JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 115, D14301, doi:10.1029/2009JD012900, 2010

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Mosses Indicating Atmospheric Nitrogen Deposition and Sources in the Yangtze River Drainage Basin, China

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Received 26 July 2009; revised 27 February 2010; accepted 11 March 2010; published 21 July 2010.

[1] Characterizing the level and sources of atmospheric N deposition in a large-scale area is not easy when using physical monitoring. In this study, we attempted to use epilithic mosses (*Haplocladium microphyllum* (Hedw.)) as a bioindicator. A gradient of atmospheric N deposition from 13.8 kg N ha^{-1} yr^{-1} to 47.7 kg N ha^{-1} yr^{-1} was estimated on the basis of moss tissue N concentrations and the linear equation between them. The estimated results are reliable because the highest atmospheric N deposition occurred in the middle parts of the Yangtze River, where the highest TN concentrations were also observed. Moss δ^{15}N values in cities and forests were found in distinctly different ranges of approximately −10‰ to −6‰ and approximately −2‰ to 2‰, respectively, indicating that the main N sources in most of these cities were excretory wastes and those in forests were soil emissions. A negative correlation between moss δ^{15}N values and the ratios of NH_4-N/NO_3-N in deposition ($y = -1.53\,x + 1.78$) has been established when the ratio increased from 1.6 to 6.5. On the basis of the source information, the negative moss δ^{15}N values in this study strongly indicate that NH_y-N is the dominant N form in N deposition in the whole drainage basin. These findings are supported by the existing data of chemical composition of local N deposition.

Citation: Xiao, H.-Y., C.-G. Tang, H.-W. Xiao, X.-Y. Liu, and C.-Q. Liu (2010), Mosses Indicating Atmospheric Nitrogen Deposition and Sources in the Yangtze River Drainage Basin, China, *J. Geophys. Res.*, *115*, D14301, doi:10.1029/2009JD012900.

1. Introduction

[2] 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.*, 1996; *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; *Krupa*, 2003]. Therefore, it is important to quantify atmospheric N deposition and identify its sources. The assessment of levels of atmospheric N pollution is critical for environmental health. However, until now only nutrient load in rivers has been measured, and atmospheric N deposition has been neglected in the Yangtze River drainage basin.

[3] In China, elevated concentrations of NH_4^+-N and NO_3^--N in precipitation have been observed in many cities since the 1980s [e.g., *Xiao and Liu*, 2002]. Although emission of reactive oxidized nitrogen (NO_y) and reduced nitrogen (NH_y) is considerable and expected to increase, influences of atmospheric N deposition on environments have received little attention in China [e.g., *Zhao and Wang*, 1994; *Galloway et al.*, 1996]. This may be mainly because measurement of N deposition by physical methods is a complex task with a wide range of compounds in the gas phase, in aerosols, and in precipitation, which has made it very difficult and expensive to undertake long-term instrumental monitoring, especially in remote areas [*Solga et al.*, 2005; *Pitcairn et al.*, 2006]. Owing to the scarcity of physical monitoring, information about atmospheric N deposition and major atmospheric N sources is still lacking in many regions. Therefore, a less costly alternative to physical measurement of N deposition is needed.

[4] One potentially reliable approach is to use moss as a biomonitor, an easy and low-cost way to shed light specifically on integrative and long-term N deposition [*Hicks et al.*, 2000; *Pitcairn et al.*, 2001]. Mosses receive their N exclusively via atmospheric deposition, and studies have shown that N levels in mosses can be used to quantify levels of N deposition in areas with scarce environmental monitoring. In the past few decades, this form of biomonitoring has been used to assess N deposition rates in areas with scarce direct measurements. [*Gerdol et al.*, 2002; *Liu et al.*, 2007]. Several studies have shown that moss N concentrations can be used to quantify atmospheric N deposition [e.g., *Pitcairn et al.*, 1995, 2001], especially to reflect the level and variation of N deposition within an area with scarce

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0148-0227/10/2009JD012900

Table 1. Sampling Site Description[a]

Sites	Latitude	Longitude	Altitude (m)	Concentrations in Rainwater (μeq/L)				Air concentrations (μeq/m^3)	
				Years	NH_y-N	NO_x-N	NH_y-N/ NO_x-N	NH_y-N	NO_x-N
Cities									
Suzhou (SZ), Jiangsu Province	31°18′N	120°37′E	3	1986	93.6	14.4	6.5	n.d.	n.d.
Nanjing (NJ), Jiangsu Province	32°02′N	118°50′E	9	1992–2003	194.3	40.0	4.9	0.94	0.13
Hefei (HF), Anhui Province	31°51′N	117°18′E	30	1986	117.3	31.8	3.7	n.d.	n.d.
Nanchang (NC), Jiangxi Province	28°39′N	115°53′E	22	1990–2000	77.0	24.3	3.2	n.d.	n.d.
Wuhan (WH), Hubei Province	30°37′N	114°21′E	23	2003	104.3	57.3	1.8	n.d.	n.d.
Changsha (CS), Hunan Province	28°12′N	112°59′E	45	1993–2002	72.2	24.0	3.0	n.d.	n.d.
Guiyang (GY), Guizhou Province	26°34′N	106°42′E	1,100	2001	69.4	13.9	5.0	0.21	0.05
Zunyi (ZY), Guizhou Province	27°42′N	106°53′E	1,300	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chongqing (CQ)	29°32′N	106°31′E	300	1996–2002	151.1	27.9	3.6	0.22	0.07
Chengdu (CD), Sichuan Province	30°40′N	104°04′E	500	1995–2003	173.5	52.3	3.3	n.d.	n.d.
Forests									
Mt. Lushan (LSM), Jiangxi Province	29°33′N	115°58′E	1,474	1998	43.7	19.1	2.3	n.d.	n.d.
Mt. Hengshan (HSM), Hunan Province	27°12′N	102°50′E	1,290	1989	115.0	26.3	4.4	0.14	0.07
Mt. Leigong (LGM), Guizhou Province	26°22′N	108°11′E	1,735	2002–2003	30.5	18.5	1.6	0.9	0.03
Mt. Fanjing (FJM), Guizhou Province	28°50′N	108°47′E	2,572	1986	107.0	34.0	3.1	n.d.	n.d.
Mt. Emei (EMM), Sichuan Province	29°31′N	103°20′E	3,098	1984–1985	98.3	19.2	5.1	n.d.	n.d.
Mt. Gongga (GGM), Sichuan Province	29°34′N	101°55′E	7,556	1986	3.44	0.16	21.5	n.d.	n.d.

