Atmospheric Environment 159 (2017) 1–10

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Nitrogen concentrations and nitrogen isotopic compositions in leaves of *Cinnamomum Camphora* and *Pinus massoniana* (Lamb.) for indicating atmospheric nitrogen deposition in Guiyang (SW China)

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HIGHLIGHTS

- N concentrations in camphor and Masson pine leaves can indicate N deposition.
- $\delta^{15}N$ of vascular plant leaves can provide an indication of the main N sources.
- ^{15}N-enriched traffic NO_x-N was the dominant atmospheric N source in urban areas.
- ^{15}N-depleted agricultural NHx-N was the main atmospheric N source in rural areas.

ARTICLE INFO

Article history:
Received 23 November 2016
Received in revised form
24 March 2017
Accepted 27 March 2017
Available online 28 March 2017

Keywords:
Leaf
Moss
Soil
$\delta^{15}N$
N deposition

ABSTRACT

Nitrogen (N) concentrations and $\delta^{15}N$ signatures in soil and camphor (*Cinnamomum Camphora*) and Masson pine (*Pinus massoniana* Lamb.) leaves collected along an urban-rural gradient in Guiyang (SW China) were investigated systematically. N concentrations in camphor (1.01–2.37%) and Masson pine (0.99–2.42%) leaves showed a significant decrease from central Guiyang (0–6 km) to suburban areas (18–24 km), while slightly increased leaf N concentrations reemerged at areas more than 24 km from the city center. The $\delta^{15}N$ values in camphor and Masson pine leaves also decreased from central Guiyang to the rural area, with more positive leaf $\delta^{15}N$ in the urban area and ^{15}N-depleted leaf $\delta^{15}N$ in the rural area. No significant differences were observed for soil N concentrations and soil $\delta^{15}N$ in these areas, which suggested that the decrease in leaf N concentrations was due to decreased atmospheric N deposition along the urban-rural gradient and that there were two isotopically different atmospheric N sources in Guiyang city: foliar $\delta^{15}N$ values in urban areas were mainly influenced by ^{15}N-enriched atmospheric NO_x-N from traffic emissions, while those in rural areas were primarily affected by ^{15}N-depleted atmospheric NH_x-N from agricultural activities. However, the pattern of moss (collected ten years prior, with lower traffic density and wastewater treatment rate in the urban area) $\delta^{15}N$ variation in the urban area (0–12 km) was contrary to that of the camphor and Masson pine leaves, indicating that the $\delta^{15}N$ values in previously collected urban mosses were mainly controlled by isotopically light NH_x-N from untreated wastes and sewage, but were much less affected by traffic. For the trees in the urban area, N concentrations in camphor and Masson pine leaves varied in parallel with their $\delta^{15}N$ values ($P < 0.0001$), and we thus applied a mass balance equation to estimate the $\delta^{15}N$ value (about 7‰) in the atmospheric N deposition in the urban area. This indicated that the greater $\delta^{15}N$ in urban camphor and Masson pine leaves reflected a higher contribution of NO_x-N to N deposition. This study shows that the analysis of N and $\delta^{15}N$ in camphor and Masson pine leaves is a promising method to indicate N deposition.

1. Introduction

Anthropogenic N emission has increased substantially during the recent decades, particularly in the many regions of Asia

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http://dx.doi.org/10.1016/j.atmosenv.2017.03.049
1352-2310/

experiencing rapid industrialization and urbanization (Kim and Cho, 2003; Galloway et al., 2008; Liu et al., 2011). The production and use of N fertilizers in China exceeded the sum of the European Union and the United States around 2000; however, more than half of the fertilizer N applied in China is lost to the environment in dissolved (NO_3^- and NH_4^+) or gaseous (NH_3, N_2, NO and N_2O) forms (Zhu and Chen, 2002; Ju et al., 2009). These fluxes, as well as N compounds from industrial and transport sectors, have resulted in dramatically increasing concentrations of N compounds in the atmosphere. Increased atmospheric N compound concentrations, through deposition in terrestrial and aquatic ecosystems, can lead to soil acidification, alter water chemistry, cause plant nutrient imbalances or deficiencies, reduce biological diversity and influence the air quality of cities (Vitousek et al., 1997; Driscoll et al., 2003; Clark and Tilman, 2008; Stevens et al., 2009; Kan et al., 2012). It has been widely recognized that the total emission of NH_3-N was higher than NO_x-N emission in China, and thus, NH_x-N was the dominant form in atmospheric N deposition. In fact, the mounting motor vehicle population (20.8-fold growth between the 1980s and the 2000s) and coal-based energy consumption structure (3.2-fold growth between the 1980s and the 2000s) have caused the ratio of NO_x-N to NH_x-N in total N deposition to increase significantly from about 0.2 to 0.5 between the 1980s and the 2000s in six regions of China (Southwest China, Southeast China, Tibetan Plateau, North China, Northeast China and Northwest China) (Liu et al., 2013). For Guiyang city, continuous development of the regional economy in recent years has led to sharply increasing emissions of NO_x and SO_2 (Tian et al., 2013); additionally, enhanced agricultural activities and continued population growth (increased excretory waste) have contributed large amounts of NH_3 emission (Liu et al., 2008a). Therefore, a better understanding of the current status of atmospheric N pollution, distribution of atmospheric N deposition and their possible sources in Guiyang city is of great significance.

The fact that a wide range of N compounds exists in the atmosphere (aerosols, gas phase and precipitation) has made it very complex and expensive to conduct instrumental measurements of N deposition. Thus, bio-monitoring has been regarded as an easier and less expensive way to monitor N deposition. Because they absorb mineral nutrients mainly from the atmosphere and precipitation, naturally growing mosses have been widely used to indicate N deposition (Pitcairn et al., 1998, 2006; Liu et al., 2007). Previous studies have demonstrated the positive relationship between moss N concentrations and atmospheric N deposition (Pitcairn et al., 2003; Xiao et al., 2010a). However, mosses will not grow or cannot be collected easily in seriously polluted regions, especially in urban centers with high densities of population and traffic. In contrast, tall arbors (e.g., *Cinnamomum Camphora* and *Pinus massoniana* Lamb.) are widely distributed in Guiyang city and readily sampled. We already know that N concentrations in vascular plant leaves can be influenced by atmospheric N and soil N, so the response of vascular plants to N pollutants may differ from mosses. Thus, very few studies have used vascular plant leaf N concentrations as a biomarker of atmospheric N deposition. Limited studies have mainly focused on dwarf shrubs and grasses. For example, a study by Hicks et al. (2000) in northern Britain suggested that foliar N concentrations increased linearly with total N deposition for *Calluna vulgaris*, *Erica cinerea*, *Deschampsia flexuosa* and *Nardus stricta*, and a study by Power and Collins (2010) also showed a quantitative relationship between N concentrations in *Calluna vulgaris* leaves and atmospheric N deposition. Therefore, more studies on tall arbors are urgently needed, which could provide further valuable information on vascular plants as bio-monitors of atmospheric N deposition.

