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Total N content and $\delta^{15}N$ signatures in moss tissue for indicating varying atmospheric nitrogen deposition in Guizhou Province, China

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HIGHLIGHTS

- Atmospheric N deposition in Guizhou province was first reported.
- TN deposition was 27.74 kg N ha^{-1} yr^{-1} with significant spatial variation.
- NH_4^+-N and NO_3^--N contributed 52% and 44% of wet N deposition.
- Urban sewage and agricultural NH_3 were the main N sources.
- Opposite trends between N deposition and N emission were observed in this study.

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ABSTRACT

Unsurprisingly, the amount of reactive nitrogen circulating annually on land has been doubled because of increasing anthropogenic activities. Exceedingly large amounts of reactive nitrogen (N_r) are likely to disrupt N dynamics and negatively impact the environment and human health. Guizhou Province, a major energy-producing province in southwest China, is suffering from serious long-term acid deposition. However, little work has been done to quantify the levels of atmospheric N deposition in this province, in which some ecologically vulnerable areas have resulted from rocky desertification. In this study, tissue N contents and $\delta^{15}N$ signatures in 109 epilithic mosses were analyzed by the ordinary kriging (OK) interpolation technique to determine atmospheric N deposition. Moss N content (1.36–2.65%) showed a significant decrease from west to east, indicating that the spatial variance of TN deposition was the same as that of moss N content, with an average of 27.74 kg N ha^{-1} yr^{-1}. Moss $\delta^{15}N$ ranged from −5.89‰ to −0.72‰ and showed an opposite spatial variance compared with moss N contents. Negative $\delta^{15}N$ indicated that the main sources for N deposition were urban sewage and agricultural NH_3. According to Moss $\delta^{15}N$ values, it could be concluded that NH_4^+-N and NO_3^--N were the main components of wet deposition, accounting for 52% and 44% of TN, respectively. The deposition fluxes were 14.49 kg N ha^{-1} yr^{-1} and 12.16 kg N ha^{-1} yr^{-1}, respectively. Although the emission flux of NO_3^--N far exceeded that of NH_4^+-N, the amount of NH_4^+-N deposited on land was larger than that of NO_3^--N. N deposition in 99.6% of the province exceeded the critical load for terrestrial ecosystems. High N deposition is the main environmental problem facing Guizhou Province, and recommendations regarding regulatory strategies for mitigating atmospheric N pollution are urgently needed.

1. Introduction

Since the Haber-Bosch process was established, the emission of N_r into the atmosphere increased dramatically (Galloway and Cowling, 2002). In large regions of the world, average nitrogen deposition rates have exceeded natural rates (~0.5 kg N ha^{-1} yr^{-1}) by more than an order of magnitude and are greater than 10 kg N ha^{-1} yr^{-1} (Erisman et al., 2008). N deposition is an important nutrient source that supports maintaining plant productivity in terrestrial ecosystems (Liu et al., 2010; Ti et al., 2011); however, excessive N deposition rapidly creates issues that threaten the “health” of the ecosystem and humans, causing eutrophication (Liu et al., 2011; Smith, 2003), loss of biodiversity

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(Bobbink et al., 2010; Hettelingh et al., 2015), and various types of illness and death (Brunekreef and Holgate, 2002; Peel et al., 2012; Townsend et al., 2003). Recent studies indicate that global N total deposition has reached 106.3 Tg yr^{-1} and will increase to 200 Tg yr^{-1} by 2050 (Galloway et al., 2008; Vet et al., 2014). Because of its remarkable and unprecedented increases in urbanization and industrialization, China has become the largest creator and emitter of N_r globally, surpassing the USA and Europe (Liu et al., 2013). The annual N deposition rate has increased from 13.2 kg N ha^{-1} yr^{-1} to 21.1 kg N ha^{-1} yr^{-1} over 20 years and is expected to further increase over the next few decades (Liu et al., 2013).