[a]Data of N concentration in wet and dry deposition are from *Hu et al.* [2002], *Li* [1999], *Liu et al.* [2005], *Mei et al.* [2005], *Wang et al.* [1992], *Xiao and Liu* [2002, 2004], and *Zhou et al.* [2003]. N.d.: no data.

monitoring [*Pitcairn et al.*, 2006; *Liu et al.*, 2008]. Some species have been thought to be excellent bioindicators of national and regional atmospheric N deposition, such as *Pleurozium schreberi* (Brid.) Mitt. and *Scleropodium purum* (Hedw.) Limpr. [*Solga et al.*, 2005], *Sphagnum* from ombrotrophic mires [*Press et al.*, 1986; *Pitcairn et al.*, 1995], epilithic *Haplocladium microphyllum* at open sites [*Liu et al.*, 2007], and also mixtures species [*Pearson et al.*, 2000].

[5] Isotopic composition of atmospheric NH_y and NO_x has been increasingly used to assess the sources of inputs to a wide variety of soil and plant environments [*Evans and Ehleringer*, 1993; *Durka et al.*, 1994]. Compared with direct analysis of δ^{15}N in atmospheric N deposition, moss δ^{15}N was assumed as an integrator of the isotopic signatures of atmospheric N sources. Isotopic fractionation during N uptake has been assumed to be absent or very low for mosses [*Bragazza et al.*, 2005]. Accordingly, the different δ^{15}N signatures of reactive N forms in the atmosphere [see, e.g., *Heaton*, 1986] would make isotopic composition of mosses a reliable monitor of N emission sources [*Liu et al.*, 2008].

[6] In this study, we investigated the N concentrations and the δ^{15}N signatures of epilithic mosses in some cities and forests in the Yangtze River drainage basin, aiming to describe how N concentrations and isotopic signatures of N in mosses can effectively be used to assess N deposition. The following specific questions are addressed: (1) What is the level of atmospheric N deposition, and how does it vary spatially in the drainage basin? (2) What are the main sources of atmospheric N deposition, and what is the dominant N form in N deposition?

2. Materials and Methods

2.1. Study Area

[7] The enormous Yangtze River drainage basin lies between 91°E and 122°E, and between 25°N and 35°N. The Yangtze River is the third longest river in the world and is the largest river in China, with a drainage area of 1.8 × 10^6 km^2 and a population of 400 million living in the river drainage basin. Wandering 6300 km eastward to the East China Sea, it contributes 9 × 10^{11} m^3 of freshwater annually into its estuary and is a major pathway of nutrients.

[8] In the Yangtze River drainage basin, NH_4^+-N and NO_3^--N levels in precipitation have been reported for some cities and forests since the 1980s (Table 1). The reported results indicate that NH_4^+-N is the dominant inorganic N species in precipitation.

2.2. Sample Collection and Treatment

[9] The moss materials *Haplocladium microphyllum* (Hedw.) at all study sites were collected in 2006 (Figure 1). Urban mosses were mainly collected around parks or hills. Forests selected in the Yangtze River drainage basin are usually >100 km away from cities and are not polluted by anthropogenic N sources. The sampling sites in the forested areas were evenly distributed and were selected to be located in open habitats such as heaths or clearings at least 500 m away from main roads and at least 100 m away from other roads or houses. All mosses were obtained from natural rocks without canopies or overhanging vegetation, ensuring no influence from throughfall N compounds. Sampling was performed only at those sites above ground level to avoid surface water splashes. Sites possibly disturbed by domestic animals or other point sources were also avoided. We collected 5–10 subsamples at each site and combined them into one representative sample. Only green, healthy samples were taken; yellow or dark samples were avoided.

[10] Fresh mosses were stored in cleaned plastic bags en route to the laboratory. Using the treatment method described by *Liu et al.* [2007], samples were gently rinsed with 1.5 mol L^{-1} HCl solution, then sonicated and washed with deionized water several times until no N (NH_4^+ and NO_3^-) was detected in the washed water (using spectrophotometry; limit of detection <0.005 mg L^{-1}). The main purpose of this

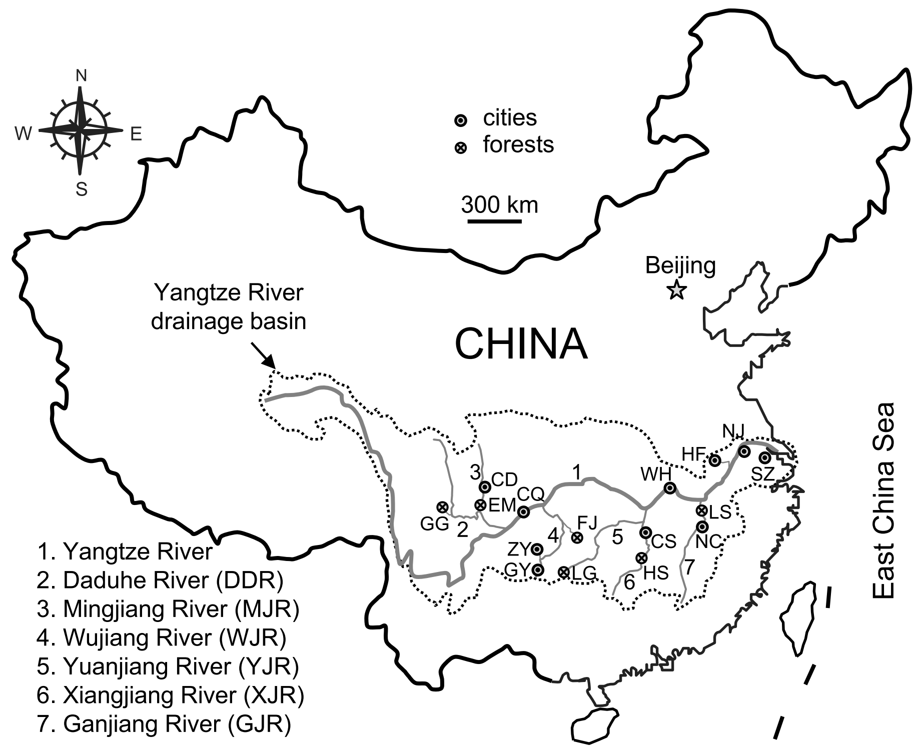

Figure 1. Map of China showing the sampling sites in the Yangtze River drainage basin. The abbreviations of the sampling sites are presented in Table 1.

washing procedure was to remove adsorbed pollutants. All samples were dried in a vacuum oven at 70°C and redried after being ground separately in liquid nitrogen into fine powders using a mortar and pestle.

