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Atmospheric transport of urban-derived NH_x: Evidence from nitrogen concentration and $\delta^{15}N$ in epilithic mosses at Guiyang, SW China

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Tissue N concentration and $\delta^{15}N$ in epilithic mosses may be indicators for atmospheric transport of urban-derived NH_x.

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ABSTRACT

Nitrogen concentration and $\delta^{15}N$ in 175 epilithic moss samples were investigated along four directions from urban to rural sites in Guiyang, SW China. The spatial variations of moss N concentration and $\delta^{15}N$ revealed that atmospheric N deposition is dominated by NH_x-N from two major sources (urban sewage NH_3 and agricultural NH_3), the deposition of urban-derived NH_x followed a point source pattern characterized by an exponential decline with distance from the urban center, while the agricultural-derived NH_x was shown to be a non-point source. The relationship between moss N concentration and distance ($y = 1.5e^{-0.13x} + 1.26$) indicated that the maximum transporting distance of urban-derived NH_x averaged 41 km from the urban center, and it could be determined from the relationship between moss $\delta^{15}N$ and distance [$y = 2.54 \ln(x) - 12.227$] that urban-derived NH_x was proportionally lower than agricultural-derived NH_x in N deposition at sites beyond 17.2 km from the urban center. Consequently, the variation of urban-derived NH_x with distance from the urban center could be modeled as $y = 56.272e^{-0.116x} - 0.481$ in the Guiyang area.

1. Introduction

Atmospheric N deposition increased dramatically during the second half of the 20th century, at scales ranging from highly localized to regional or even global (Galloway et al., 1995; Erisman et al., 2003). Due to the high population density and intensive industries, anthropogenic N emissions from cities have inevitably become prominent sources for elevated regional N pollution, which influences the air quality of cities and poses threats to surrounding ecosystems (Jung et al., 1997; Cowling et al., 1998; Krupa, 2003). Therefore, it is important to identify the sources and behavior of urban-derived atmospheric N pollutants, which is of great value for reducing urban N release and protecting the environment around cities. However, atmospheric N deposition includes a wide range of gaseous compounds, aerosols and particulates, which has made it very difficult and expensive to undertake long-term instrumental monitoring and simultaneous $\delta^{15}N$ measurements (Solga et al., 2005; Pitcairn et al., 2006). Therefore, information of N deposition variation around cities is really rare.

One potentially reliable approach is to use moss as a bio-monitor, an easy and low-cost way to specifically shed light on integrative and long-term N deposition (Soares and Pearson, 1997; Hicks et al., 2000; Pitcairn et al., 2001). Several studies have shown that moss N concentration can be used to quantify atmospheric N deposition (e.g. Pitcairn et al., 1998, 2003), especially to reflect the level and variation of N deposition within an area with scarce monitoring (Pitcairn et al., 2006; Liu et al., 2008a). Due to the direct influx of N to the living moss cells, no significant isotopic fractionation was assumed to occur during N absorption by mosses (Bragazza et al., 2005). In contrast to root uptake of vascular plants, the initial signature of atmospheric N compounds should not change significantly as the deposited N is promptly utilized by mosses without undergoing changes in soil processes (Evans, 2001). Accordingly, increasing attention has been given to investigations of atmospheric N deposition using moss $\delta^{15}N$ signatures. For examples, studies by Pearson et al. (2000) in the London area and Gerdol et al. (2002) in northern Italy have found that moss $\delta^{15}N$ can effectively decipher atmospheric N sources from urban traffic NO_x (relatively positive signature) and from rural animal NH_3 (relatively negative signature). Solga et al. (2005) in western

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Germany and Bragazza et al. (2005) in 11 European countries established a negative correlation between moss δ^{15}N and the ratio of NH_x-N/NO_x-N in atmospheric deposition. Recent studies further showed that moss δ^{15}N was a good indicator for both temporal and spatial variations of NH_x-N in atmospheric deposition, the more enriched in NH_x-N the atmospheric deposition was, the more negative the moss δ^{15}N signature was (Harrison et al., 1999; Solga et al., 2006; Kosior et al., 2008; Liu et al., 2008b).

According to these studies, moss N concentration and δ^{15}N have the potential to provide more concrete and quantitative information in bio-monitoring of N deposition. Until now, little such work has been done out of Europe (e.g. Solga et al., 2006) and more related studies are strongly needed to achieve a better understanding of regional atmospheric N sources and their spatial variations.

China is known as an area with high atmospheric NH_x deposition (Galloway et al., 1996). In 1990, NH_3 amounts released from urban wastewater and agriculture were 2.3–5.7 Tg and 1.9–3.8 Tg, respectively, which accounted for 55% of the total amount in Asia (Zhao and Wang, 1994; Galloway et al., 1996). In 1993, total NH_3 emissions in China reached 12 Tg with 52% from livestock excretion, 33% from fertilizer application, and 13% from human wastes (Sun and Wang, 1997). However, owing to the scarcity of physical monitoring, the variations of these major atmospheric N sources are still not well understood. Although bryophytes are very abundant in China, no studies have examined moss N concentration and δ^{15}N in relation to atmospheric NH_x deposition in this region. Therefore, this study was designed to give a systematic investigation of N concentration and δ^{15}N in epilithic mosses in the Guiyang area (SW China), trying to find more specific bio-monitoring evidence for the deposition of urban-derived NH_x.