Guizhou Province is a typical hotspot of acid deposition and is known as a “coal city” in southwest China. Previously, this province was a main contributor of sulfur dioxide (SO_2) pollution in China (Xiao and He, 2011). Although the emission of SO_2 and nitrogen oxides (NO_y) have decreased in recent years, the increased emission and usage rates of domestic sewage and nitrogen fertilizer are leading to a build-up of atmospheric ammonia (NH_3) (Environmental Protection Bureau of Guizhou Province; Guizhou Provincial Bureau of Statistics). As a result, N deposition is gradually rising (Lü and Tian, 2007; Xiao and He, 2011). A few studies on regional variations in precipitation chemistry showed that the concentrations of NH_4^+-N and NO_3^--N were high in precipitation in other parts of Guizhou Province (Wei et al., 2010; Zhao et al., 2014). However, previous studies focused on atmospheric deposition in Guiyang, the capital of Guizhou (Liu et al., 2008a, c; Xiao and Liu, 2002). Therefore, comprehensive assessment of the status of atmospheric N deposition throughout Guizhou Province is needed.

In contrast to vascular plants, mosses without a root system to acquire nutrients from soil are lack of a cuticular barrier to atmospheric inputs (Gerdol et al., 2002). These characteristics lead mosses to be sensitive to environmental pollution. With the special physiological properties, the epilithic moss was employed for surveying atmospheric N deposition in this study. Several studies have shown that moss N content was proportional to atmospheric N inputs, which could reflect the level and variation of N deposition especially for an area with scarce monitoring (Liu et al., 2008b; Pitcairn et al., 2006). To further investigate the quantitative importance of different N sources, moss $\delta^{15}N$ has successfully been applied (Bragazza et al., 2005). Reduced (NH_x) and oxidized nitrogen (NO_y) released by humans are the two main sources of atmospheric N. NH_x tends to have negative $\delta^{15}N$ values compared to NO_y, which usually has more positive $\delta^{15}N$ values (Liu et al., 2008c). Due to the direct uptake of N from the atmosphere, N can be efficiently retained in moss tissues with little isotope fractionation, thus moss $\delta^{15}N$ is regards as an efficient method to identify different atmospheric N sources (Liu et al., 2008a; Xiao et al., 2010a).

In recent years, spatial interpolation methods that are integrated with Geographic Information System (GIS) are widely used for simulation of the spatial patterns of atmospheric nitrogen deposition (Jia et al., 2014; Lü and Tian, 2014; Zhu et al., 2015). These are powerful tools for transforming limited data from discrete points to spatially continuous surfaces and for predicting surface values at unsampled sites (Atkinson, 2005; Li and Heap, 2011). For this study, the ordinary kriging (OK) method was used to assess atmospheric N deposition in Guizhou Province. Our objectives were: 1) to assess the level of N deposition based on the epilithic moss N content and characterize its spatial pattern, 2) to identify the composition of N deposition and its main sources through moss $\delta^{15}N$ signatures, 3) to explore changes in N deposition with N pollutant emissions, and 4) to estimate the status of N deposition throughout the whole province and predict its future trend. We hope to facilitate creating an effective policy for N pollution abatement by quantifying atmospheric N deposition across Guizhou Province.

2. Materials and methods

2.1. Sampling and treatment

The study was conducted in July and August 2014. In total, 42 study sites were located throughout Guizhou Province, including 6 cities and 3 autonomous prefectures. The geographical distribution of these sites is mapped in Fig. 1. Based on these sites, we can explore the pattern of atmospheric nitrogen deposition at a regional scale.

All sampling sites were located in open habitats. 109 mosses were collected from natural rocks above ground level to avoid the influence of surface water splashes, overlapping by canopies and buildings, and other anthropogenic pollution. If mosses were collected around urban parks or hills, the sampling sites were located at least 500 m from main roads and at least 100 m from other roads or houses. At each site, 5–10 subsamples were collected and combined into one representative sample. All selected samples were green and healthy (Xiao and Liu, 2011).

