogen concentration of moss in the rural area was primarily derived from NH_3 volatilization from fertilizer

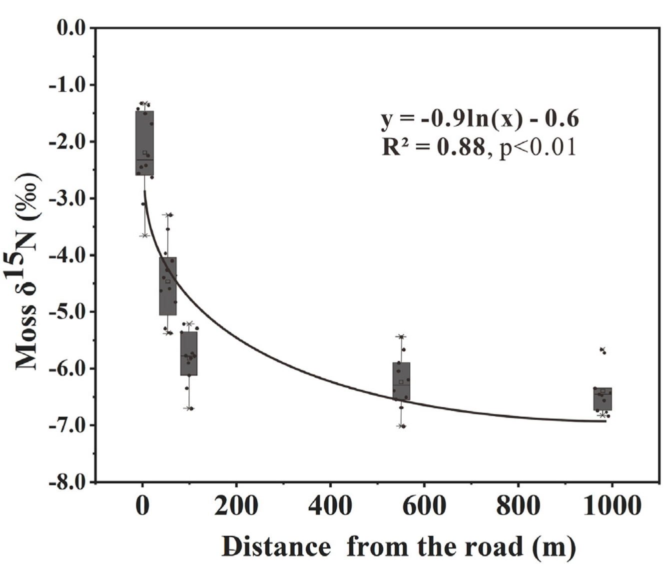

Fig. 4. The variation of the $\delta^{15}N$ value of moss along a distance gradient from the road. The boxes encompass the 25th to 75th, and the whiskers represent the SD values. The square and line in each box show the mean and median, respectively. Significant and spatial differences in moss $\delta^{15}N$ are marked with lowercase letters ($p < .05$).

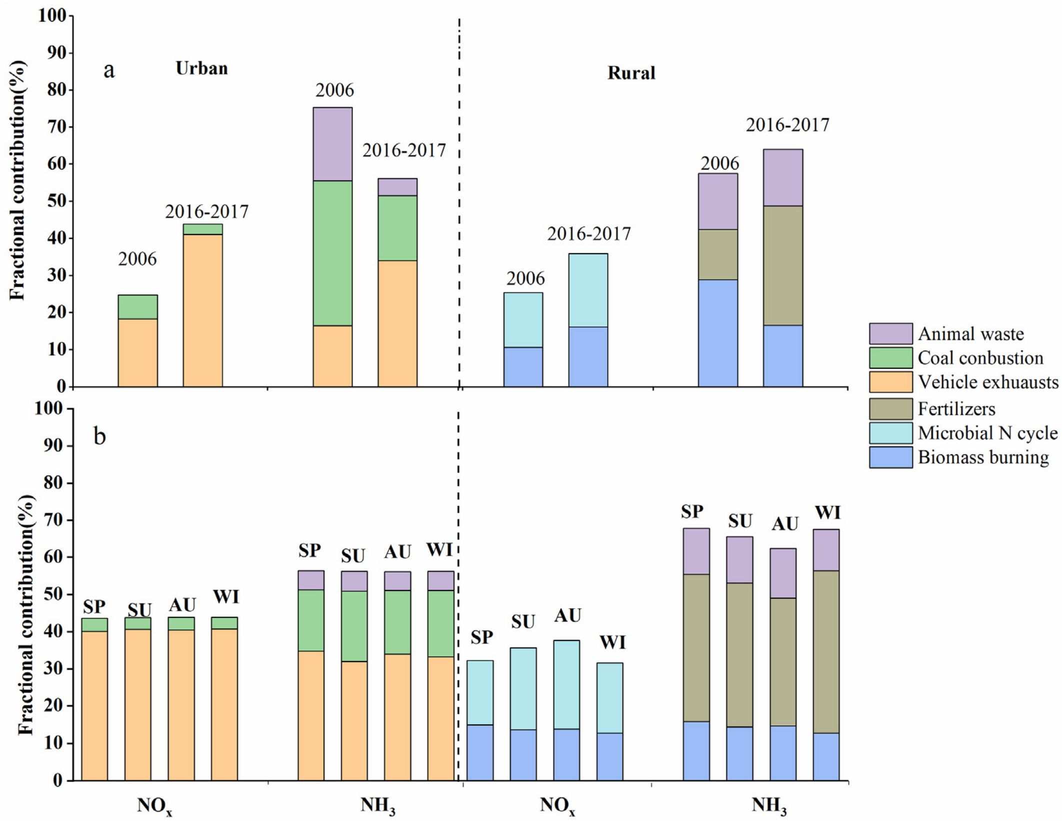

Fig. 5. a: Fractional contributions of dominant N sources to moss bulk N at Guiyang center and the rural in 2016–2017 and in 2006. b: Seasonal various of proportional contribution for different source at Guiyang center and the rural in 2016–2017. The boxes encompass the 25th to 75th, and the whiskers represent the SD values. SP: Spring, SU: Summer, AU: Autumn, WI: Winter.