It has been well documented from moss δ^{15}N signature that atmospheric N deposition in the Guiyang area is dominated by NH_x-N mainly from urban sewage NH_3 and agricultural NH_3 (Liu et al., 2008a, 2008b), which was also supported by existing studies on the chemical composition (Table 1) and δ^{15}N of atmospheric N deposition (Xiao and Liu, 2002). In this study, we mainly focus on the quantitative relations between moss N concentration, δ^{15}N and distance from the urban center, in the specific aim to investigate:

(1) the deposition patterns of urban-derived NH_x and agricultural-derived NH_x;
(2) the mechanisms and factors influencing the distribution of urban-derived NH_x deposition;
(3) how far and to what extent the urban-derived NH_x could disperse or be transported from the urban area to the neighboring rural areas.

2. Materials and methods

2.1. Study area

The city of Guiyang, the capital of Guizhou Province, is located in the Karst region of SW China with average altitude of 1250 m above mean sea level. The study area ranges between 26°18′N and 26°54′N latitude and between 106°21′E and 107°01′E longitude (Fig. 1). Guiyang city has a subtropical monsoon climate with an annual average temperature of 15.3 °C, annual rainfall averages 1174.7 mm, average relative humidity (RH) is about 86% and annual prevailing wind is from North by East (NbE) (Guiyang Environmental Protection Bureau, 2006). With the mild climate and widespread naked carbonate rocks in the Karst rocky desertification region, there are abundant mosses on rock surfaces, which are suitable to carry out moss bio-monitoring studies of atmospheric deposition.

Guiyang is one of the world's most densely populated cities with more than 40% of its inhabitants living in the urban area (mean radius ≈ 5 km, Fig. 1). According to a census in 2000 (data cited from http://www.gzgov.gov.cn/), the population density was as high as 3×10^4/km^2 in the central urban area (for comparison, during the same period, the population density was 14,694/km^2 for Beijing, 8811/km^2 for New York, 8071/km^2 for Paris and 4554/km^2 for London), in 2005 the population of Guiyang city exceeded 2 million.

Atmospheric N deposition in Guiyang is characterized by a low NO_x concentration, but high NH_x concentration (Table 1), due to low traffic intensity, workshops with heavy pollution being forced to shut down or relocate in 1997, and 49% of the city residents replacing coal with natural gas (Xiao and Liu, 2004). Higher atmospheric NH_x is mainly attributed to discharge of sewage with high ammonia content, which is a pressing environmental problem in this city because of the low level of wastewater treatment (17.2% in 2004 and 20% in 2005, Guiyang Environmental Protection Bureau, 2006). The average NH_x deposition in the Guiyang urban area was 31 kg N ha^{-1} yr^{-1} in 2003 (Xiao et al., unpublished data), while the average agricultural NH_x deposition reported by Wang et al. (1997) in the rural area was 14.3 kg N ha^{-1} yr^{-1}.

2.2. Species collection and sample treatment

In April 2006, sampling of epilithic mosses was conducted at 175 sites along four directions (NE, SW, NW and SE) from urban to rural areas in the Guiyang area; sampling along the SE direction was restricted by high mountains with good vegetative cover and a lack of eligible sampling species (Fig. 1). All moss samplings were performed under stable weather conditions characterized by sunny or cloudy days without rain. Urban mosses were mainly collected around parks or hills, sampling sites in the rural areas were located at least 500 m from main roads and at least 100 m from other roads or houses. All mosses were obtained from natural rocks without canopies or overhanging vegetation. Sampling was performed only at those sites above ground level to avoid surface water splashes. Sites possibly disturbed by domestic animals or pets were also avoided. We collected 5–10 subsamples at each site and combined them into one representative sample. Only green, healthy samples were taken, avoiding yellow or dark samples; a subjective assessment of sample age (the upper green leafy shoot) was made to keep every sample as uniform as possible.

Fresh mosses were stored in cleaned plastic bags enroute to the laboratory. After identification, species that could not be found at every site have been discarded, so finally each sample was composed of four species: *Haplocladium microphyllum* (Hedw.) Broth, *Haplocladium angustifolium* (Hampe et C. Muell.) Broth, *Brachythecium salebrosum* (Web. et Mohr.) B.S.G and *Eurohypnum leptothallum* (C. Muell.) Ando. Species of *Haplocladium* are pleurocarpous mosses with pinnated and interweaved branches morphologically, which have been used to evaluate heavy metal pollution in urban environments in China (An et al., 2006), Liu et al. (2007) showed that δ^{15}N of *H. microphyllum* on open rocky surfaces could be used for indicating atmospheric N sources. As for the later two species, no references were available, possibly because until now little attention has been paid to them in the context of bio-monitoring, however, they are widespread epilithic mosses in the Guiyang area, characterized by drought and sunshine tolerance.