Fresh mosses were stored in clean plastic bags and returned to the laboratory. The samples were gently rinsed with 1.5 mol/L HCl, washed with deionized water, and sonicated several times until no N was detected in the washed water (spectrophotometry, the limit of detection was <0.005 mg/L). The main purpose of this wash procedure was to remove absorbed pollutants. Subsequently, all samples were dried in a vacuum oven at 70 °C. We used a mortar and pestle to separately grind the oven-dried samples into fine powders in liquid nitrogen and then re-dried the samples.

2.2. Chemical analyses

The total N (TN) contents of the mosses were analyzed by an elemental analyzer (Model PE-2400 II, PerkinElmer, USA). The analytical precision was 1%. $\delta^{15}N$ was measured on a Finnigan MAT 252 gas isotope ratio mass spectrometer after combustion at 850 °C and purification with liquid nitrogen. Three to five replicate measurements per sample were implemented with high-purity N_2 reference gas. The obtained results represented the averages of these measurements, and the precision (±SD, $n = 5$) was ±0.2‰. We used potassium nitrate standard (MOR 2386-01) from Shoko Co., Ltd., Tokyo, Japan (+1.9‰) for our analysis, which gave a mean (±SD) $\delta^{15}N_{air}$ value of 1.9 ± 0.2‰. All experimental analyses were performed in the State Key Laboratory of Environmental Geochemistry at the Institute of Geochemistry, Chinese Academy of Sciences.

2.3. N deposition estimates

Atmospheric TN deposition was estimated using tissue N contents of mosses based on the significant linear correlation between them (Xiao et al., 2010b):

$$TN_{dep} = 19.23x - 14.03 \tag{1}$$

where TN_{dep} is total N deposition (kg N ha^{-1} yr^{-1}), and x is moss N content (%).

A negative correlation between moss $\delta^{15}N$ values and the ratios of NH_4^+-N/NO_3^--N was found at $\delta^{15}N$ values between −8.17 and −0.67 (Xiao et al., 2010b). Thus, the deposition fluxes of NH_4^+-N and NO_3^--N were estimated by the equation:

$$y = -1.53x + 1.78 \tag{2}$$

where y is moss $\delta^{15}N$ value, and x is the NH_4^+-N/NO_3^--N ratio.

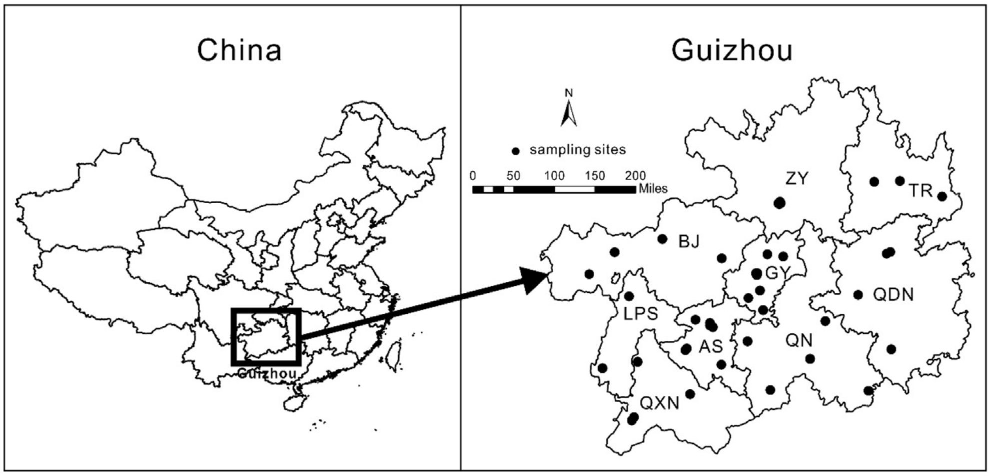

Fig. 1. The distribution of sampling points in different cities inGuizhou Province: Guiyang (GY), Anshun (AS), Zunyi (ZY), Tongren (TR), QianDongnan (QDN), Qiannan (QN), QianXinan (QXN), Liu Panshui (LPS), andBijie (BJ).