The isotopic composition of atmospherically derived N has been known to provide reliable integrated information on the potential N sources of atmospheric inputs to various plant and soil environments (Evans and Ehleringer, 1993; Xiao et al., 2010b). In addition, the $\delta^{15}N$ values associated with NO_x-N from fossil fuel combustion are generally more positive than those associated with NH_x-N from agriculture and excretory wastes (Table 1). As is well known, moss $\delta^{15}N$ has been a desired tool to identify N emission sources because of its very low or even absent isotopic fractionation during N uptake (Bragazza et al., 2005). However, the $\delta^{15}N$ values in vascular plant leaves may be an integrated result of many factors, which can be summarized by the following aspects: atmospheric N, soil N, root depth, the influence of canopy trees, plant mycorrhizal status, isotopic fractionation in N uptake and anthropogenic N addition (Högberg, 1997; Evans, 2001; Choi et al., 2002; Asada et al., 2005; Xiao et al., 2011). Thus, although many researchers have reported that tree ring $\delta^{15}N$ could also respond to atmospheric N pollution (Savard et al., 2009; Kwak et al., 2009; Sun et al., 2010), vascular plants have been less commonly considered as bio-indicators of N deposition than mosses. Nevertheless, changes in foliar $\delta^{15}N$ could also be observed when plants were exposed to different nitrogenous pollutants. These limited studies were mostly conducted at forest ecosystems and mainly used coniferous trees as bio-indicators. For example, Ammann et al. (1999) found that more positive $\delta^{15}N$ values (+2‰) occurred in Norway spruce needles collected near a road, significantly different from the $\delta^{15}N$ values in needles (−3‰) sampled 980 m away. Saurer et al. (2004) reported that *Picea abies* needle $\delta^{15}N$ could be clearly used to identify inputs of NO_x from traffic exhausts.

Urban environments make an important contribution to local biodiversity, and few studies have been performed to examine the $\delta^{15}N$ values in vascular plant leaves in city areas. In this study, we investigated N concentrations and $\delta^{15}N$ values in soils and camphor and Masson pine leaves systematically from central Guiyang to the rural area to determine whether (1) N concentrations in camphor and Masson pine leaves can be used to identify areas of excess N deposition; (2) there are any differences in $\delta^{15}N$ values between soils and leaves; and (3) the $\delta^{15}N$ values in camphor and Masson pine leaves can be used to distinguish the main sources of atmospheric N deposition in the Guiyang area.

2. Materials and methods

2.1. Sampling area description

Guiyang city, the capital of Guizhou province (SW, China), is located in a karst region and is characterized by a subtropical monsoon climate with an annual mean temperature of 15.3 °C. The average altitude of Guiyang city is 1250 m. The prevailing wind direction in Guiyang city is southeast in the summer and northeast all year (Guiyang Environmental Protection Bureau, 2006). Two plant species, camphor (*Cinnamomum Camphora*) and Masson pine (*Pinus massoniana* Lamb.), are widely distributed in Guiyang city. The study area lies between 26°19′-26°45′ N latitude and between 106°19′-106°47′E longitude (Fig. 1). The major soil type in this study area is acid yellow soil (in the Chinese classification system) with strongly weathered, low base saturation and high aluminum concentration (Bohan et al., 1997; Larssen et al., 1998).

The urban center (the southern part of Yunyan and the northern part of Nanming) has a population density of 30,000/km^2 and over 100,000 motor vehicles (Li et al., 2012). Guiyang city has high-density traffic with a motor vehicle population of 225,400 in 2005 and 610,800 in 2010 (He, 2013), and the number increased to 790,000 in 2014 (General Office of Guiyang People's Government, 2014). Total emissions of NO_x in Guiyang in 2010 were 36.6 kt yr^{-1} (45.6 kg N ha^{-1} yr^{-1}), while the NO_x from vehicle

Table 1
N isotopic compositions of potential N sources in the atmosphere.

Sources		$\delta^{15}N$ (‰)	References
NO_x	Vehicle exhausts	+5.7 ± 2.8 (NO_2); +3.1 ± 5.4 (NO)	Ammann et al. (1999)
	Vehicle exhausts	+1.3 to +6.4 (NO_2)	Saurer et al. (2004)
	Coal combustion	+6.0 to +13.0	Heaton (1990)
	Guiyang rainwater	+2.0 ± 4.4	Xiao and Liu (2002)
NH_x	Sewage and wastes	−15 to −4	Freyer (1978), Heaton (1986, 1987)
	Fertilizer use	−5 to 0	Freyer (1978)
	Jülich (agricultural areas, Germany) rainwater	−12.1 ± 1.5	Freyer (1978)
	Guiyang rainwater	−12.2 ± 6.7	Xiao and Liu (2002)