Samples were gently rinsed with 1.5 mol L^{-1} HCl solution, then sonicated and washed with deionized water for several times until no N (NH_4^+ and NO_3^-) was detected in the washed water (spectrophotometry, the limit of detection was <0.005 mg L^{-1}). The main purpose of this washing procedure was to remove adsorbed pollutants. All samples were dried in a vacuum oven at 70 °C and re-dried after being ground separately in liquid nitrogen into fine powders using a mortar and pestle.

Table 1
Comparison of NH_x-N and NO_x-N concentrations in atmospheric deposition in the Guiyang area

Sites	Deposition	Year	NH_x-N	NO_x-N	References
Urban	Wet (μeq L^{-1})	1984	60.56	10.00	Galloway et al., 1987
Urban	Wet (μeq L^{-1})	2001	69.44	13.87	Xiao and Liu, 2002
Urban	Wet (μeq L^{-1})	2006	126.11	26.77	Unpublished data from Liu Xueyan
Rural	Wet (μeq L^{-1})	2006	63.89	17.42	Unpublished data from Liu Xueyan
Urban	Aerosol (μeq m^{-3})	2003	0.21	0.05	Xiao and Liu, 2004
Urban	Gaseous (μeq m^{-3})	2005	0.42 (NH_3)	0.32 (NO_2)	Xiao et al., Unpublished data; Guiyang Environmental Protection Bureau, 2006

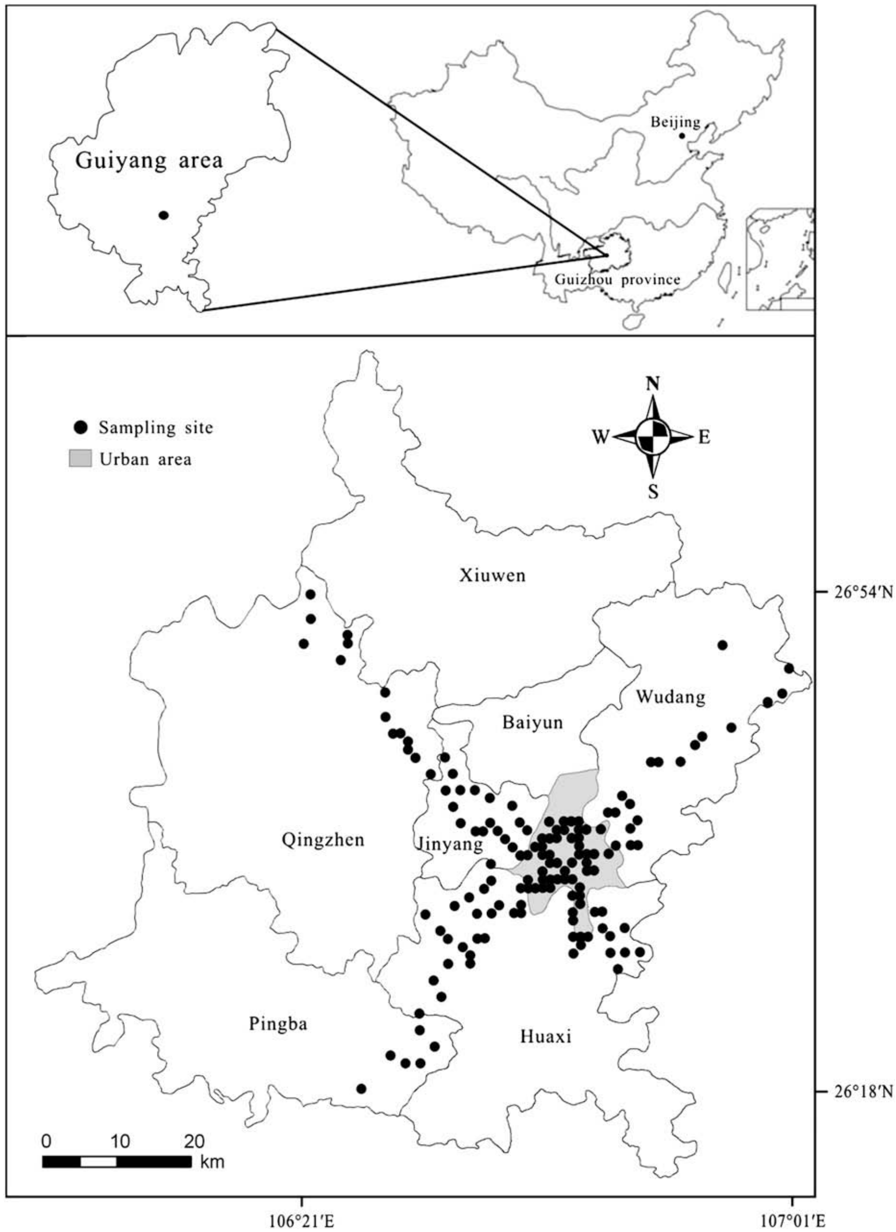

Fig. 1. Map showing the location of the Guiyang area and the sampling sites of epilithic mosses.