2.4. Geostatistical analyses

To explore the spatial distribution of N deposition in Guizhou Province, a geostatistical method was used to produce spatially continuous estimates from discrete sampling sites. Geostatistical analysis was performed by ordinary kriging (OK), which is a common geostatistical interpolation technique. Attempting to minimize the error variance and systematically setting the mean of the prediction errors to zero, OK method yields optimal and unbiased estimates. Prior to OK interpolation, SPSS 19.0 software was employed to determine whether the original data followed a normal distribution and thereby determine whether a data transformation was needed. Subsequently, the Explore Data tool of ArcGIS 10.2 software was used to conduct further data analysis, including outlier identification and trend analyses. Then, the optimal semivariogram model and parameters were generated. All graphs were created with CorelDRAW X7.

3. Results and discussion

3.1. Moss N content and $\delta^{15}N$ signature

In this study, the tissue N content of epilithic moss ranged between 1.36% and 2.65%, with an average of 2.23 ± 0.25% (Fig. 2A). A decreasing gradient in tissue N content was observed from west to east. The highest moss N content (2.65%) was observed in the Guiyang urban area and was similar to that (2.97%) reported by Liu et al. (2008c). The lowest moss N content (1.36%) was observed in southeastern Guizhou Province and was higher than that (0.71–0.84%) found in western Germany (Solga et al., 2005). Moss N content, significantly correlated with atmospheric N deposition even at low levels, is widely used to substitute direct measurements of N deposition at locations without instrumental monitoring (Liu et al., 2008b; Skinner et al., 2006). According to some previous data, Liu et al. (2009) summarized an integrated relationship between N deposition and tissue N contents in mosses, and assessed the level of atmospheric N deposition in Guiyang. This good linear pattern was also successfully applied to the estimation of atmospheric N deposition in Yangtze River drainage basin (Xiao et al., 2010b). As shown in Fig. 2A, the high moss N contents in most regions of Guizhou Province indicated that these regions have been subject to inputs of atmospheric N. Based on Pitcairn et al. (1998) estimation that a deposition rate of 20 kg N ha^{-1} yr^{-1} would result in a corresponding moss N content of 2%, it can be concluded that the level of N deposition in Guizhou Province has exceeded 20 kg N ha^{-1} yr^{-1}. These assessments contribute to our understanding of the ecological effects of atmospheric N deposition in Guizhou Province, especially in the rocky Karst areas.

As shown in Fig. 2B, epilithic mosses showed negative $\delta^{15}N$ signatures in this study, ranging from −5.89‰ to −0.72‰. The spatial pattern of moss $\delta^{15}N$ was opposite to that of moss N content, increased from the western to eastern regions, with the highest $\delta^{15}N$ value in southeastern Guizhou Province. Moss $\delta^{15}N$ can be effectively used to identify different atmospheric N sources. Gerdol et al. (2002) found that moss $\delta^{15}N$ values in northern Italy could be used to effectively distinguish between the sources of atmospheric N deposition from rural NH_3 and urban NO_y. According to the $\delta^{15}N$ inventories of atmospheric NH_3 (Freyer, 1978), the sources of N deposition in Guizhou Province were city sewage and wastes ($\delta^{15}NH_3 = -15$ to −5‰) and agricultural NH_3 ($\delta^{15}NH_3 = -5$ to 0‰). In the present study, moss $\delta^{15}N$ was concentrated in the range of −5~0‰ (Fig. 2B). Thus, considering these less negative moss $\delta^{15}N$ values, it can be concluded that the atmospheric N source was associated with agricultural activities in the study region. The result was consistent with previous studies that reported that agricultural NH_3 released from fertilizer application in China was the main source of N deposition in rural areas, and that the fertilizer used in China was capable of causing greater NH_3 volatilization in areas with calcareous soil, such as the Karst region (Wang et al., 1997; Zhu et al., 1989).