2.3. Chemical Analyses

[11] Moss N concentrations were measured by an elemental analyzer (Model PE-2400 II, PerkinElmer) with an analytical precision of 1%. After combustion at 850°C and high purification with liquid N, nitrogen isotope ratios were determined using a Finnigan MAT 252 mass spectrometer. Analysis of potassium nitrate standard (MOR2386-01), provided by Shoko Co., (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‰.

2.4. Estimation of Deposition Fluxes Using Air Concentrations

[12] Dry deposition fluxes were estimated using the measured air concentrations and the model-estimated dry deposition velocities [*Aneja et al.*, 1986]. Dry deposition flux (F_d) (mmol m^{-2} month^{-1}) is written as $F_d = 2.592 \times 10^4 C_{air} V_d$, where C_{air} is the atmospheric concentration of that substance (mmol m^{-3}), V_d is the dry deposition velocity (cm s^{-1}), and 2.592×10^4 is a unit conversion factor [*Gao*, 2002].

[13] An estimate of wet deposition could be obtained by multiplying the concentrations by precipitation amounts. The rainfall, or wet deposition, flux (F_w) is computed as $F_w = I_w C_w$, where I_w is the precipitation intensity obtained in terms of precipitation amount collected within a projected time scale (e.g., mm h^{-1}) and C_w is the rainwater concentration.

[14] Using the above methods, total N deposition of five sites in the Yangtze River drainage basin was estimated on the basis of the concentrations of ammonium and nitrate in rainwater and in dry deposition (Table 1).

2.5. Statistical Analysis

[15] Statistical analysis was conducted using SPSS 11.5, and graphs were mainly created with SigmaPlot 2000 software (both SPSS, Chicago, IL). A multiple comparison test (Tukey's honestly significant difference test and Tukey's least significant difference test) was used to determine significant differences between mean values, and correlations were analyzed by one-way analysis of variance.

3. Results

3.1. Moss N Concentrations

[16] Tissue N concentrations of epilithic mosses in the study varied widely from 1.19% to 4.05%, with a mean of 2.45 ± 0.55%, as shown in Figure 2. The mean concentration of urban mosses was 2.57 ± 0.52%, significantly higher ($p < 0.001$) than that in forests (2.17 ± 0.57%).

[17] For urban mosses, those sampled in Wuhan (WH) had the highest mean tissue N concentration (3.21%), followed by those in Changsha (CS; 3.12%) and in Nanchang (NC; 2.93%), all located in the middle parts of the Yangtze

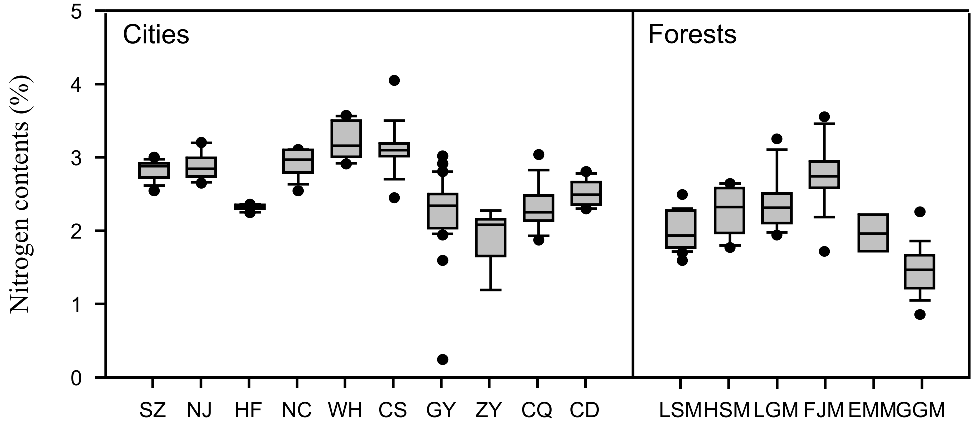

Figure 2. Moss tissue N contents in cities and forests. Boxplots display the 10th, 25th, 50th, 75th, and 90th percentiles as solid lines. Symbols indicate 5th and 95th percentiles.

River. Mosses in two cities of Guizhou Province, Zunyi (ZY) and Guiyang (GY), showed the lowest mean tissue N concentration at 1.89% and 2.26%, respectively. For forested mosses, those in Leigong Mountain (LGM) had the highest mean tissue N concentration (2.77%), followed by those in Fanjing Mountain (FJM; 2.41%). The minimum tissue N concentration of 1.45% occurred at a remote area (Gongga Mountain) in the upper parts of the Yangtze River.

3.2. Moss δ^{15}N Signature

[18] Epilithic mosses showed negative δ^{15}N signatures, except for some sampled in Chongqing (CQ) and Chengdu (CD). Compared to those in cities (−6.07 ± 3.51‰), epilithic mosses sampled in forests were less ^{15}N-depleted (−1.82 ± 3.44‰) than those sampled in a rural area of Guiyang [*Liu et al.*, 2008].