2.3. Elemental analysis and isotopic determination

Moss N concentration was measured by an elemental analyzer (Model PE-2400 II, USA) with an analytical precision of 0.1%. After combustion at 850 °C and high purification with liquid N, N isotope ratios were determined on a Finnigan MAT 252 mass spectrometer. Analysis of potassium nitrate standard (MOR2386-01) provided by Shoko Co., Ltd., Tokyo, Japan (+1.9‰) gave a mean (±SD) $\delta^{15}N_{air}$ value of 1.9 ± 0.2‰ ($n = 5$). High purity N_2 reference gas was run with each analysis. Three to five replicate measurements per sample were carried out, and values were presented as the average of these measurements. The analytical precision (SD, $n = 5$) for $\delta^{15}N$ was ±0.2‰.

Isotope data are reported as $\delta^{15}N$ values, which represent relative difference expressed in per mil (‰) between the isotopic composition of the sample and that of atmospheric dinitrogen:

$$\delta^{15}N\ (‰\ \text{vs at-air}) = [(R_{sample}/R_{standard}) - 1]1000$$

where R_{sample} represents the isotope ratio ($^{15}N/^{14}N$), and $R_{standard}$ is $^{15}N/^{14}N$ for atmospheric N_2, or 0.0036765. All experimental analyses were performed at the State Key Laboratory of Environmental Geochemistry, at the Institute of Geochemistry, Chinese Academy of Sciences.

2.4. Statistical analysis

Regression analysis was calculated to evaluate changes of N concentration and $\delta^{15}N$ in mosses over distance from the urban center. For examining relations between distance and the dependent variables (moss N concentration and $\delta^{15}N$), Pearson product–moment correlation coefficients were calculated. Statistical analysis was conducted by using SPSS 12.0, and graphs were mainly created with SigmaPlot2000 software (both SPSS Science, Chicago, USA).

3. Results

Nitrogen concentration of epilithic mosses in this study varied widely from 0.85% to 2.97%, and decreased with distance from the urban center along each direction (Fig. 2). When all moss samples were considered (Fig. 3), the general correlation between moss N concentration and distance from the urban center presented an exponential decay ($y = 1.5e^{-0.13x} + 1.26$) within 30 km from the urban center. For sites

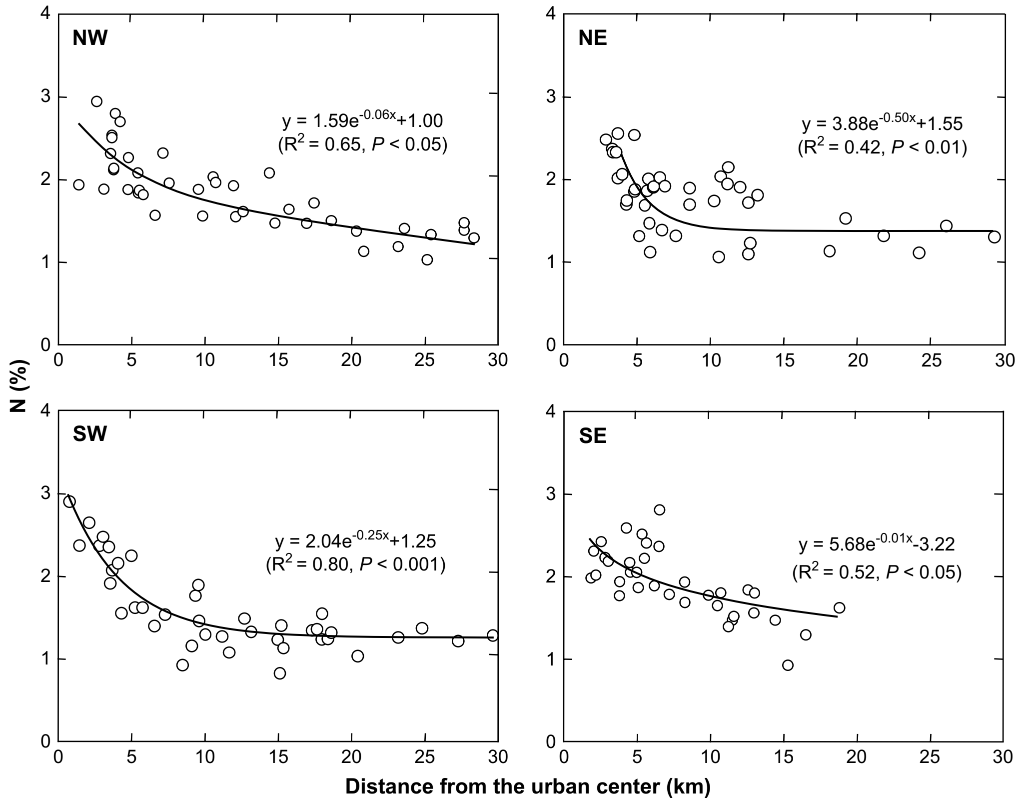

Fig. 2. Variations of N concentration in epilithic mosses with distance (30 km) from the urban center along four directions.

beyond 30 km, slightly higher moss N concentrations were observed although the increase was not significant ($y = 0.012x + 1.16$).