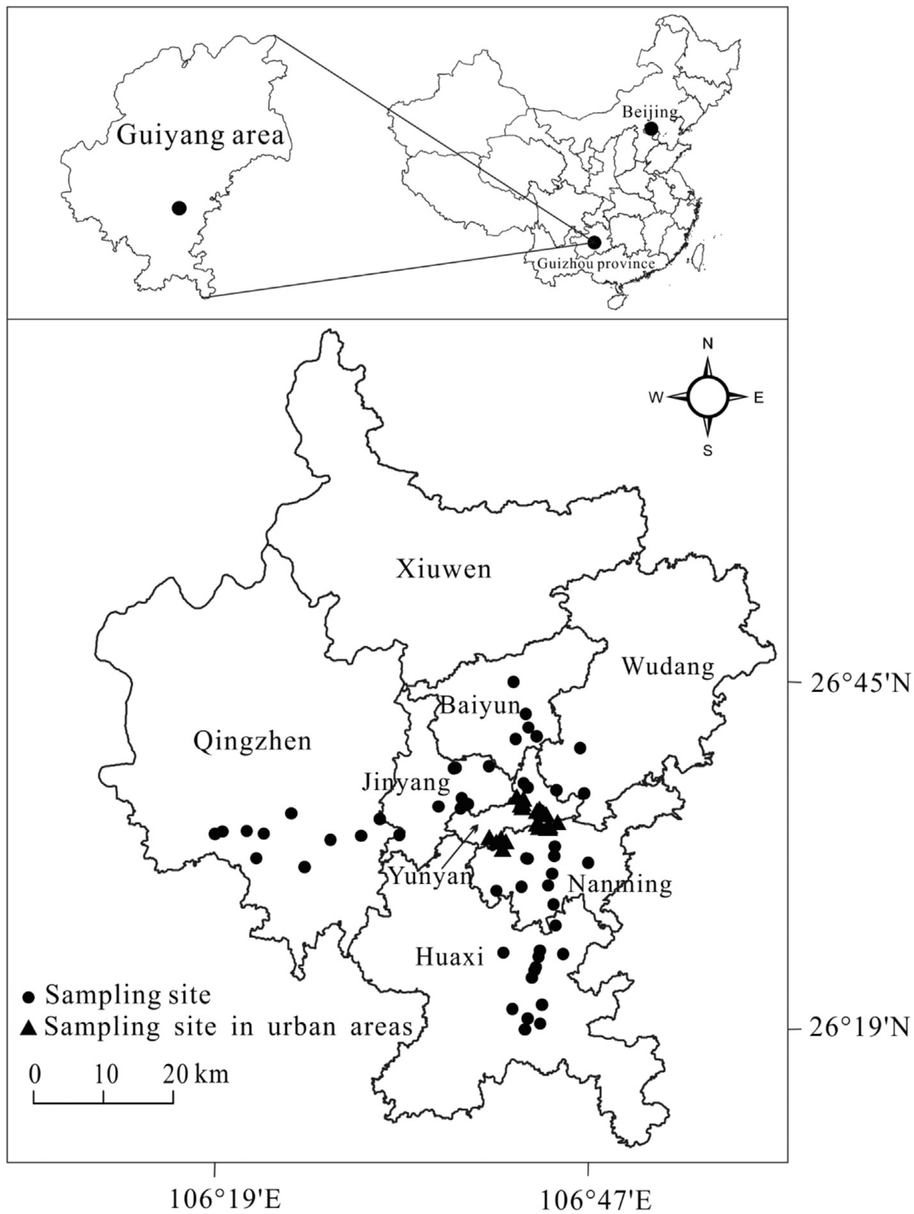

Fig. 1. Map showing the location of the Guiyang area and leaf sampling sites.

emissions (20.2 kt yr^{-1}) accounted for nearly half the amount of total NO_x emissions (He, 2013; Tian et al., 2013). Moreover, emissions of NO_x were 12 times greater than NH_3 emissions in 2010 throughout Guizhou province (MEP, 2011). In the past, the low NO_x-N/NH_x-N ratio in the N deposition of Guiyang city was mainly attributed to substantial NH_3 emission from wastewater (the rate of wastewater treatment was 17.2% in 2004 and 20% in 2005) (Guiyang Environmental Protection Bureau, 2006), while in recent years, wastewater treatment has centralized, and the rate of wastewater treatment has exceeded 90% (Guiyang Environmental Protection Bureau, 2016a). Therefore, rapidly increasing emission of NO_x from vehicles and decreasing NH_3 emission caused by centralized wastewater treatment have led to a higher NO_x-N/NH_x-N ratio in N deposition in the Guiyang area. For example, the NO_x-N/NH_x-N ratio in wet N deposition was only 0.17 in 1984 (Galloway et al., 1987), 0.20 in 2001 (Xiao and Liu, 2002) and 0.51 in 2007–2008 (Han et al., 2011), while in 2014 the ratio had climbed to 0.82 (Qu et al., 2016).

2.2. Sampling and treatment

Samples were collected in May and June 2015. Sampling was conducted from central Guiyang to the rural area (Fig. 1). At each site, one camphor tree and one Masson pine tree were selected, and the distance between the camphor and Masson pine at each site was less than 1 km for most of the sites. Urban camphor samples were collected around parks and hills (at least 60 m away from main roads), and Masson pine sampling sites in the city center were mainly located at parks and hills (at least 80 m away from main roads). In rural areas, camphor and Masson pine leaves were collected at least 200 m away from main roads. Camphor and Masson pine trees chosen for sampling were about 15 years old (about 8 m in height) and about 25 years old (about 13 m in height), respectively. About 4–8 g of mature current-year Masson pine leaves were collected, and about 10 g of mature current-year camphor leaves (10–30 cm^2 surface area) were sampled. All samples were collected from outer branches at the east, south, west, and north directions (cut about 12 m above the ground for Masson pine and about 7 m for camphor). To estimate the level of atmospheric N deposition, mosses (*Haplocladium microphyllum* (Hedw.) Broth) were collected immediately from the surrounding exposed rocks (less than 50 m away from trees chosen for leaf sampling) after leaves were sampled at each site. Three to five moss samples were collected at each area (3–5 subsamples were combined into one sample). Sampling was performed under stable weather conditions without rain and needed to avoid the disturbance of local pollution sources. Only green and healthy samples were taken; dead samples were avoided.

Soils (about 100 g) were collected from the rooting zone (at depths of 0–10 cm) before leaves were sampled at each site. Roots and leaf litter were removed from the soil samples immediately. Fresh samples were stored in clean plastic bags and placed in a chilled storage box. In the lab, all samples were washed. Half of each leaf sample was dried at 80 °C for 24 h. Soil samples were also dried at 80 °C for 24 h. Then, they were ground to a fine homogeneous powder. The powder samples were stored in a desiccator before analysis.

2.3. Analyses

N concentrations (%; dry weight) were tested using a vario MACRO cube elemental analyzer (Elementar, Frankfurt, Germany). The analytical precision (SD, n = 3) of N concentrations was better than 0.02%. The $\delta^{15}N$ values in samples were tested using a Thermo MAT 253 mass spectrometer (Thermo Finnigan, Bremen, Germany) coupled to a Flash EA 2000 analyzer (Thermo Scientific, Bremen, Germany). An analytical precision of ±0.1‰ could be obtained for $\delta^{15}N$ analysis. Potassium nitrate (IAEA-NO-3, $\delta^{15}N = +4.7‰$) and ammonium sulfate (IAEA-N-1, $\delta^{15}N = +0.4‰$) standards were used to calibrate the $\delta^{15}N$ values. All reported data were a mean of 3–5 repeated measurements for each sample. The $\delta^{15}N$ values were calculated as parts per thousand:

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

where R was the $^{15}N/^{14}N$ ratio.

2.4. Estimation of atmospheric N deposition

In this study, atmospheric N deposition at each sampling area was estimated using the highly credible relationship between moss N concentrations (y) and atmospheric N deposition (x) ($y = 0.052x + 0.73$, $R^2 = 0.70$, $P < 0.001$) (Xiao et al., 2010a). Estimated atmospheric N deposition values are shown in Table 2.

2.5. Data analysis

Differences between groups of samples were tested using a one-way ANOVA with a Tukey-HSD test in SPSS 19 (IBM, Chicago, USA), and the results were accepted as $P < 0.05$. Graphs were created with Origin 9.0 (OriginLab Corporation, Massachusetts, USA).

3. Results

3.1. N concentrations in leaves and soils

Spatial variations of N concentrations in camphor and Masson pine leaves from central Guiyang to the rural area are presented in Fig. 2. N concentrations in camphor and Masson pine leaves varied from 1.01% to 2.37% and from 0.99% to 2.42%, respectively. Moreover, the average values of camphor leaf N concentrations within each 6 km from the urban to the rural area were always higher than those in Masson pine leaves. The highest mean camphor and Masson pine foliar N concentrations within each 6 km from central Guiyang to the rural area occurred in the urban center (0–6 km), corresponding to higher average NO_2 concentration in the air and atmospheric N deposition (Table 2). The average values of N concentrations in the two types of leaves within each 6 km from the city center to the rural area both showed a decreasing trend; however, both of the lowest values 1.53± 0.20% for camphor leaves and 1.19± 0.13% for Masson pine leaves (Table 3) did not occur in the rural area (30–36 km), but rather in the 18–24 km area, which had lower NO_2 concentration and atmospheric N deposition (Table 2).