3.2. Atmospheric TN deposition

Atmospheric TN deposition in our study was approximately 27.74 kg N ha^{-1} yr^{-1}, as shown in Table 1. It was approximately 2–4 times that estimated in highly industrialized USA and Europe (Holland et al., 2005; Zhang et al., 2012), and was significantly higher than the national average level (18.02 kg N ha^{-1} yr^{-1}) estimated by Zhu et al. (2015) based on the measurements from 41 monitoring sites for the whole of China.

In Guizhou Province, the magnitude and spatial pattern of TN deposition differed significantly according to region (Fig. 2C). The spatial variation of TN deposition was the same as moss N content. It was also supported by the results proposed by Xiao and He (2011). TN deposition was greatest in the center of GY city, with peak values of 36.84 kg N ha^{-1} yr^{-1}, and the lowest deposition

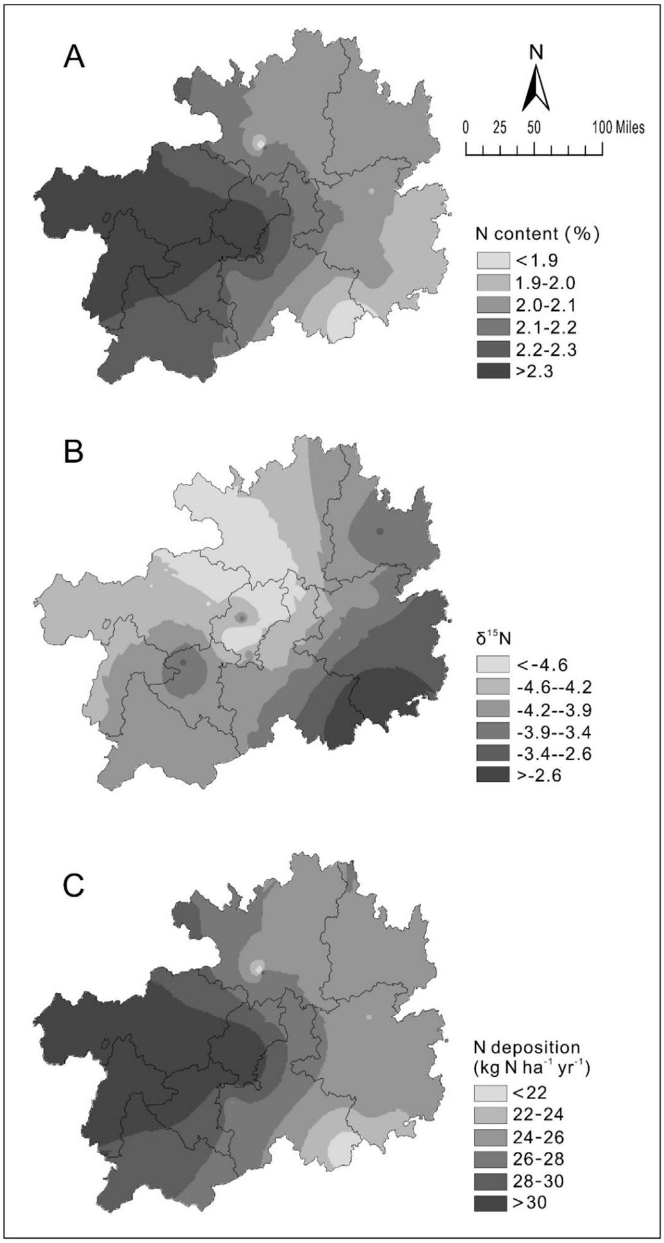

Fig. 2. The spatial pattern of moss N content (A), $\delta^{15}N$ (B) and atmospheric TN deposition (C) in Guizhou Province.