The $\delta^{15}N$ signatures of all moss samples in this study were negative, ranging from −12.50‰ to −1.39‰, showing uniform logarithmic increases with distance from the urban center in all the directions sampled (Fig. 4). The general correlation between moss $\delta^{15}N$ and distance from the urban center was $y = 2.54 \ln(x) - 12.23$ (Fig. 5). According to the mean $\delta^{15}N$ values of mosses within each 5 km increment, there was no statistical difference for moss $\delta^{15}N$ beyond 15 km at the level of $P < 0.05$ (Liu et al., 2008b).

The varying gradients (slopes) of moss N concentration and $\delta^{15}N$ with distance were different along the different directions; the NE direction had significant higher gradients (0.5 for moss N concentration and 3.15 for $\delta^{15}N$) than those in the SW direction (0.25 for N concentration and 2.02 for $\delta^{15}N$) (Figs. 2 and 4).

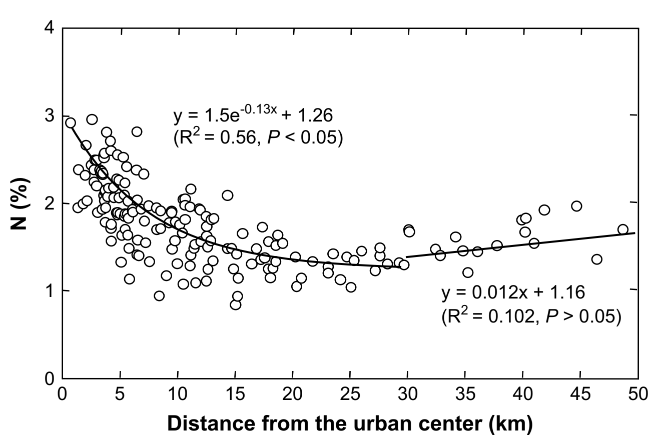

Fig. 3. The relationship between N concentration in epilithic mosses and distance from the urban center. The regression (negative exponential decay) was calculated taking into account moss samples within 30 km ($n = 158$).

4. Discussions

4.1. Moss $\delta^{15}N$ and atmospheric NH_x sources

Moss $\delta^{15}N$ was assumed as an integrator of the isotopic signatures of atmospheric N sources over the lifetime of the moss so that measuring moss $\delta^{15}N$ and comparing these data to source $\delta^{15}N$ signatures could potentially determine the sources of atmospheric N deposition. As shown in Fig. 5, more negative $\delta^{15}N$ signature in urban mosses (between −12‰ and −6‰) typically indicated the contribution of NH_3 released from untreated city sewage and wastes ($\delta^{15}NH_3 = -15$ to −5‰), while relatively less negative $\delta^{15}N$ for rural mosses (mainly in −5 to −2‰) was largely derived from agricultural NH_3 ($\delta^{15}NH_3 = -5$ to 0‰) (Freyer, 1978; Heaton, 1986).

According to Xiao and Liu (2002), who reported a more negative signature of $\delta^{15}N$ for NH_4^+ (−12.2 ± 6.7‰) than for NO_3^- (+2.0 ± 4.4‰) in urban rainwater at Guiyang, it could be calculated through the mean $\delta^{15}N$ of mosses at the urban area (−8.87‰ ± 1.65‰, <5 km) that about 76% of N in urban mosses was derived from NH_x-N, whereas NO_x-N contributed to about 23%.

4.2. Urban- and agricultural-derived NH_x

As higher moss N concentration indicates higher atmospheric N inputs, moss N concentration has been applied for mapping the spatial variation of atmospheric N deposition in many studies (e.g. Baddeley et al., 1994; Pitcairn et al., 1995, 2006; Solga et al., 2005). Figs. 2 and 3 showed that the highest atmospheric N deposition occurred at the urban area and decreased with distance from the urban center. Furthermore, the source signal of moss $\delta^{15}N$ in Figs. 4 and 5 indicated that the spatial variation of N deposition around Guiyang city was controlled by urban-derived NH_x. Therefore, the variations of moss N concentration and $\delta^{15}N$ with distance from the