Table 2
Atmospheric N deposition and atmospheric NO_2 concentrations (in parentheses minimum and maximum values) at different sampling areas.[a]

Sites (km)	Estimated N deposition (kg N ha^{-1} yr^{-1})	Reported in the literature (kg N ha^{-1} yr^{-1})	The average NO_2 concentrations in the atmosphere in 2010 (μg m^{-3})	The average NO_2 concentrations in the atmosphere in 2016 (April 4th-June 15th) (μg m^{-3})
0–6	32.22	29.21 ± 6.17	34.9 (7.0; 94.0)	40.2 (20.0; 70.0)
6–12	21.63	21.98 ± 8.34	27.9 (8.0; 116.0)	34.1 (18.0; 57.0)
12–18	17.84	17.93 ± 7.49	12-24 km: 20.1 (4.0; 83.0)	21.5 (9.0; 40.0)
18–24	11.68	11.95 ± 3.95		
24–30	19.01	16.70 ± 2.76	24-36 km: 14.7 (3.0; 67.0)	13.8 (2.0; 43.0)
30–36	22.90	20.86 ± 3.72		
Average	20.88	19.77	24.4	27.4

[a] Data of atmospheric NO_2 concentrations and atmospheric N deposition are from Tian et al. (2013), Liu et al. (2009) and Guiyang Environmental Protection Bureau (2016b).

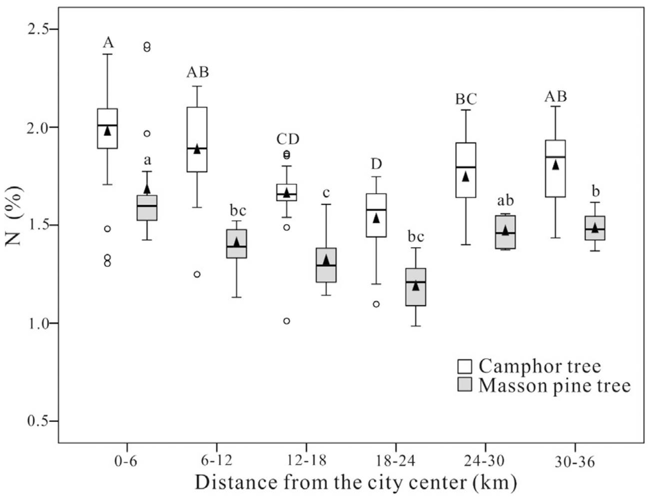

Fig. 2. Variations of N concentrations in camphor and Masson pine leaves from central Guiyang to the rural area. The boundaries of the boxes indicate the 25th and 75th percentiles; the solid lines and triangles within the boxes mark the median and the mean, respectively. Significant and spatial differences in camphor leaf N concentrations are marked with uppercase letters, while those in Masson pine leaf N concentrations are marked with lowercase letters ($P < 0.05$).

In areas beyond 24 km from the urban center, the average N concentration values in both types of leaves did not continue to decrease, but increased slightly instead. The patterns of leaf N concentration clearly indicated that the variations of leaf N concentrations may be related to atmospheric N deposition. This was supported by a correlation analysis. As presented in Fig. 3, N concentrations in both camphor and Masson pine leaves increased linearly with atmospheric N deposition estimated by moss N analysis ($P < 0.05$).

Total N concentrations of soil in camphor and Masson pine rooting zones were in the range of 0.06%–0.34% and 0.12%–0.57%, respectively. Mean values of soil N concentrations between sampling areas exhibited no significant differences ($P > 0.05$) (Table 3).

3.2. The $\delta^{15}N$ values in leaves and soils

As shown in Fig. 4, the $\delta^{15}N$ values in camphor and Masson pine leaves both varied substantially and presented a decreasing trend from the urban to the rural area. The $\delta^{15}N$ values in camphor and Masson pine leaves ranged from −5.0‰ to +7.6‰ and from −5.4‰ to +6.5‰, respectively. This large leaf $\delta^{15}N$ ranges clearly suggested that camphor and Masson pine leaves may be highly sensitive to the variation of atmospheric N deposition. According to average $\delta^{15}N$ values in leaves within each 6 km from central Guiyang to the rural area (Fig. 4), the most positive averages of camphor and Masson pine leaf $\delta^{15}N$ both occurred in the urban center (+4.2 ± 1.7‰ for camphor leaves and +3.6 ± 1.9‰ for Masson pine leaves), while significantly more negative averages of leaf $\delta^{15}N$ were observed in the rural area. Moreover, averages of Masson pine leaf $\delta^{15}N$ within each 6 km from the urban to the rural area were found to be lower than those of camphor leaves.

In contrast, the range of soil $\delta^{15}N$ values was limited from +1.1‰ to +8.1‰ from the urban to the rural area (Table 3). Although the mean values of soil $\delta^{15}N$ within each 6 km from the urban to the rural area showed a slightly decreasing trend, the decrease was not significant ($P > 0.05$) (Table 3). Across all the sampling sites, the $\delta^{15}N$ values in camphor and Masson pine leaves were lower than those in soils.

3.3. The relationship between leaf N and $\delta^{15}N$

A correlation between soil $\delta^{15}N$ and leaf $\delta^{15}N$ was not seen ($P > 0.05$), and N concentrations of soil were also not significantly related to foliar N concentrations and $\delta^{15}N$ values ($P > 0.05$). However, foliar N concentrations were found to be related to atmospheric N deposition ($P < 0.05$). Therefore, we wondered whether a relationship existed between foliar N concentrations and $\delta^{15}N$ values. A two-member mixing model has been reported in the studies of Keeling (1958) and Bauer et al. (2004); briefly, N input to leaves was assumed to originate from background N (N_b) and atmospheric N (N_a) with different $\delta^{15}N$ values ($\delta^{15}N_b$ and $\delta^{15}N_a$, respectively), and $\delta^{15}N_{leaf} = \delta^{15}N_a + N_b \times (\delta^{15}N_b - \delta^{15}N_a)/N_{leaf} = \delta^{15}N_a + \text{constant}/N_{leaf}$. Based on this model, a positive correlation between leaf $\delta^{15}N$ and 1/leaf N concentrations was found in the urban area (0–12 km) (Fig. 5). This model explained the variability of data well in the urban area (0–12 km), while significant correlations between leaf $\delta^{15}N$ and 1/leaf N concentrations were not observed in other areas using this procedure. The intercept of the above linear equation indicated the mean $\delta^{15}N$ values of atmospheric N sources. As shown in Fig. 5, the intercept of about 7‰ for the data from the urban area was closer to the $\delta^{15}N$ values associated with NO_x from fossil fuel combustion (Table 1).