[19] As shown in Figure 3, the highest mean δ^{15}N value among urban mosses was found in Chengdu (CD; 0.0‰), then in Chongqing (CQ; −0.8‰). Epilithic mosses in Suzhou (SZ), Nanjing (NJ), Nanchang (NC), and Guiyang (GY) showed very negative mean δ^{15}N values (less than −7‰). Among forested mosses, the lowest mean values occurred in Emei Mountain (EEM; −6.5‰) and Gongga Mountain (GGM; −5.0‰). More than 50% of the samples were found to be distributed in two distinctly different ranges: −10‰ to −6‰ for urban mosses and −2‰ to +2‰ for forested mosses (Figure 4), indicative of their different N sources.

[20] As shown in Figure 5, the δ^{15}N values between urban and forested mosses in the same province are significantly different, except in Hunan Province. In Jiangxi Province and Guizhou Province, forested mosses were more ^{15}N-enriched than urban mosses. But a contrary trend appeared in Sichuan Province, with less negative values occurring in urban mosses.

3.3. Atmospheric N Deposition

[21] Atmospheric N deposition was estimated using air concentrations in wet deposition and dry deposition and was available for only five locations (Table 1). There existed a linear correlation ($y = 0.052\,x + 0.73$) between the estimated atmospheric N deposition (x) and moss tissue N concentrations (y) of these five locations and other data from previous studies (Figure 6). Atmospheric N deposition estimated on the basis of the equation in cities and forests in the Yangtze River drainage basin is shown in Figure 7. The Yangtze River drainage basin spanned a wide gradient of

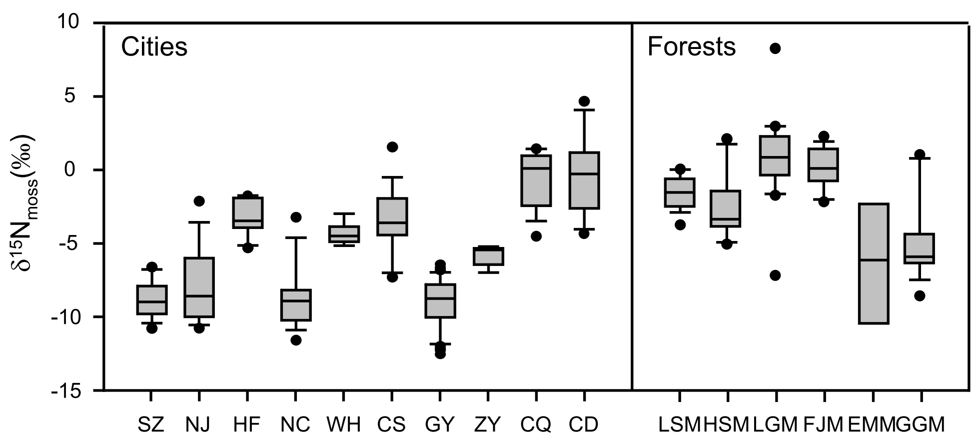

Figure 3. The δ^{15}N signatures in urban and forested mosses. Boxplots display the 10th, 25th, 50th, 75th, and 90th percentiles as solid lines. Symbols indicate 5th and 95th percentiles.

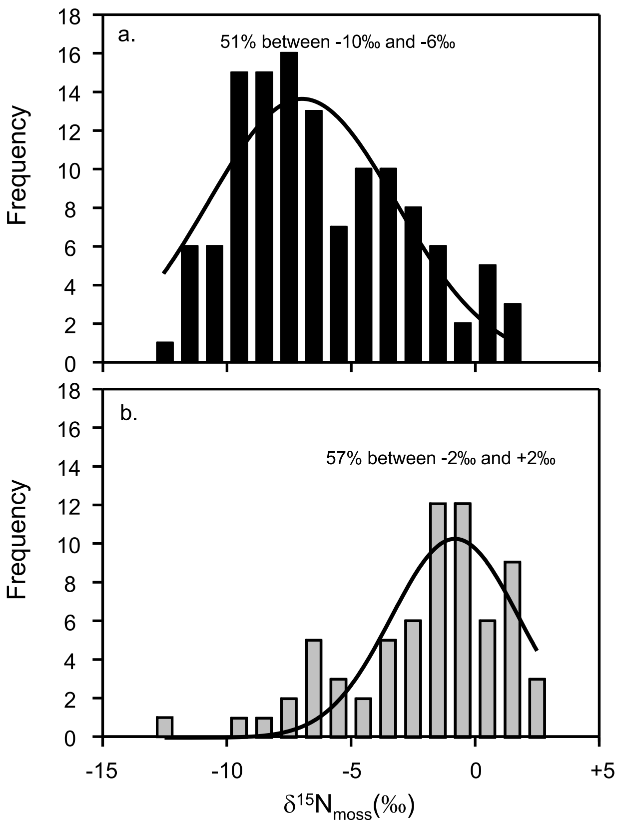

Figure 4. Frequency histograms of moss δ^{15}N values in (a) cities and in (b) forests. The difference between cities and forests is significant (p < 0.001).

atmospheric N deposition from 13.8 kg N ha^{-1} yr^{-1} in Gongga Mountain (GGM) to 47.7 kg N ha^{-1} yr^{-1} in Wuhan (WH).

4. Discussion

4.1. Estimation of Atmospheric N Deposition

[22] The N concentrations in mosses have been recognized to be sensitive and reliable tools to assess the level of regional atmospheric N deposition [e.g., *Pitcairn et al.*, 1995; *Skinner et al.*, 2006]. At very low atmospheric N deposition, N is completely and rapidly absorbed by the *Sphagnum* layer because of the limited role played by N supply [*Aerts et al.*, 1992; *Bragazza et al.*, 2004]. Accordingly, The N concentration of certain moss species has been shown to be correlated with atmospheric N deposition at low levels. Hence, concentrations of N in mosses can be used to substitute direct measurements of N deposition at locations without instrumental monitoring, but where natural growing mosses were available. However, owing to the lack of site-based N deposition data, only a few studies have established the quantitative relation between N concentrations in natural growing mosses (y) and the corresponding atmospheric N deposition (x).