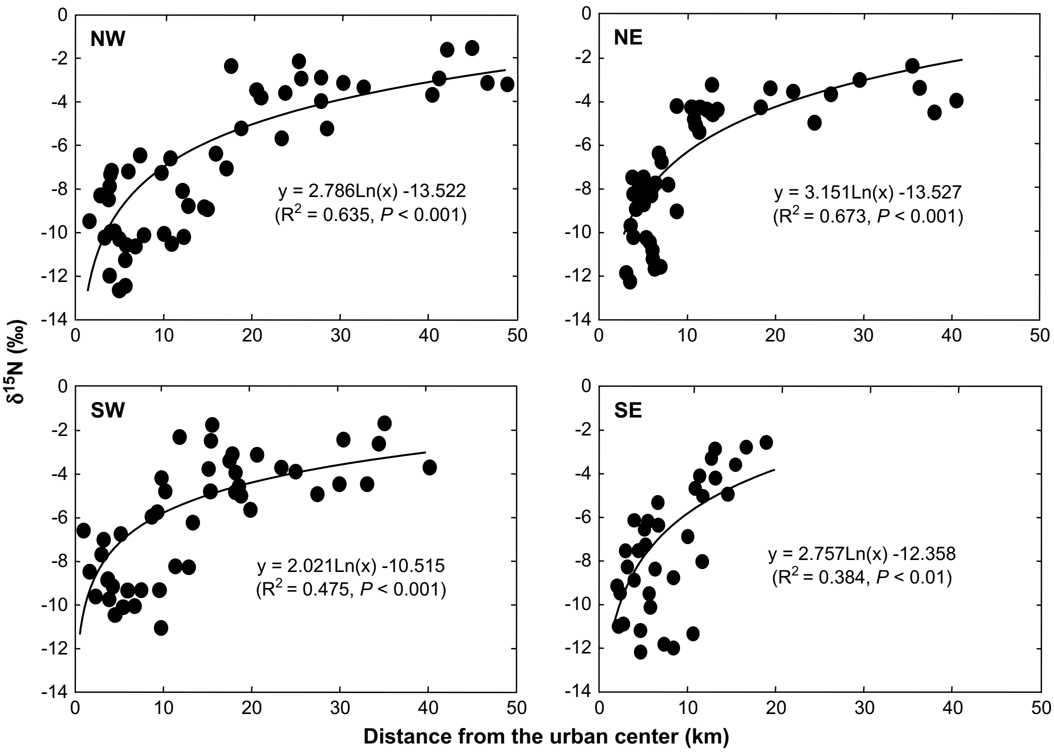

Fig. 4. Variations of $\delta^{15}N$ signature in epilithic mosses with distance from the urban center along four directions.

urban center reflect the deposition pattern of urban-derived NH_x around the city.

Moss N concentration exhibited an exponential decay with distance, while moss $\delta^{15}N$ increased logarithmically with distance from the urban center. These results from Guiyang city are similar to those found around point sources of NH_3 such as poultry barns. For example, a study by Pitcairn et al. (1998) around a poultry farm showed that moss N concentration decreased exponentially with decreasing atmospheric N deposition. Harrison et al. (1999) found that mosses around poultry buildings have more negative $\delta^{15}N$ (−9.3 to −11.5‰) than those growing 276 m away (−6.8 to −8.8‰) from NH_3 sources, while the corresponding instrumental data for NH_3 concentration showed exponential decrease within this distance (Pitcairn et al., 2004), showing that moss $\delta^{15}N$ can provide important evidence for atmospheric NH_3 transport from poultry buildings. In the same way, patterns of moss N concentration and

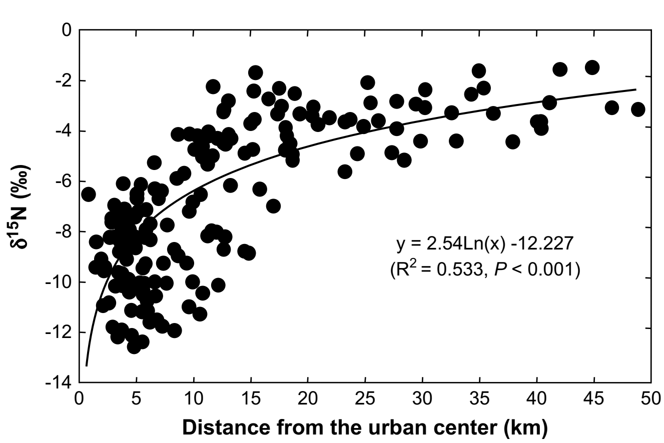

Fig. 5. The logarithmic relation between moss $\delta^{15}N$ and distance from the urban center. The regression was calculated taking into account all moss samples ($n = 175$).

$\delta^{15}N$ observed in our study revealed that the deposition of urban-derived NH_x followed an exponential decay (nonlinear) around Guiyang city. This conclusion was consistent with recent experimental studies by Skinner et al. (2004, 2006), where they reported that moss N concentration and atmospheric NH_3 decreased exponentially with distance from NH_3 point sources, while the corresponding moss $\delta^{15}N$ signature became less negative logarithmically with decreases in atmospheric NH_3 concentration. Pitcairn et al. (2006) also concluded that moss N concentration was a good indicator of enhanced N deposition at sites close to point sources of NH_3. Consequently, the urban area could be seen as a NH_3 point source in the Guiyang area for its similar evidences of both moss N concentration and $\delta^{15}N$ variations.