occurred in QDN, with the lowest value of 12.10 kg N ha^{-1} yr^{-1}. TN deposition was >26 kg N ha^{-1} yr^{-1} in most regions of Guizhou Province. Many factors are significantly correlated with atmospheric N deposition, such as precipitation, agricultural activities and meteorological conditions (Cui et al., 2014; Fan et al., 2009; Zhu et al., 2015). In our study, the spatial pattern of TN deposition could be explained by the industrial structure and various meteorological factors. Guizhou Province has experienced industrial restructuring on three occasions, yielding the industrial pattern of "secondary industry, primary industry and tertiary industry" (Guizhou Provincial Bureau of Statistics). Heavy industries were mainly located in the central, west and southwest areas of Guizhou Province, and the nitrogen pollutants emitted by these industries far exceeded those produced by agriculture (Environmental Protection Bureau of Guizhou Province). The distribution of the wind direction in summer is shown in Fig. 3, revealing that at the study site, the prevailing wind direction was south. In August, the east and southeast winds in July became weaken, whereas the south-southeast and northeast winds became strengthen. High local emissions and N-species transported by the prevailing wind led to the spatial pattern of TN deposition shown in Fig. 2C.

Table 1
Comparison of N deposition results obtained in different studies.

Site	Wet deposition (kg N ha^{-1} yr^{-1})		TN (kg N ha^{-1} yr^{-1})	Reference
	NH_4^+-N	NO_3^--N		
USA	1.35	1.35	6.75	Zhang et al. (2012)
Europe	4.20	2.56	11.32	Holland et al. (2005)
China	7.25	5.93	18.02	Zhu et al. (2015)
This study	14.49	12.16	27.74	

3.3. Components of atmospheric wet N deposition

The deposition flux of NH_4^+-N was 14.49 kg N ha^{-1} yr^{-1}, and the remainder of wet deposition was NO_3^--N, with a mean deposition rate of 12.16 kg N ha^{-1} yr^{-1} (Table 1). In other words, NH_4^+-N and NO_3^--N inputs in Guizhou Province were approximately 0.26 and 0.21 Tg N yr^{-1}, respectively. NH_4^+-N and NO_3^--N were the main components of wet deposition, accounting for 52% and 44% of TN, respectively. And their fluxes were higher than those in the USA and Europe (Table 1). The deposition distributions of NH_4^+-N and NO_3^--N were similar. Regions of high nitrogen deposition were mainly concentrated in GY, LPS and BJ (Fig. 4). The difference was that NH_4^+-N deposition was greatest in BJ, whereas the greatest NO_3^--N deposition occurred in GY.

NH_4^+-N is an end product of dissolution of emitted NH_3 and scavenging of particulate NH_4^+. It is generally thought that the main anthropogenic sources of NH_4^+-N are human and animal excrement, NH_3 volatilizing from fertilizer and biomass burning, which are closely correlated with agricultural activities (Prospero et al., 1996). NO_3^--N exists as a result of a series of gas-phase photochemical and heterogeneous reactions involving N oxides, which are primarily derived from the combustion of fossil fuels by power plants and automobiles (Gao et al., 2007). Thus, NH_4^+-N/NO_3^--N ratio might reflect the relative contributions of reactive N from anthropogenic activities to wet deposition on the regional scale (Zhao et al., 2009). The average ratio of NH_4^+-N/NO_3^--N was 1.19, which compared well with the national level (1.22) (Table 1). Compared to developed countries, the NH_4^+-N/NO_3^--N ratio in our study was higher than those in highly industrialized USA, but was less than those in Europe (Table 1). This result indicated that NH_4^+-N from agricultural activities and urban sewage contributed more than NO_3^--N from industrial activities and transportation.