[23] Some recent studies reported a different issue that N saturation occurred in *Sphagnum* tissues under increasing atmospheric N deposition [*Lamers et al.*, 2000; *Berendse et al.*, 2001], which would cause an exponential decrease along the gradient of N deposition with N concentrations [*Bragazza et al.*, 2005]. However, *Bragazza et al.* [2004] reported that *Sphagnum* plants, subject to the high atmospheric N input, were expected to absorb further N supplies even if nutritional conditions were no longer N-limited. In N fertilization experiments with artificial N supply up to 10-fold greater than the amount in bulk deposition, total N concentration in *Sphagnum* capitula was found up to ~2.0% [*Berendse et al.*, 2001; *Heijmans et al.*, 2001]. This was attributed to an effective metabolic adaptation of *Sphagnum* plants to a broad range of external N supplies.

[24] In the Yangtze River drainage basin, the N deposition at five sites where N concentrations in both wet and dry deposition are available (Table 1) were estimated. In Figure 6, we integrated these previous data and those of the five sites as a linear pattern ($y = 0.052\,x + 0.73$, $R^2 = 0.70$, $p < 0.001$) and an exponential pattern ($y = 2.80^*[1 - \exp(-0.061x)]$, $R^2 = 0.58$, $p < 0.001$) for calculating atmospheric N deposition (x) with moss N concentrations (y) in this study. The exponential equation has an R^2 of 0.58, worse than 0.70 for the linear equation. The N deposition (x) cannot be calculated using the exponential equation at sites where >2.8% of moss N concentration (y) was observed. For those data calculated using the two equations, the differences between them are small ($p < 0.001$). Considering all of the above factors, we used the linear equation and moss N concentrations to calculate N deposition (x) in this study. Additionally, the following comparison also indicated that the estimated results using the linear equation were reliable.

[25] As shown in Figure 7, the highest N deposition calculated occurred in Wuhan (WH), Changsha (CS), and Nanchang (NC), the middle parts of the Yangtze River where the highest TN concentration were also found [*Zhang et al.*, 1999], reflecting a reliable estimate of N deposition using moss nitrogen concentrations.

4.2. The Main Sources of Atmospheric N Deposition

[26] Atmospheric NH_4^+ is derived from heterogeneous reactions involving ammonia (NH_3), and the major sources of NH_3 are animal excrement, soil emissions, and fertilizer application [*Dentener and Crutzen*, 1994]. The main

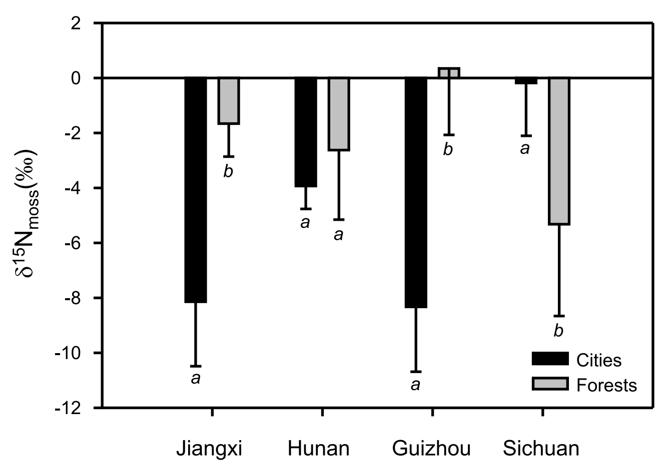

Figure 5. Comparisons of δ^{15}N values between urban and forested mosses. Data from different sampling sites that do not share a letter below the bars are significantly different at p < 0.05.

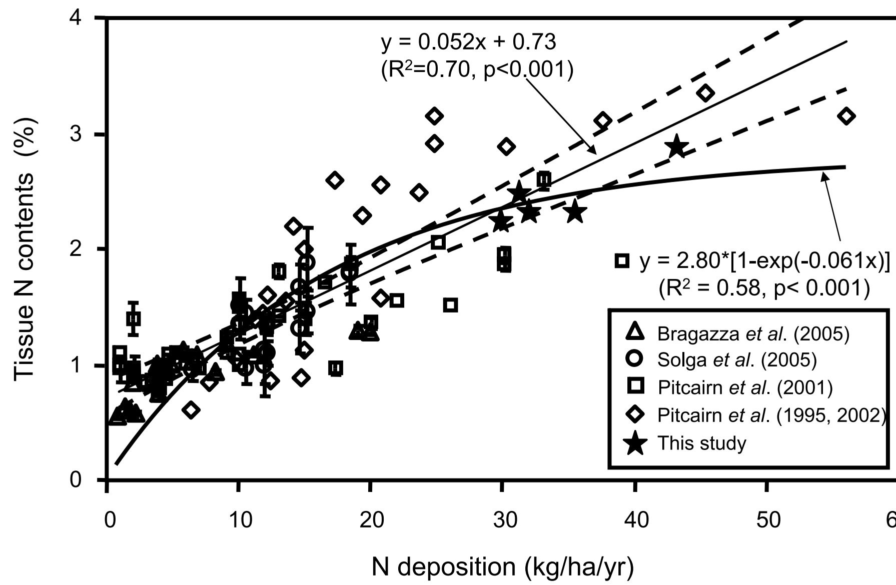

Figure 6. Linear and exponential relations between atmospheric N deposition and moss N contents integrated in this study and from previous studies. The dashed lines represent the 95% confidence interval for the linear regression.

anthropogenic sources for NO_x emissions are fossil fuel combustion during transport, industry, and energy production. The $\delta^{15}N$ signatures of these potential sources are shown in Table 2.