The influence of agricultural-derived NH_x ($\delta^{15}NH_3 = -5$ to 0‰, Freyer, 1978) was observed from 15 km to 50 km from the urban center with mean moss $\delta^{15}N$ of -3.83 ± 0.82‰ to -2.48 ± 0.95‰ within every 5 km (Liu et al., 2008b). This broad distribution demonstrated that agricultural-derived NH_x was a non-point source (Sommer, 1988), occurring anywhere with agricultural practices. As shown in Fig. 3, slightly higher moss N concentration re-emerged at rural sites beyond 30 km, but it did not change significantly with distance ($y = 0.012x + 1.16$, $R^2 = 0.102$, $P > 0.05$), reflecting little spatial difference for agricultural-derived NH_x; the higher moss N concentration at sites beyond 30 km was possibly caused by more intensive agricultural activities in remote areas.

4.3. Dispersal and transport of urban-derived NH_x

The exponential decay pattern of urban-derived NH_x deposition around Guiyang city should be attributed to the short residence time of atmospheric NH_3 (Erisman et al., 1987; Asman et al., 1998; Krupa, 2003), which would strongly affect the dispersal or transport of atmospheric NH_3 from the source area to outer areas (Asman et al., 1989, 1998; Skinner et al., 2004). Therefore, urban-derived NH_x deposited largely near the urban area and decreased quickly with distance away from the urban center. At present, there was no report on how far urban-derived NH_x could be transported in a city area, but studies of some smaller NH_3 sources have shown that there was a rapid decrease of atmospheric NH_3 concentration with distance from source. Erisman et al. (1987) reported a 50% reduction at 600 m, a 70% decrease at 4 km was determined by Asman et al. (1989), and a most recent work by Pitcairn et al. (2002) around livestock buildings in the UK showed a 95% reduction in NH_3 concentrations (from 60 $\mu g\,m^{-3}$ to 3 $\mu g\,m^{-3}$) at 650 m, while the corresponding moss N concentration declined from 4.5% to 1.6% at 650 m, and a N concentration lower than 1% was measured in mosses from remote background sites such as North West Scotland (Pitcairn et al., 1995).

According to the relationship between moss N concentration and distance ($y = 1.5e^{-0.13x} + 1.26$, Fig. 3), the variable ($1.5e^{-0.13x}$) stands for the decrease of urban-derived NH_x with distance, the intercept ($y = 1.26\%$) could be assumed as a concentration without contribution of urban-derived NH_x ($1.5e^{-0.13x} = 0$). By limit calculation, when the distance (x, km) approached 41 km, moss N concentration (y, %) approached the baseline of 1.26%. Therefore, it could be concluded that the maximum distance of urban-derived NH_x transport was about 41 km from the urban center in the Guiyang area. Similarly, in the relationship between moss $\delta^{15}N$ and distance [$y = 2.54\ln(x) - 12.23$] (Fig. 5), the intercept ($\delta^{15}N = -12.23‰$) could be considered as the initial $\delta^{15}N$ of urban-derived NH_x, which almost equaled the mean $\delta^{15}N$ of NH_4^+ (−12.2‰) in urban rainwater reported by Xiao and Liu (2002). Thus, the variable [$2.54\ln(x)$] showed the decline of urban-derived NH_x with increasing distance from urban center, when the distance (x, km) approached 17.2 km, moss $\delta^{15}N$ (y, ‰) approached −5‰ ($\delta^{15}NH_{3\text{-agriculture}} = -5$ to 0‰, Freyer, 1978; Heaton, 1986). This threshold of distance reflected that mosses within 17.2 km from the urban center were mainly influenced by urban-derived NH_x, but beyond 17.2 km they were mainly controlled by agricultural-derived NH_x. Consequently, the contribution of urban-derived NH_x to atmospheric NH_x deposition was lower than 50% beyond 17.2 km from the urban center, and no contribution from urban-derived NH_x beyond 41 km.

4.4. Pattern of atmospheric NH_x deposition at Guiyang area

From the above discussion, the exponential relationship between the urban-derived NH_x deposition ($kg\,N\,ha^{-1}\,yr^{-1}$) and distance from the urban center (km) in the Guiyang area could be described as:

$$[NH_x\ \text{deposition}] = ae^{-b[\text{distance}]} + c$$

In the urban area (<5 km), the level of NH_x deposition was 31 $kg\,N\,ha^{-1}\,yr^{-1}$, which was calculated according to annual mean values (NH_3 and NH_4^+) in both dry and wet deposition (Xiao et al., unpublished data). The minimum level (0 $kg\,N\,ha^{-1}\,yr^{-1}$) of urban-derived NH_x occurred at 41 km, and at 17.2 km, the urban-derived NH_x deposition could be considered to account for 50% of total NH_x deposition (14.3 $kg\,N\,ha^{-1}\,yr^{-1}$), which was estimated based on agricultural NH_3 emission in rural areas (Wang et al., 1997). Schlesinger and Hartley (1992) reported that the total NH_3 emission was in reasonable agreement with NH_x deposition from the atmosphere, the major fate of atmospheric NH_3. The corresponding equations are:

$$ae^{-5b} + c = 31$$
$$ae^{-41b} + c = 0$$
$$ae^{-17.2b} + c = 7.15$$

By solving the above three equations, the variation of urban-derived NH_x deposition with distance from the urban center in the Guiyang area could be modeled as:

$$[NH_x\ \text{deposition}] = 56.272e^{-0.116[\text{distance}]} + 0.481$$

where some variations could not be well understood in this study. As shown in Fig. 6, the variation of NH_x deposition within the urban area (<5 km) was still unclear, the level of agricultural-derived NH_x within 17.2 km could not be reasonably predicted, and it was difficult to quantify the slight oscillation of agricultural NH_x in rural areas.