4. Discussion

4.1. Implications of leaf N

Published works have shown that highly consistent responses of mosses to atmospheric N inputs were significantly higher leaf N concentrations (Pitcairn et al., 2003, 2006; Xiao et al., 2010b; Harmens et al., 2011). For example, Xiao et al. (2010a) integrated a great deal of published data and found a robust relationship between moss N concentrations (y) and atmospheric N deposition (x) ($y = 0.052x + 0.73$, $P < 0.001$), and similar quantitative relationships had been established in an earlier study by Pitcairn et al. (1998). Additionally, there is a further problem wherein foliar N concentrations of vascular plants can be influenced by different N

Table 3
N concentrations in camphor and Masson pine leaves and soil and soil $\delta^{15}N$ at different sampling areas (in parentheses minimum and maximum values).

Areas (km)	Sample (n)		N concentration (%)				Soil $\delta^{15}N$(‰)
	Camphor	Pine	Camphor leaf	Soil	Pine leaf	Soil	
0–6	22	20	1.95 ± 0.27	0.24 ± 0.07 (a)	1.68 ± 0.27	0.22 ± 0.07 (a)	5.4 ± 1.8 (2.4; 7.1) (A)
6–12	20	15	1.89 ± 0.23	0.20 ± 0.09 (a)	1.39 ± 0.11	0.20 ± 0.05 (a)	5.3 ± 1.6 (3.6; 8.1) (A)
12–18	23	20	1.65 ± 0.17	0.15 ± 0.07 (a)	1.32 ± 0.12	0.29 ± 0.15 (a)	3.9 ± 2.0 (1.2; 7.2) (A)
18–24	13	19	1.53 ± 0.20	0.15 ± 0.08 (a)	1.19 ± 0.13	0.18 ± 0.05 (a)	4.4 ± 1.7 (2.3; 7.0) (A)
24–30	12	16	1.76 ± 0.20	0.19 ± 0.04 (a)	1.46 ± 0.07	0.25 ± 0.07 (a)	3.4 ± 1.3 (1.2; 5.7) (A)
30–36	16	12	1.82 ± 0.20	0.23 ± 0.04 (a)	1.49 ± 0.07	0.22 ± 0.05 (a)	3.3 ± 1.5 (1.1; 6.1) (A)

Same letters indicate no significant difference between groups of samples (marked with lowercase letters for soil N concentrations, marked with uppercase letters for soil $\delta^{15}N$) ($P > 0.05$).

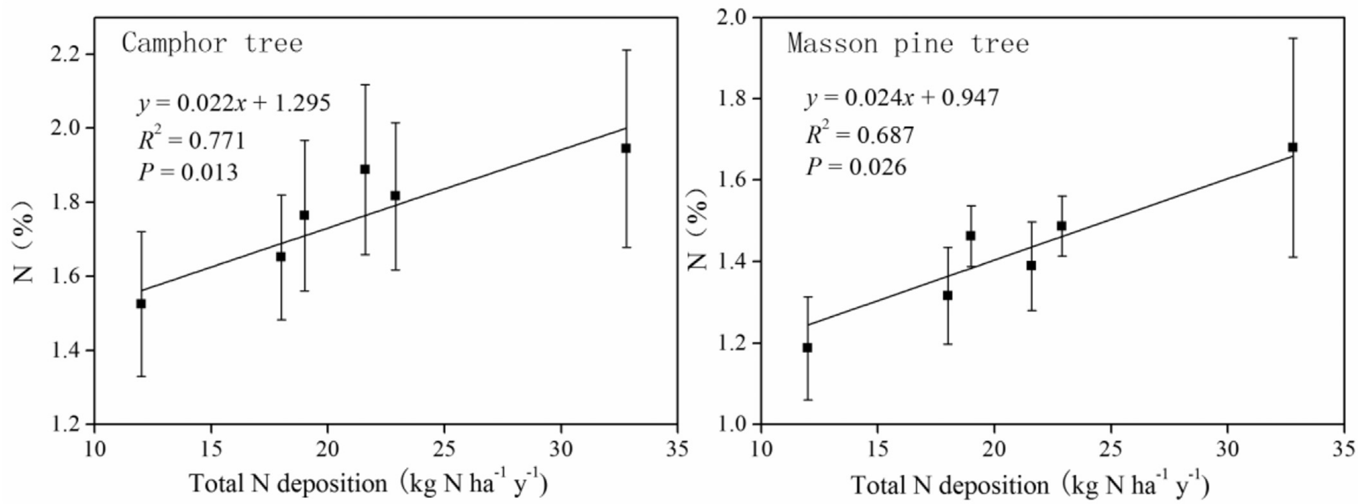

Fig. 3. The relationship between N concentrations in camphor and Masson pine leaves and total N deposition. Error bars represent standard deviations.

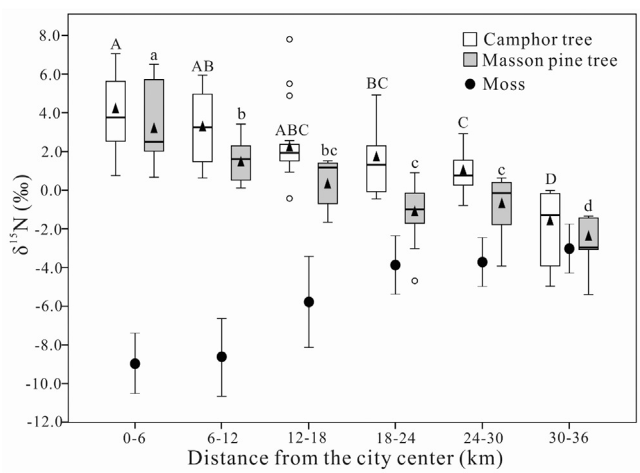

Fig. 4. Variations of $\delta^{15}N$ values in camphor and Masson pine leaves and mosses from central Guiyang to the rural area. The boundaries of the boxes indicate the 25th and 75th percentiles; the solid lines and triangles within the boxes mark the median and the mean, respectively. Significant and spatial differences in camphor leaf $\delta^{15}N$ are marked with uppercase letters, while those in Masson pine leaf $\delta^{15}N$ are marked with lowercase letters (*P < 0.05*). The data of moss $\delta^{15}N$ (Mean ± *SD*) is cited from Liu et al. (2008b).

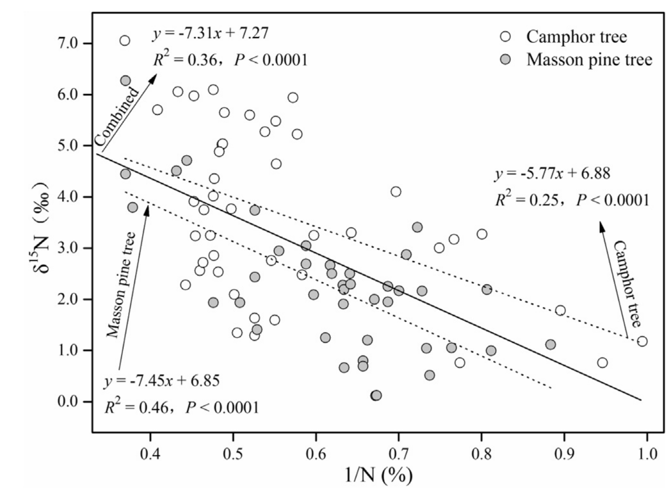

Fig. 5. The relationship between the inverse of the N concentrations in camphor and Masson pine leaves and the $\delta^{15}N$ values for the data from the area of 0–12 km.