3.4. Relationship between atmospheric N deposition and emission fluxes of nitrogen pollutants

As seen in Fig. 5, the emission fluxes of NO_3^--N in most regions were much higher than that of NH_4^+-N in the Guizhou Province (Emission data cited from http://www.gzhjbh.gov.cn/). The opposite trend was observed in the composition of atmospheric wet N deposition (Fig. 4). Regions with high emission fluxes of nitrogen pollutants were concentrated in GY, LPS and BJ. Emission fluxes in GY and LPS, with high emissions and small regional areas, were higher than that in other regions. The average emission flux of NH_4^+-N was 18.56 kg ha^{-1} yr^{-1} throughout the entire province, and the average rate of NH_4^+-N deposition was 14.49 kg N ha^{-1} yr^{-1} (Table 1). In contrast, in the context of low deposition (12.16 kg N ha^{-1} yr^{-1}) (Table 1), the average emission flux of NO_3^--N

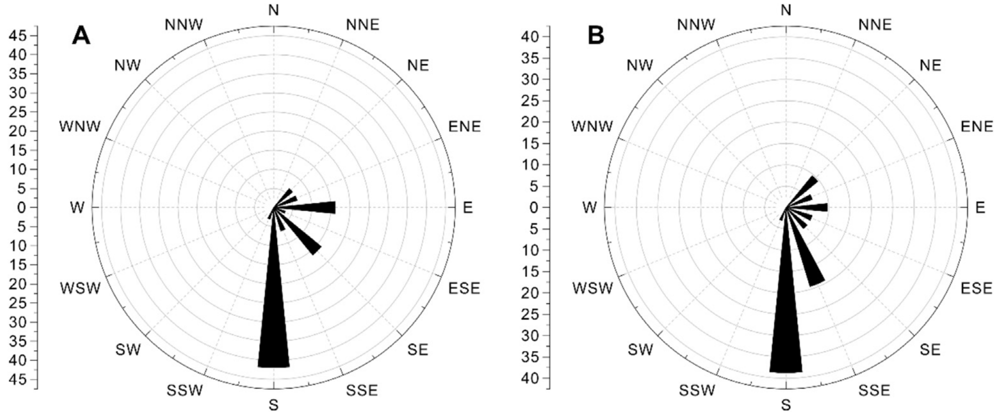

Fig. 3. Distribution of wind direction frequency in July and August 2014. A, wind direction frequency in July; B, wind direction frequency in August.

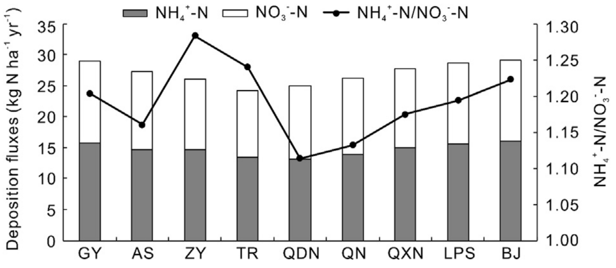

Fig. 4. Regional fluxes and composition of wet N deposition in Guizhou province.

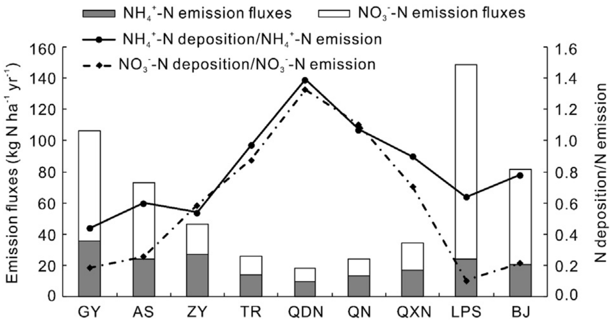

Fig. 5. Regional fluxes of N emission and comparison of the emission and deposition in 2014.

was approximately 1.7 times higher than that of NH_4^+-N, reaching 31.63 kg ha^{-1} yr^{-1}. This phenomenon was attributed to the long-distance transport and chemical reactions of NO_2 in the atmosphere; emitted NH_3 has a shorter lifetime and is more readily deposited (Zhang et al., 2011).