(32.3%; Fig. 5a). The estimation of $\delta^{15}N$ values performed in 2006 indicated that the bulk nitrogen concentration of moss was primarily derived from coal combustion (45.5%) and animal waste (19.8%). The NH_3 emissions of coal combustion had higher contributions (39.0%) than NO_x emissions (6.5%; Fig. 5a). Fossil-derived NH_3 contributed more to nitrogen concentrations (55.5%) than fossil-derived NO_x (24.8%; Fig. 5a). Accordingly, fossil-derived nitrogen emissions substantially contributed to urban nitrogen pollution in 2006, while in rural areas, nitrogen pollution was primarily derived from biomass burning (56.9%; Table 2).

4. Discussion

Previous studies found that the atmospheric nitrogen deposition in Guiyang was dominated by NH_y-N (Liu et al., 2008a, 2008b, 2008c, 2012, 2017; Xiao et al., 2010a, 2010b, 2012; Qu et al., 2016). A systematic analysis of nitrogen content and $\delta^{15}N$ values of epilithic mosses from the urban center to rural areas in Guiyang in 2006 confirmed this assertion (Liu et al., 2008c). However, our data obtained between 2016 and 2017 reveals a different trend. Our previous study revealed an opposite trend between moss nitrogen contents and $\delta^{15}N$ values along the urban-rural gradient in Guiyang (Liu et al., 2008c): moss nitrogen contents decreased with increasing distance from the city center, while $\delta^{15}N$ values increased with increasing distance from the city center (< 30 km) in 2006 (Fig. 6). The pattern of moss nitrogen contents and $\delta^{15}N$ variation in 2006 indicated that the level of nitrogen deposition decreased away from the urban environment and that NHy-N was the dominant nitrogen form deposited in the Guiyang area,

Table 2
Fractional contribution (F, %) of dominant N precursors and sources to bulk N of mosses at Guiyang center and the rural in 2016–2017 and 2006. Values (mean ± SD, $n = 10^4$) were calculated based on the output of the SIAR model.

	Urban		Rural	
	2006	2016–2017	2006	2016–2017
F_{NH3}	75.3 ± 15.4	56.1 ± 8.9	57.5 ± 12.9	64.1 ± 12.4
F_{NOx}	24.8 ± 9.4	43.9 ± 10.8	42.5 ± 13.3	35.9 ± 10.3
F_{NH3}/F_{NOx}	3.04	1.28	1.35	1.78
F_{fossil}	80.3 ± 13.4	95.4 ± 11.6		
$F_{coal\ combustion}$	45.5 ± 13.4	20.3 ± 4.0		
$F_{vehicle\ exhausts}$	34.8 ± 13.4	75.1 ± 19.3		
$F_{non\text{-}fossil}$	19.7 ± 11.3	4.6 ± 11.6		
$F_{NH3\ volatilization}$			13.5 ± 9.7	32.3 ± 10.7
$F_{biomass\ burning}$			56.9 ± 17.8	32.7 ± 11.3

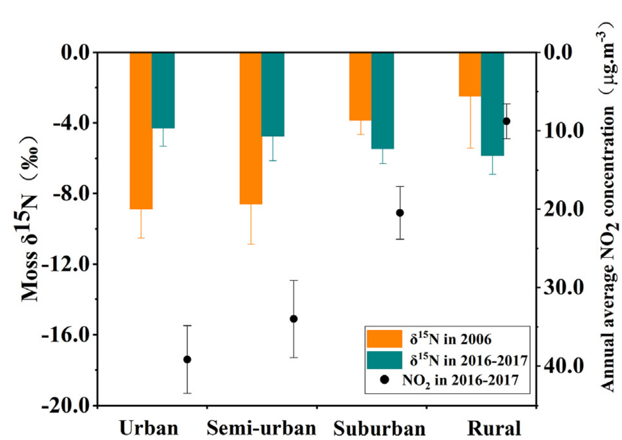

Fig. 6. Variations of moss $\delta^{15}N$ values in different study areas in 2006 and 2016–2017 and annual average NO_2 concentration in Guiyang in 2016–2017. The border of the boxes encompasses the 25th to 75th, and the whiskers represent the SD values.