sources (e.g., atmospheric N and soil N). Thus, only a few studies have been conducted using vascular plants as bio-indicators of atmospheric N deposition, and available studies mainly concentrated on dwarf shrubs (*Calluna vulgaris* and *Erica cinerea*) (Pitcairn et al., 2001; Power and Collins, 2010) or grasses (*Nardus stricta* and *Deschampsia flexuosa*) (Hicks et al., 2000). This shows that it is urgent and important to research the feasibility of tall arbors as bio-indicators of atmospheric N pollution. In this study, no significant difference in soil N concentrations between sampling areas was found (*P > 0.05*), and N concentrations in both camphor and Masson pine leaves increased linearly with atmospheric N deposition (*P < 0.05*) (Fig. 3). This indicated that although vascular plant leaf N concentrations can be influenced by different N sources, it is possible to use N concentrations in tall arbor leaves to indicate the different levels of N deposition. Therefore, the robust relationships between foliar N concentrations and atmospheric N deposition for camphor and Masson pine trees in this study further implied that vascular plant foliar N concentrations may be used to identify areas of excess N deposition.

Liu et al. (2013) collected a total of 981 observations of vascular plant foliar N concentrations across the whole of China and found that woody plant leaf N concentrations (in unfertilized and non-agricultural ecosystems) increased about 27.5% when the average atmospheric N deposition increased from 13.2 kg N ha^{-1} yr^{-1} in the 1980s to 21.1 kg N ha^{-1} yr^{-1} in the 2000s. It is apparent that higher average leaf N concentrations in a certain area may be connected to higher atmospheric N deposition. Similarly, Han et al. (2005) collected a total of 2094 observations from the published literature (between 1980 and 2005, corresponding levels of atmospheric N deposition between 13.2 kg N ha^{-1} yr^{-1} and 21.1 kg N ha^{-1} yr^{-1}) on higher plant leaf N concentrations across 127 sampling sites in China (including the Guizhou area) and reported that the geometric mean of N concentrations in conifer leaves was 1.17%. The geometric mean of Masson pine leaf N concentration in this study was 1.41% (greater than the mean of 1.17%), suggesting that the average level of atmospheric N deposition in the Guiyang area may have exceeded 13.2 kg N ha^{-1} yr^{-1} and was closer to 21.1 kg N ha^{-1} yr^{-1}, similar to the average value of 19.77 kg N ha^{-1} yr^{-1} in the Guiyang area (Liu et al., 2009). This average N deposition level was higher than the critical load of N for some terrestrial ecosystems. For example, the critical load of N was set at 10 kg N ha^{-1} yr^{-1} for heathland, ombotrophic bogs and fens and was set at 10–12 kg N ha^{-1} yr^{-1} or 3–14 kg N ha^{-1} yr^{-1} for coniferous forests (Nilsson and Grennfelt, 1988; Schulze et al., 1989; Krupa, 2003; Pitcairn et al., 2003). We can therefore infer that most of the Guiyang area has been influenced by inputs of anthropogenic N to some extent.

The patterns of N concentration in camphor and Masson pine leaves along an urban-rural gradient as shown in Fig. 2 clearly implied the spatial variation of atmospheric N deposition in the Guiyang area. Average N concentrations in both types of leaves decreased from the city center to the 18–24 km area, which corresponded to the variations of atmospheric N deposition and atmospheric NO_2 concentration (Table 2). This result may be attributed to the large amount of anthropogenic N inputs from the heavy traffic density and the rapidly expanding industrial activities in the urban area, while in the combining area between the urban and rural areas, N pollutants from the urban area decreased. Slightly risen leaf N concentrations in areas beyond 24 km from the city center indicated increased atmospheric N deposition in these areas, which was possibly caused by increased NH_3 emission associated with agricultural activities (fertilizer application and animal excrement). In general, the positive relationships between foliar N concentrations and atmospheric N deposition provide robust evidence to show the value of vascular plants as bio-indicators of N deposition, particularly in urban areas where heavy pollution and available habitat have severely limited the use of mosses as bio-indicators of atmospheric N pollution. Furthermore, assessment of the level of atmospheric N deposition based on the above relationship can facilitate the understanding of the ecological effects of atmospheric N deposition to the rocky karst area (desired bryophyte species will not grow).

4.2. *The pattern of soil $\delta^{15}N$*

It is generally known that the soil $\delta^{15}N$ values can be influenced by a variety of factors including atmospheric N input, microbial cycling of N, nitrification, root depth and anthropogenic N addition. The lack of long-term historical data on atmospheric N deposition and soil $\delta^{15}N$ in Guiyang city (especially in the remote rural area) made it difficult to prove the direct correlation of atmospheric N deposition and soil $\delta^{15}N$. To date, reports on soil $\delta^{15}N$ associated with atmospheric N deposition are rare, although Kuang et al. (2011) reported that increased atmospheric N deposition from motor vehicles and industrial activities in south China contributed substantially to the changes in forest soil $\delta^{15}N$. In this study, while soil $\delta^{15}N$ showed a slightly decreasing trend from the urban to the rural area, the decrease was not significant ($P > 0.05$) (Table 3). The fact that we observed a slightly decreasing trend of soil $\delta^{15}N$ from central Guiyang to the rural area is likely caused by isotopically different N input sources.

On the one hand, foliar litter with differing $\delta^{15}N$ values could provide continuous N input into soil, and isotope fractionation will occur in subsequent mineralization, which has been shown to cause a decreasing gradient of soil $\delta^{15}N$ with increasing distance from the highway (Ammann et al., 1999). As shown in Fig. 4, the $\delta^{15}N$ values of camphor and Masson pine leaves both showed a strong distance gradient from the urban to the rural area, with more positive foliar $\delta^{15}N$ in the urban area and ^{15}N-depleted leaves in the rural area. Accordingly, isotopically different leaf litter between sampling areas may lead to this pattern of soil $\delta^{15}N$. In addition, rapidly increasing NO_x emission (from increased motor vehicles and coal consumption) has become an important contributor to acid rain in the urban area of Guiyang, while enhanced agricultural activities have caused huge amounts of NH_3 emission in the rural area of Guiyang. Increased concentrations of N compounds in the atmosphere (such as NO_x and NH_3) could contribute to a great deal of available plant N sources (Vitousek et al., 1997; Wang et al., 2010). NH_x-N has generally more negative $\delta^{15}N$ values than NO_x-N (Table 1). Therefore, NO_x-N with high $\delta^{15}N$ continuous input into the urban soil and the strongly ^{15}N-depleted NH_x-N input into the rural soil may be the important reason causing the slightly decreasing trend of soil $\delta^{15}N$ from the urban to the rural area.