[27] In the Yangtze River drainage basin, epilithic mosses sampled in forests were found to be less ^{15}N-depleted (−1.82 ± 3.44%) than those in cities (−6.07 ± 3.51%). This result is different from the previous findings in European studies. For example, studies by *Pearson et al.* [2000] in the London area and *Gerdol et al.* [2002] in northern Italy found that moss $\delta^{15}N$ values were higher in urban areas than in rural areas. They attributed the relatively positive signatures of urban mosses to urban traffic NO_x whereas the relatively negative signatures of rural mosses were attributed to the rural animal NH_y. According to the $\delta^{15}N$ signatures of potential sources of N in the atmosphere, NH_y deposition should be predominant in the Yangtze River drainage basin because of the low moss $\delta^{15}N$ and similar values to those of NH_y sources (Table 2). This is in accordance with the report by *Galloway et al.* [1996] that China is known as an area with high atmospheric NH_3 deposition. In the most populated regions of China, agricultural activities, in particular livestock farming and fertilizer application, are important sources of atmospheric NH_3 [*Schlesinger and Hartley*, 1992; *Zhao and Wang*, 1994; *Galloway et al.*, 1996]. In 1990, NH_3 released from urban sewage and agriculture was approximately 2.3 to 5.7 Tg and approximately 1.9 to 3.8 Tg, respectively, in China, 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 waste [*Sun and*

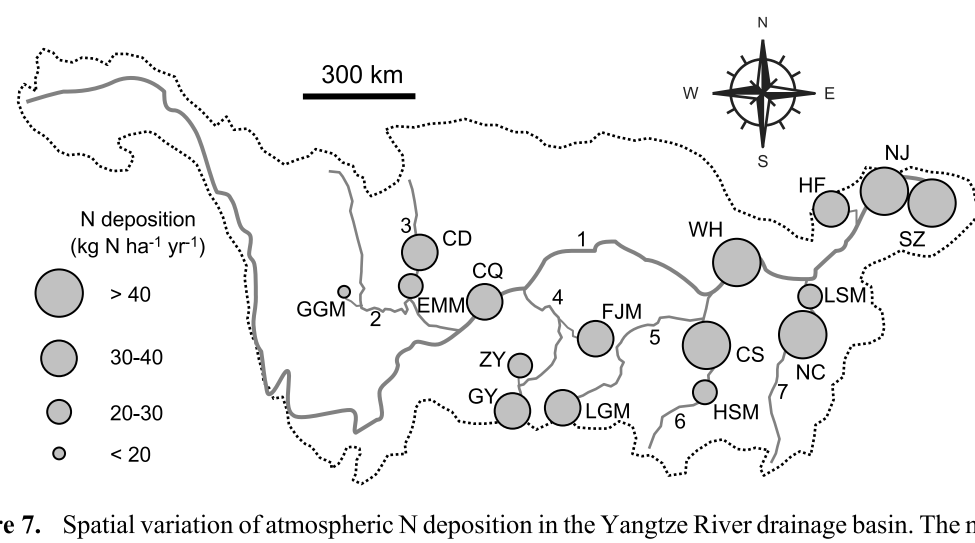

Figure 7. Spatial variation of atmospheric N deposition in the Yangtze River drainage basin. The numbers of the rivers are as in Figure 1.

Table 2. Nitrogen Isotopic Composition of Potential Sources of N in the Atmosphere

Sources	δ^{15}N (%)	References
NH_x		
From excretory wastes	−15 ~ −4	*Freyer* [1978], *Heaton* [1987]
From soils	−5.8 ~ −3.3	*Freyer* [1978]
NO_x		
From vehicle exhausts	−1.8 ~ +3.7	*Moore* [1977], *Freyer* [1978]
From coal combustion	+6 ~ +13	*Heaton* [1990]

Wang, 1997]. An exception was found in Sichuan Province (Figure 5). That is, more positive values are observed in urban mosses than in forested mosses in the province. This may be related to coal combustion used in cities for electricity generation, which also results in serious acid rain in the two cities [*Liu et al.*, 2001].

[28] Our recent studies in Guiyang area further showed that moss δ^{15}N value was also a good indicator for different sources of NH_y-N in atmospheric deposition [*Liu et al.*, 2008]. Because moss δ^{15}N values in the Guiyang area were regulated mainly by NH_y-N from urban sources (excretory wastes approximately −15% to −5%) and soil sources (approximately −5.8 to −3.3%), variations of moss δ^{15}N values from the urban to the rural area should be controlled by the ratios of urban-derived NH_y to soil-derived NH_y in N deposition. The distinctly different δ^{15}N signatures between urban and forested mosses (Figure 4) in this study indicated that NH_y sources in cities and forests were excretory wastes and soil emissions, respectively. This finding can be used to explain why less negative δ^{15}N values were found in forests than in cities in Jiangxi Province and Guizhou Province (Figure 5).

4.3. The Main N Form of Atmospheric N Deposition

[29] Because both sources of the reduced N (NH_y-N) generally have more negative δ^{15}N values than both sources of the oxidized N (NO_x-N) in atmospheric deposition (Table 2), it is expected that mosses are more ^{15}N-depleted when the contribution of NH_y is higher, no matter which of the NH_x sources is more important. So, moss δ^{15}N can be used to differentiate the dominant N form in atmospheric N deposition. *Solga et al.* [2005] and *Bragazza et al.* [2005] established the negative correlation between moss δ^{15}N values and the ratios of NH_y-N/NO_x-N in N deposition. *Solga et al.* [2005] reported that in western Germany, the δ^{15}N values of two pleurocarpous mosses (*Pleurozium schreberi* and *Scleropodium purum*) decreased linearly from −2.86% to −7.89% when the ratio of NH_4-N/NO_3-N in deposition increased from 0.87 to 1.90, and a similar survey by *Bragazza et al.* [2005] in 11 European countries showed that the δ^{15}N values of ombrotrophic *Sphagnum* decreased linearly from −3.5% to −8% when NH_4-N/NO_3-N in deposition increased from 0.5 to 2.5. In this study, negative correlation between them also existed when the ratio increased from 1.6 to 6.5 (Figure 8). Therefore, the pattern of moss δ^{15}N variation found in this study can be explained by the mechanism of moss δ^{15}N responding to the ratios of NH_y-N/NO_x-N in N deposition.