respectively. However, moss nitrogen contents and $\delta^{15}N$ values, as well as the annual average NO_2 concentration, decreased with increasing distance from central Guiyang in the current study (2016–2017) (Fig. 6). This opposing trend in the gradient of $\delta^{15}N$ values along the urban-rural gradient in 2006 compared to 2016–2017 may indicate a change in nitrogen source in Guiyang. Further, the $\delta^{15}N$ values of moss showed a significant decreasing trend along a distance gradient from the road (<100 m) (Fig. 4). High-density traffic in urban areas not only causes a large amount of NO_x emissions (Asman et al., 1998), but also increases the NH_3 emissions from traffic sources (NOx emissions are still higher than NH_3) (Pearson et al., 2010; Liu et al., 2017). The largest NO_x emissions in urban areas come from on-road traffic, which is the largest contributor to pollutant emissions in urban areas (Colvile et al., 2001; Boulter et al., 2012). Moreover, in the current study, $\delta^{15}N$ values of mosses in urban and semi-urban areas were 4.0 to 6.0‰ higher than those values from moss in 2006 (Fig. 6). Over the past decade, increased car ownership (Fig. 1a) has contributed to an exponential increase in the average annual NO_2 concentration from 2006 to 2016 (Fig. 1a). According to the SIAR model estimations, the bulk nitrogen concentration of mosses in the urban area (2016–2017) was mainly derived from NO_x emissions from vehicle exhausts. Further, the SIAR model estimations show that the nitrogen concentration of mosses in the urban area in 2006 was mainly derived from coal combustion, animal waste, and fossil-derived nitrogen emissions. The contribution of NO_x to moss nitrogen concentrations in urban areas is much greater than that in rural areas, and the anthropogenic nitrogen in moss primarily comes from NO_x from coal combustion emissions. However, Liu et al. (2008c) attributed the relatively lower moss $\delta^{15}N$ values (more ^{15}N-depleted; $\delta^{15}N = -8.87 \pm 1.65‰$) in urban areas to NH_3 from sewage. Accordingly, NH_3 emissions from domestic waste and sewage might be overestimated and fossil fuel-derived N may be underestimated in previous studies (Xiao and Liu, 2011, Liu et al., 2008c; Liu et al., 2012; Xiao et al., 2013). According to the SIAR model estimations, NH_3 emissions from coal combustion had a greater contribution to moss nitrogen than NO_x emissions. In fact, coal combustion produces more NO_2 than NH_3. This can be explained by the fact that moss preference NH_y-N over NO_x-N has been reported in previous studies (Varela et al., 2013; Christian et al., 2014; Varela et al., 2016; Dong et al., 2017). In summary, these findings not only suggest that nitrogen pollution from urban traffic is gradually replacing traditional coal-burning as the most significant source of nitrogen pollution in the urban areas of Guiyang, but also indicate that the dominant constituent of urban regional atmospheric nitrogen pollution is changing from NH_y-N to NO_x—N.

The negative moss $\delta^{15}N$ values in the rural area ($\delta^{15}N = -2.48 \pm 0.95‰$) in the previous study by Liu et al. (2008c) indicate that atmospheric nitrogen deposition in the rural area is dominated by agricultural NH_y—N. Atmospheric NH_3 is mainly derived from animal waste and the application of chemical fertilizers (Pearson and Stewart, 1993; Zhao and Wang, 1994; Galloway et al., 1996; Pearson et al., 2000). It has been reported that NH_3 emissions from agricultural activities account for 61% of the total NH_3 emissions in Guiyang (Liu et al., 2017), which is consistent with the present study (>65.3% of NH_3 emissions from agricultural activities) (Fig. 1b). As shown in Fig. 6, the $\delta^{15}N$ values of mosses in the rural and suburban areas in 2016–2017 were lower (2 to 4‰) than the values from moss samples collected in 2006. A higher level of agricultural ammonia (fertilizer use and emissions, livestock, and poultry) in 2016 (an increase from 40.4 in 2006 to 57.7 kt in 2016) (Fig. 1b), which indicate increasing in ammonia emissions in the rural area and result in a relatively lower $\delta^{15}N$ value than in 2006. According to the SIAR model estimations, the dominant source of nitrogen in the rural area was biomass burning in 2006, while in 2016–2017, the dominant source was NH_3 volatilization from nitrogen fertilizers. Biomass burning contributed less NO_x than NH_3 to moss nitrogen in the rural area in 2006 and 2016–2017. Higher production of NH_3 than NO_x from biomass burning has been documented previously (Crutzen and Andreae, 1990).