4.3. *$\delta^{15}N$ variations during soil and plant processes*

The $\delta^{15}N$ values in plants and soil are widely used to assess ecological and environmental impacts of anthropogenic N inputs and trace N input sources (Bergstrom et al., 2002; Pardo et al., 2006, 2007; Power and Collins, 2010). In this study, the $\delta^{15}N$ values of camphor and Masson pine leaves were found to be lower than those of soil. Many studies have also shown this pattern (Gebauer and Dietrich, 1993; Kuang et al., 2011; Xiao et al., 2011). As mentioned in the introduction, the $\delta^{15}N$ values in vascular plant leaves reflect the net effect of many factors. In this study, the influences from root depth and canopy height between these sampled trees may be small because camphor trees with similar size, similar age and similar canopy height were chosen, and the same for the Masson pines. Under natural conditions, the organic layer of soil can provide N input into the mineral soil, while mineralization discriminates against the heavier ^{15}N, so that ^{15}N enrichment of the lower soil layer (0–10 cm) can be found (Gebauer et al., 1994). In addition, the major pathways of N transformation in soil (e.g., ammonia volatilization, nitrification, denitrification and microbial immobilization of soil ammonium) can cause a long-term ^{15}N enrichment of residual N (Högberg, 1990; Högberg et al., 1995; Michelsen et al., 1998). Ammonia volatilization could be the exclusive pathway for soil ^{15}N enrichment in this study since elevated emissions of SO_2 and NO_x in Guiyang city have been important sources to acid rain, and thus, a large amount of acid material has entered the soil (Xiao et al., 2013). For most vascular plants, nitrate and ammonium in soil were the primary natural N sources available for root uptake (Gebauer and Schulze, 1991; Seith et al., 1994), while subsequent assimilation and translocation processes of N within the plants tended to decrease the $\delta^{15}N$ values of the original soil N sources (Ammann et al., 1999; Xiao et al., 2011). Therefore, when soil N sources (especially for nitrate) are taken up by camphor and Masson pine roots, higher soil $\delta^{15}N$ will be found.

Because relatively small isotope fractionation has been associated with N uptake and assimilation of roots in N-limited ecosystems (Michelsen et al., 1996, 1998), leaf $\delta^{15}N$ may represent the ^{15}N abundance of soil N sources. However, N supply will exceed the N demand of plants in most urban ecosystems. As in this study, all trees chosen for leaf sampling were exposed to high level of atmospheric N deposition, so atmospheric N deposition may become an important factor affecting N isotopic composition in leaves. We already know that the uptake of atmospheric N compounds (e.g., NO, NO_2, HNO_3 and NH_3) through the leaves is considerable. In addition, as leaves can directly gain those atmospheric N compounds through the stoma, the isotope fractionation caused by leaf uptake of these compounds may be small compared to N transformation occurring in soil and plant processes (Handley and Raven, 1992). Accordingly, if plants are exposed to higher level of atmospheric N deposition and can obtain much of their N requirements by direct leaf absorption of atmospheric N, while leaf $\delta^{15}N$ of vascular plants may be affected by many factors as mentioned above, foliar $\delta^{15}N$ in plants grown in polluted areas with high atmospheric N concentrations would be closer to the $\delta^{15}N$ values of atmospheric N sources. In addition, average $\delta^{15}N$ values in

Masson pine leaves were found to be lower than those in camphor leaves from the urban to the rural area. Factors including leaf morphology and leaf surface trichomes or cutin would affect foliar wettability and N residence time and further lead to different leaf uptakes of atmospheric N. Thus, probably because camphor leaves had greater surface area and longer N residence time than Masson pine leaves, camphor leaf $\delta^{15}N$ may be more susceptible to atmospheric N input than Masson pine leaf $\delta^{15}N$.

Through the above discussion, we interpreted isotopic fractionation during soil and plant processes to be able to cause more positive $\delta^{15}N$ values in soil than those in leaves. But even so, atmospheric N deposition can still influence the N isotope composition in leaves. Therefore, we expect to derive more information on atmospheric N sources from the N isotope composition in leaves.

4.4. Implications of leaf $\delta^{15}N$

Generally, moss $\delta^{15}N$ can provide accurate information on the prevailing N sources in the surroundings because mosses obtain nutrients mainly from the atmosphere (Pearson et al., 2000; Bragazza et al., 2005; Zechmeister et al., 2008). However, mosses are often covered by other plants and are difficult to be collected in heavily polluted urban regions. Although foliar $\delta^{15}N$ of vascular plants can be controlled by many factors as discussed above, information on atmospheric N sources could still be recorded by foliar $\delta^{15}N$ values. For example, in Switzerland, positive $\delta^{15}N$ of *Picea abies* needles occurred in near a motorway, becoming more negative with distance from the motorway (Saurer et al., 2004). Camphor leaves growing near roads had more positive $\delta^{15}N$ levels (up to +2.5‰), while strongly ^{15}N-depleted camphor leaves (low as −11.8‰) were observed near a chemical fertilizer plant (Xiao et al., 2011). A study by Stewart et al. (2002) also suggested that the $\delta^{15}N$ values in leaves sampled in a polluted area would be closer to the $\delta^{15}N$ values of mainly atmospheric N pollutants. In this study, the fact that the $\delta^{15}N$ values in vascular plant leaves can be used as indicators of atmospheric N deposition in a larger geographic region can be further demonstrated by the following discussion.

The ranges of leaf $\delta^{15}N$ were very large from central Guiyang to the rural area, while soil $\delta^{15}N$ remained relatively stable. This large leaf $\delta^{15}N$ range suggested that camphor and Masson pine leaves may be extremely sensitive to the variation of atmospheric N deposition. In addition, we found that the difference in soil and leaf $\delta^{15}N$ increased with increasing distance from the urban center. The isotopic fractionation occurring in plant and soil processes could not result in the significant differences between leaf $\delta^{15}N$ in different areas since both soil $\delta^{15}N$ and soil N concentrations were not significantly different in this study (Table 3). Therefore, the only reason causing the differences in soil and leaf $\delta^{15}N$ increases with increasing distance from the city center was the varying atmospheric N deposition.