[30] In Guiyang city, our previous studies [*Liu et al.*, 2008] showed that negative δ^{15}N signatures of urban mosses were rather closer to the $\delta^{15}NH_4^+$ value (−12.2 ± 6.7%) than to the $\delta^{15}NO_3^-$ value (+2.0 ± 4.4%) in rainwater [*Xiao and Liu*, 2002], suggesting that urban mosses were influenced more by the reduced form of N (NH_y-N) than by the oxidized N species (NO_x-N) [*Xiao and Liu*, 2002; 2004]. Similar to those in Guiyang (GY), mosses also expressed very negative δ^{15}N signatures at other cities where NH_y-N/NO_x-N was high in N deposition (Figure 8). The higher the NH_y-N/NO_x-N ratios in N deposition, the more negative the moss δ^{15}N values. On the basis of the source information, the negative δ^{15}N values of mosses in cities and forests in this study strongly indicate that NH_y-N is the dominant N form in N deposition on a regional scale. These findings have also been supported by the existing data of chemical composition of local N deposition (Table 1). Therefore, on a regional scale, deposition of reduced N exceeds that of oxidized N in the Yangtze River drainage basin and arises mainly from excretory wastes and soil emissions.

[31] The more ^{15}N-depleted mosses in cities than in forests in this study is different from those reported in some European cities and polluted areas. Research by *Pearson et al.* [2000] in London showed distinctly positive moss δ^{15}N values, which was supported by the finding that local atmospheric N species were dominated by oxidized N (NO_x-N) from industrial and traffic emission. In addition, *Gerdol et al.* [2002] observed similar evidence at Ferrara in northern Italy. Relatively higher δ^{15}N signatures of mosses sampled in one of the most polluted and acidified areas in Europe seem to be related to the higher contribution of NO_x forms emitted by industrial activities, primarily fossil fuel combustion [*Bragazza et al.*, 2005]. Because of lower NH_y-N/NO_x-N ratios in N deposition in cities (CD, 3.3) than in forests (EMM, 5.1; and GGM, 21.5) in Sichuan Province (Table 1), less ^{15}N-depleted mosses were found in the former, which is contrary to the findings in Jiangxi Province and Guizhou Province (Figure 5). In Hunan Province, relatively lower NH_y-N/NO_x-N ratios (3.0) in deposition and more ^{15}N-depleted N sources (excretory wastes) in Changsha (CS) than in Hengshan Mountain (HSM) led to there being no significant difference between them.

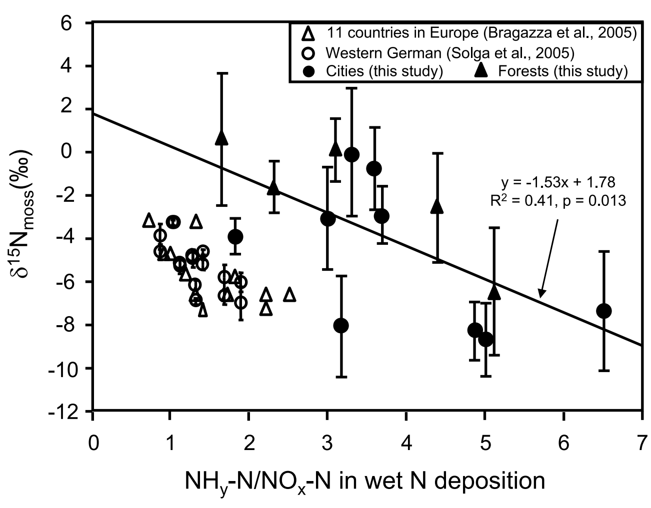

Figure 8. Linear relation between moss δ^{15}N values and NH_y-N/NO_x-N ratio in wet N deposition. Site of GGM and the previous data are not included in the equation $y = -1.53x + 1.78$.

[32] **Acknowledgments.** This work was kindly supported by the National Natural Science Foundation of China through grants 40573006 to H. Y. Xiao and 40721002 to C. Q. Liu, and by a grant from West Light Foundation of The Chinese Academy of Sciences to H. Y. Xiao.

References

Aerts, R., B. Wallén, and N. Malmer (1992), Growth-limiting nutrients in *Sphagnum*-dominated bogs subjected to low and high atmospheric nitrogen supply, *J. Ecol.*, *80*, 131–140.

Aneja, V. P., H. H. Rogers, and W. P. Stahel (1986), Dry deposition of ammonia at environmental concentrations on selected plant species, *J. Air Pollut. Control Assoc.*, *36*(12), 1338–1341.

Berendse, F., et al. (2001), Raised atmospheric CO_2 levels and increased N deposition cause shifts in plant species composition and production in *Sphagnum* bogs, *Global Change Biol.*, *7*, 591–598.

Bragazza, L., et al. (2005), Nitrogen concentration and δ^{15}N signature of ombrotrophic *Sphagnum* mosses at different N deposition levels in Europe, *Global Change Biol.*, *11*, 106–114.

Bragazza, L., et al. (2004), Nutritional constraints in ombrotrophic *Sphagnum* plants under increasing atmospheric nitrogen depositions in Europe, *New Phytol.*, *163*, 609–616.

Dentener, F. J., and P. J. Crutzen (1994), A three-dimensional model of the global ammonia cycle, *J. Atmos. Chem.*, *19*, 331–369.

Durka, W., et al. (1994), Effects of forest decline on uptake and leaching of deposited nitrate determined from ^{15}N and ^{18}O measurements, *Nature*, *372*, 765–767.

Erisman, J. W., P. Grennfelt, and M. Sutton (2003), The European perspective on nitrogen emission and deposition, *Environ. Int.*, *29*, 311–325.

Evans, R. D., and J. R. Ehleringer (1993), A break in the nitrogen cycle in arid lands? Evidence from δ^{15}N of soils, *Oecologia*, *94*, 313–317.

Freyer, H. D. (1978), Seasonal trends of NH_4^+ and NO_3^- nitrogen isotope composition in rain collected at Jülich, Germany, *Tellus*, *30*, 83–92.

Galloway, J. N., et al. (1996), Nitrogen mobilization in the United States of America and the People's Republic of China, *Atmos. Env.*, *30*, 1551–1561.

Gao, Y. (2002), Atmospheric nitrogen deposition to Barnegat Bay, *Atmos. Env.*, *36*, 5783–5794.

Gerdol, R., et al. (2002), Use of moss (*Tortula muralis Hedw.*) for monitoring organic and inorganic air pollution in urban and rural sites in northern Italy, *Atmos. Env.*, *36*, 4069–4075.

Heaton, T. H. E. (1986), Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review, *Chem. Geol.*, *59*, 87–102.