To discuss the relationship between N deposition and the emission fluxes of nitrogen pollutants in each region, the deposition and emission fluxes of NH_4^+-N and NO_3^--N were compared using ratios (Fig. 5). The ratios of deposition and emission of NH_4^+-N and NO_3^--N in QDN were higher than those in other areas, likely because of low emission in this region and the influence of pollutants transported from surrounding cities. Similar results were found in TR, QN and QXN. However, the lower ratios in GY and LPS were not in accordance with results found in the aforementioned regions. The emission of nitrogen pollutants in these two regions was high, and the emitted pollutants readily impacted the rest of the province. In most regions, the ratio of the deposition and emission of NH_4^+-N was higher than that of NO_3^--N, confirming the conclusions from Zhang et al. (2011).

3.5. The present and the future of atmospheric N deposition in Guizhou Province

We highlighted five sensitive regions based on the critical load of N deposition in Chinese terrestrial ecosystems (Table 2). Many studies have suggested that short-term or moderate N deposition increased plant growth, whereas long-term or excessive N deposition would lead to a severe reduction through acidification and nutrient imbalances (Bleeker et al., 2011; Bobbink and Hicks, 2014). International concern over environmental issues promoted the development of an effect threshold approach for assessing the impacts of N deposition, known as "critical loads" (CLs) (Sutton et al., 2014). The CLs approach has been a valuable tool to assess present and future risks of adverse effects of N deposition on the environment and human health (Hettelingh et al., 2014). As shown in Table 2, most areas of Guizhou Province were slightly sensitive to N deposition. However, regions corresponding to approximately 30% of the province exist in insensitive zones. Our findings demonstrated that the N deposition in 99.6% of the province exceeded the critical load for terrestrial ecosystems, which is approximately 10–20 kg N ha^{-1} yr^{-1} (Bobbink et al., 2010). If the growth rate of N deposition in Guizhou Province is consistent with the national annual average growth rate of 0.41 kg ha^{-1} yr^{-1} proposed by Liu et al. (2013), all regions in the province will be insensitive to atmospheric N deposition after 9 years.

4. Conclusions

N content and δ^{15}N in epilithic mosses were reliable indicators for the deposition and source of atmospheric N in this study. The spatial variation of moss N content revealed that TN deposition declined from west to east, with an average deposition rate of

Table 2
Sensitivity classification of atmospheric N deposition in Guizhou Province and the ratio of the critical load area to the total land area.

Sensitivity classification	Critical loads (kg N ha^{-1} yr^{-1})[a]	Ratio of critical load area to total land area (%)
High insensitivity	>40	–
Insensitivity	30–40	28.21
Slight sensitivity	20–30	71.39
Sensitivity	10–20	0.40
High sensitivity	<10	–

[a] Critical loads of atmospheric N deposition in China (Duan et al., 2002).

27.74 kg N ha^{-1} yr^{-1}. It was estimated that the level of N deposition in a large part of Guizhou Province has exceeded 26 kg N ha^{-1} yr^{-1}, where were slightly sensitive to N deposition. In space, moss δ^{15}N presented an opposite trend to moss N content. Negative δ^{15}N values (−5.89‰ to −0.72‰) suggested that city sewage and agricultural NH$_3$ were the atmospheric N sources in Guizhou Province. The region with higher δ^{15}N value was influenced by more intensive agricultural activities.

In this study, moss δ^{15}N was used to determine the main N form of N deposition. NH$_4^+$-N and NO$_3^-$-N were the main components of wet deposition, with the deposition fluxes of 14.49 kg ha^{-1} yr^{-1} and 12.16 kg ha^{-1} yr^{-1}, respectively. The NH$_4^+$-N/NO$_3^-$-N ratio suggested that wet N deposition in this study region was mostly controlled by agricultural activities or urban sewage rather than industrial activities or transportation. However, the emission fluxes of NH$_4^+$-N and NO$_3^-$-N were opposite to their deposition trends. The influence of pollutants transported from surrounding cities led to a higher ratio of N deposition and N emission in low emission regions. Guizhou Province is currently experiencing high N deposition. Reducing the regional N emission and deposition by improving industrial distribution and the energy structure and managing nitrogenous fertilizer application and motor vehicles in a timely and effective manner is urgently needed.

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