4.5. Factors influencing the transport of urban-derived NH_x

As shown in Figs. 2 and 4, both moss N concentration and $\delta^{15}N$ have different gradients with distance along different directions, implying that the atmospheric transport of urban-derived NH_x was not equipotent from urban to neighboring areas around the city. Significantly higher gradients (0.5 for moss N concentration and 3.15 for $\delta^{15}N$) were observed along northeastern (NE) direction than gradients along southwestern (SW) direction (0.25 for moss N concentration and 2.02 for $\delta^{15}N$). This was mainly related to the prevailing north by east (NbE) wind direction in the study area, which likely caused more urban-derived NH_x to be transported along the SW direction (downwind). The response of moss $\delta^{15}N$ to the influence of wind direction on atmospheric NH_x transport in our study was similar to that found around poultry buildings by Harrison et al. (1999), showing more negative signatures (−9.3 to

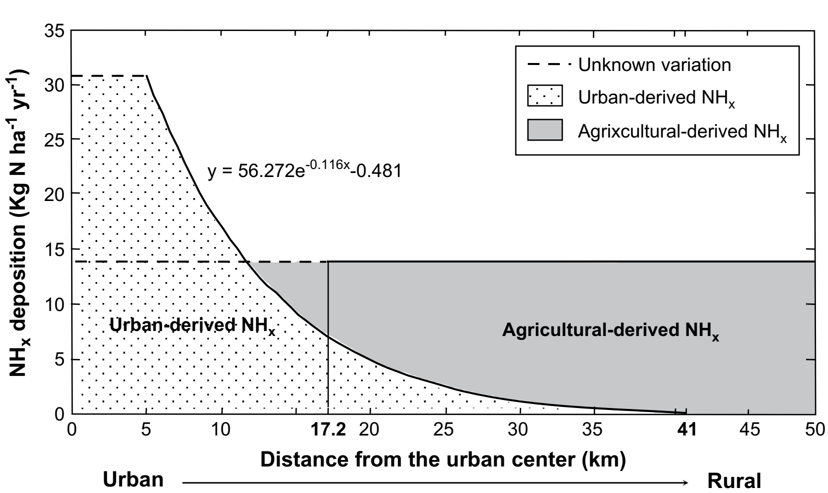

Fig. 6. The deposition pattern of atmospheric NH_x (mainly including urban-derived NH_x and agricultural-derived NH_x) in the Guiyang area.

−11.5‰) downwind than upwind (−6.8 to −8.8‰). Both the northwestern and southeastern directions showed even lower gradients that could not be accounted for by the wind direction; possible factors included differences in geographic conditions and urbanization. Areas with more flat topography and higher urbanization would be influenced more by urban-derived NH_x, so the variations of moss N concentration and $\delta^{15}N$ were relatively slower.

5. Conclusions

Nitrogen concentration and $\delta^{15}N$ in epilithic mosses were shown as reliable indicators for the deposition and atmospheric transport of urban-derived NH_x in this study. Some principal conclusions could be drawn as follows:

(1) The spatial variations of moss N concentration and $\delta^{15}N$ revealed that the deposition of urban-derived NH_x declined exponentially with distance from the urban center, which followed the deposition pattern of a point source. The deposition of agricultural NH_x followed a non-point source model displaying slight fluctuation possibly related to the intensity of agricultural activities.
(2) The quantitative relationship between moss N concentration and distance indicated that the maximum distance of urban-derived NH_x transport was 41 km from the urban center, and it could be determined from the relationship between moss $\delta^{15}N$ and distance that urban-derived NH_x was proportionally lower than agricultural-derived NH_x at sites beyond 17.2 km from the urban center. The deposition of urban-derived NH_x in the Guiyang area could be modeled as $y = 56.272e^{-0.116x} - 0.481$.
(3) The short longevity of atmospheric NH_3 is likely responsible for the exponential decrease of urban-derived NH_x with distance from the urban center. While discrepant gradients of moss N and $\delta^{15}N$ varying with distance along different directions indicated that the transport of urban-derived NH_x was not equipotent around the city, which was related to the long-term influences from wind direction, and possibly geographic conditions and urbanization in the study area.
(4) Urban-transect studies of moss N concentration and $\delta^{15}N$ can determine the distribution of urban-derived NH_x, which is useful for understanding atmospheric N pollution at congeneric cities dominated by NH_x-N and would greatly promote the application of moss N concentration and $\delta^{15}N$ in N deposition bio-monitoring.

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