Foliar $\delta^{15}N$ values notably presented an urban-rural gradient in this study, with the most positive leaf $\delta^{15}N$ in the urban center (+4.2 ± 1.7‰ for camphor leaves and +3.6 ± 1.9‰ for Masson pine leaves). This result was similar to many reports of urban moss $\delta^{15}N$. For instance, studies by Gerdol et al. (2002) in northern Italy and Pearson et al. (2000) in the London area found significantly more positive moss $\delta^{15}N$ in urban areas than in rural areas, which were attributed to greater uptake from ^{15}N-enriched atmospheric NO_x-N (from traffic and industrial emissions) by mosses in the urban areas and greater uptake of ^{15}N-depleted NH_x-N (from agricultural activities) by mosses in the rural areas. However, the reverse pattern of moss $\delta^{15}N$ (collected ten years ago) in Guiyang city proposed by Liu et al. (2008a) showed that urban moss $\delta^{15}N$ levels were more negative than those in the rural area (Fig. 4), which revealed that the $\delta^{15}N$ values in previously collected urban mosses were mainly affected by isotopically light NH_x-N deposition from untreated wastes and sewage ($\delta^{15}NH_x$-N = −15‰ to −4‰, Table 1), while being much less controlled by traffic. The rate of wastewater treatment in Guiyang city was only 17.2% in 2004, which caused N deposition in the urban center to be dominated by NH_x-N from wastewater and wastes (Liu et al., 2008a). After that, the wastewater treatment rate increased notably year-over-year (20% in 2005, more than 90% in 2015) under local policies (Guiyang Environmental Protection Bureau, 2006 and 2016a). However, during the last ten years, the sharply increased motor vehicle population and coal consumption in Guiyang city drove a more rapid increase in NO_x-N emission than in NH_3-N emission. Qu et al. (2016) reported that the emission fluxes of NO_x-N and NH_3-N in Guiyang in 2014 were 70.56 kg N ha^{-1} yr^{-1} and 7.07 kg N ha^{-1} yr^{-1}, respectively. Motor vehicles were considered to be the most polluting sector for NO_x-N, with a contribution of about 56.2% (average NO_2/NO_x ratio of 0.75 in urban area in 2010) (Tian et al., 2013). Coal consumption in the urban area, by contrast, has been reduced severely by the national policy of energy conservation promotion, such that one-half of all urban dwellers have replaced coal by natural gas, and many heavily polluting industries in urban areas were forced to reform or move to another district. Heavy traffic density has directly led to high average atmospheric NO_2 concentrations in the urban area. In the urban center, the average atmospheric NO_2 concentrations of 34.9 μg m^{-3} in 2010 and 40.2 μg m^{-3} in 2016 (April 4th-June 15th) (Table 2) were well above the critical level of 10–15 μg m^{-3} for NO_2 at the northern coniferous forests (Manninen and Huttunen, 2000) and the background value of 17.3 μg m^{-3} for NO_2 in a clean area of London (Carslaw and Carslaw, 2007). In addition, the gradient of atmospheric NO_2 concentrations from central Guiyang to the rural area was consistent with the trend of leaf $\delta^{15}N$ variation. According to the $\delta^{15}N$ inventories of potential atmospheric N sources (Table 1), the more positive leaf $\delta^{15}N$ observed at the 0–12 km area were closer to the $\delta^{15}NO_x$ value rather than the $\delta^{15}NH_x$ value. Moreover, the $\delta^{15}N$ value of atmospheric N deposition of the urban area could be estimated from the relationship between urban leaf $\delta^{15}N$ and 1/leaf N concentrations (Fig. 5), and the estimated value of about 7‰ was apparently closer to the $\delta^{15}N$ values associated with NO_x. The above discussion thus further corroborated that significantly more positive leaf $\delta^{15}N$ in the current urban area may be largely controlled by traffic-derived NO_x-N rather than NH_x-N sourced from untreated wastes and sewage. It is difficult to collect moss samples in heavy traffic regions (e.g., the urban center); conversely, the distribution of the vascular plants is actually more uniform. Therefore, the above result revealed that the main atmospheric N pollutants can be distinguished efficiently by the $\delta^{15}N$ values in vascular plant leaves.

On the other hand, foliar $\delta^{15}N$ values became less positive at 18–24 km, and lower leaf N concentrations in this area were also observed. Thus, urban-derived NO_x deposited largely near the urban area and reduced quickly with increasing distance from the urban center. Furthermore, significantly ^{15}N-depleted leaves (in the range of the δ^{15} N values of agriculture-derived NH_x-N) occurred in the rural area. The similar patterns of leaf and moss $\delta^{15}N$ in areas beyond 18 km from the city center as presented in Fig. 4 strongly implied that the main N form of atmospheric N deposition in the rural area isotopically differed from that of the urban. In the rural area of Guiyang, there are some continuous sources of atmospheric NH_3 emission, for example, animal excrement, soil emissions and fertilizer application. According to a study by Xiao et al. (2010), the total amount of NH_3 emission was 72.6 kt in Guiyang city in 2006, of which the anthropogenic NH_3 emission was 99.85%, and an important source of anthropogenic NH_3 emission was the emission of livestock, which accounted for 38.30%. In addition, China today accounts for about 33% of the world total fertilizer usage (Zhang et al., 2015), yet more than half of the fertilizer N applied in China (NH_4HCO_3 56% and urea 35%) has been lost to the environment and has caused a large amount of NH_3 volatilization (Cai et al., 1985; Zhu et al., 1989; Zhu and Chen, 2002; Ju et al., 2009), particularly in this study area (karst region) where the farmland was distributed mainly between 6° and 25° mountain regions with serious soil erosion and a lack of soil, water, and fertilizer (Lin et al., 2004). Therefore, agriculture-derived NH_x-N may be the main atmospheric N source in rural areas. Based on the above discussion, it could be concluded that the contribution of NO_x-N to atmospheric N deposition was dominant in the urban center, while NH_x-N was the main N form in N deposition of the rural area.

5. Conclusion

Variations of N concentrations in camphor and Masson pine leaves were apparently associated with atmospheric N deposition. The highest average leaf N concentrations occurred in the urban center, corresponding to a higher level of atmospheric N deposition. Then, leaf N concentrations decreased significantly from the urban center to the suburban region (18–24 km), while slightly increasing leaf N concentrations reemerged in the rural area, indicating increased N deposition in this area. Therefore, it is possible to use N concentrations in camphor and Masson pine leaves to identify areas of excess N deposition.

The difference in soil and leaf $\delta^{15}N$ increased with increasing distance from the urban center, implying that the detectable changes in leaf and soil $\delta^{15}N$ may be strongly associated with atmospheric N deposition. The patterns of leaf $\delta^{15}N$ as presented by this study showed a decreasing trend from central Guiyang to the rural area, with more positive leaf $\delta^{15}N$ in the urban center and ^{15}N-depleted leaf $\delta^{15}N$ in the rural area. However, the reverse pattern of $\delta^{15}N$ was found in previously collected urban mosses (more negative moss $\delta^{15}N$ in area of 0–12 km). These indicated that there are different sources for N deposition in the current urban and rural area: ^{15}N-enriched NO_x-N from traffic emissions was the dominant N form of N deposition in the urban area, while ^{15}N-depleted NH_x-N from agricultural activities was the dominant N form for N deposition in the rural area. The result that the more positive $\delta^{15}N$ in urban camphor and Masson pine leaves were mainly affected by isotopically heavy NO_x-N from traffic was also further confirmed by a mixing model applied to the data from the urban area (0–12 km). Therefore, this study not only showed that the detectable changes in the $\delta^{15}N$ values of soils and vascular plant leaves can provide an indication of atmospheric N deposition but may also promote the application of vascular plant leaf N concentrations and $\delta^{15}N$ as biomarkers of atmospheric N pollution.

Acknowledgments

This study was kindly supported by the National Key Research and Development Program of China through grant 2016YFA0601000 (H.Y. Xiao), the National Natural Science Foundation of China through grants 41425014, 41273027 and 41173027 (H.Y. Xiao), and by the National Basic Research Program of China through grant 2013CB956703 (H.Y. Xiao).

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