Moss $\delta^{15}N$ values did not significantly differ among the different seasons, indicating that there was no significant difference in the sources of nitrogen absorbed by moss throughout the year. We did not find any significant seasonal variation in the moss $\delta^{15}N$ values in urban and semi-urban areas ($p > .05$), but the moss $\delta^{15}N$ values in the rural and suburban areas in spring and winter were significantly higher than those in summer and autumn ($p < .05$). In this study, the rural sampling area is a karst area. The main crops are rice and winter rapeseed. The main fertilizers are ammonium bicarbonate and urea. Fertilization (using urea and compound fertilizer) is mainly concentrated in March to April and in November. Total nitrogen loss from ammonium bicarbonate and urea accounts for 30–70% of nitrogen loss, and the nitrogen loss mainly occurs within 9 to 10 days after fertilization. The higher nitrogen loss from calcareous soil is primarily due to the higher ammonia loss. As shown in Fig. 5b, the fractional contributions of NHy from fertilizer used in spring and winter were significantly higher compared to those in summer and autumn ($p < .05$), the fractional contributions of NOx from the microbial nitrogen cycle in spring and winter were significantly lower than those in summer and autumn ($p < .05$), and the fractional contributions of nitrogen from biomass burning, and NHy from animal waste to moss nitrogen, did not differ significantly between the four seasons in rural areas ($p > .05$). In addition, the higher temperatures and more rainfall resulted in stronger microbial activity and increased release of NOx from soil (^{15}N-depleted) (Freyer, 1978; Heaton, 1990). Therefore, combined with the data in Table 1, this can explain why the nitrogen isotope in summer and autumn is lower than that in spring and winter. As shown in Fig. 3, we found no seasonal variation in the $\delta^{15}N$ values of mosses in urban areas. According to the analysis, using the SIAR model, in this work, we found that the fractional contributions of corresponding sources to moss nitrogen did not differ significantly between the four seasons in urban areas ($p > .05$).

5. Conclusion

China is experiencing enhanced nitrogen deposition, which has a significant negative impact on human and ecosystem health. Here we used epilithic moss as bio-monitors (bulk nitrogen contents and their isotopic compositions) to obtain a holistic understanding of the changes in atmospheric reactive nitrogen sources in Guiyang in the last decade (2006–2016/2017). In recent years, mosses in the Guiyang urban area were found to comprise nitrogen derived mainly from vehicle exhausts, while in the rural area, mosses comprised nitrogen derived primarily from NH_3 volatilization. Our findings not only indicate that nitrogen deposition in the urban area is primarily dominated by NO_x-N deposition, but they also revealed that urban regional atmospheric nitrogen pollution has changed from NH_y-N to NO_x-N over the last decade. The regulation of nitrogen emissions from urban traffic sources is an important measure to reduce the risk of serious nitrogen pollution in Guiyang City. However, emissions from NH_3 volatilization (particularly N-fertilizer) in rural areas also need to be addressed to suppress the sharp increasing trend in reactive nitrogen emissions in China. Although the SIAR model was used to investigate the fractional contributions of major sources to moss bulk nitrogen, further research is needed to verify the boundary conditions and assumptions in this work. In particular, it is necessary to measure the $\delta^{15}N$ values of gaseous nitrogen emission sources with greater accuracy so as to reduce the uncertainty of the source $\delta^{15}N$ value. To date, on a global scale, there are few isotopic studies of gaseous nitrogen emissions from typical natural and anthropogenic sources, particularly in China. In future studies, the kinetic and equilibrium isotope effect during uptake of various nitrogen compounds should be explored and appropriately considered. This study expands the application of plant tissue isotope analysis to atmospheric nitrogen pollution monitoring, and provides essential research tools and ideas to identify the sources of atmospheric nitrogen pollution. This study also contributes a fundamental geochemical basis for the prevention and control of urban nitrogen pollution.

Declaration of interests

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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Appendix A. Supplementary data

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