Heaton, T. H. E. (1987), ^{15}N/^{14}N ratios of nitrate and ammonium in rain at Pretoria, South Africa, *Atmos. Env.*, *21*, 843–852.

Heaton, T. H. E. (1990), ^{15}N/^{14}N ratios of NO_x from vehicle engines and coal-fired power stations, *Tellus*, *42B*, 305–307.

Heijmans, M. M. P. D., et al. (2001), Effects of elevated carbon dioxide and increased nitrogen deposition on bog vegetation in the Netherlands, *J. Ecol.*, *89*, 268–279.

Hicks, W. K., et al. (2000), Can the foliar nitrogen concentration of upland vegetation be used for predicting atmospheric nitrogen deposition? Evidence from field surveys, *Env. Pollut.*, *107*, 367–376.

Hu, C. Y., X. G. Huang, and C. L. Li (2002), Pollution features and changing regularity of acid rain in Nanchang city (in Chinese with English abstract), *Acta Agricultural Universitatis Jiangxiensis*, *24*(5), 689–691.

Jung, K., et al. (1997), Anthropogenic impacts on natural nitrogen isotope variations in *Pinus sylvestris* stands in an industrially polluted area, *Env. Pollut.*, *97*, 175–181.

Krupa, S. V. (2003), Effects of atmospheric ammonia (NH_3) on terrestrial vegetation: A review, *Env. Pollut.*, *124*, 179–221.

Lamers, L. P. M., R. Bobbink, and J. M. G. Roelofs (2000), Natural nitrogen filter fails in polluted raised bogs, *Global Change Biol.*, *6*, 583–586.

Li, Z. Y. (1999), Relation between ion concentration and pH in precipitation in number of Chinese cities (in Chinese with English abstract), *Acta Scientiae Circumstantiae*, *19*(3), 303–306.

Liu, L., et al. (2005), The present situation and formative cause and countermeasure research of the acid precipitation in Changsha city (in Chinese with English abstract), *Journal of Hunan Agricultural University (Natural Sciences)*, *31*(2), 216–218.

Liu, X. Y., et al. (2007), δ^{13}C and δ^{15}N of moss (*Haplocladium microphyllum* (*Hedw.*) *Broth*) for indicating environment variations and canopy retention on atmospheric nitrogen deposition, *Atmos. Env.*, *41*, 4897–4907.

Liu, X. Y., et al. (2008), Stable carbon and nitrogen isotopes of the moss *Haplocladium microphyllum* in an urban and a background area (SW China): The role of environmental conditions and atmospheric nitrogen deposition, *Atmos. Env.*, *42*, 5413–5423.

Liu, Y. M., C. L. Chen, and Z. Y. Zhou (2001), Cause of air pollution in urban area of Chongqing and the suggestions to improve air diffusive condition (in Chinese with English abstract), *Chongqing Env. Sci.*, *23*(4), 22–25.

Mei, Z. L., et al. (2005), Analysis on the variation of acidity and chemical compositions of rainwater in Chengdu urban area (in Chinese with English abstract), *Sichuan Env.*, *24*(3), 52–55.

Moore, H. (1977), The isotopic composition of ammonia, nitrogen dioxide, and nitrate in the atmosphere, *Atmos. Env.*, *11*, 1239–1243.

Pearson, J., et al. (2000), Traffic exposure increases natural ^{15}N and heavy metal concentrations in mosses, *New Phytol.*, *147*, 317–326.

Pitcairn, C. E. R., D. Fowler, and J. Grace (1995), Deposition of fixed atmospheric nitrogen and foliar nitrogen content of bryophytes and *Calluna vulgaris* (L.) Hull, *Env. Pollut.*, *88*, 193–205.

Pitcairn, C. E. R., et al. (2006), Diagnostic indicators of elevated nitrogen deposition, *Env. Pollut.*, *144*, 941–950.

Pitcairn, C. E. R., et al. (2001), Foliar nitrogen as an indicator of nitrogen deposition and critical loads exceedance on a European scale, *Water, Air, Soil Pollution*, *130*, 1037–1042.

Pitcairn, C. E. R., et al. (2002), Defining the spatial impacts of poultry farm ammonia emissions on species composition of adjacent woodland groundflora using Ellenberg indicators, nitrous oxide and nitric oxide and foliar nitrogen as marker variables, *Env. Pollut.*, *119*, 9–21.

Press, M. C., S. J. Woodin, and J. A. Lee (1986), The potential importance of an increased atmospheric nitrogen supply to the growth of ombrotrophic *Sphagnum* species, *New Phytol.*, *103*, 45–55.

Schlesinger, W. H., and A. E. Hartley (1992), A global budget for atmospheric NH_3, *Biogeochemistry*, *15*, 191–211.

Skinner, R. A., et al. (2006), Heathland vegetation as a bio-monitor for nitrogen deposition and source attribution using δ^{15}N values, *Atmos. Env.*, *40*, 498–507.

Solga, A., et al. (2005), Nitrogen content, ^{15}N natural abundance and biomass of the two pleurocarpous mosses *Pleurozium schreberi* (*Brid.*) *Mitt* and *Scleropodium purum* (*Hedw.*) *Limpr*. in relation to atmospheric nitrogen deposition, *Env. Pollut.*, *134*, 465–473.

Sun, Q. R., and M. R. Wang (1997), Ammonia emission and concentration in the atmosphere over China (in Chinese with English abstract), *Scientia Atmospherica Sinica*, *21*, 590–598.

Wang, W., et al. (1992), Pollution characteristic of atmospheric aerosol and relationship between aerosol and acid precipitation in south China (in Chinese with English abstract), *Acta Scientiae Circumstantiae*, *12*(1), 7–15.

Xiao, H. Y., and C. Q. Liu (2002), Sources of nitrogen and sulfur in wet deposition at Guiyang, Southwest China, *Atmos. Env.*, *36*, 5121–5130.

Xiao, H. Y., and C. Q. Liu (2004), Chemical characteristics of water soluble components in TSP over Guiyang, SW China, 2003, *Atmos. Env.*, *38*, 6297–6306.

Zhang, J., et al. (1999), Human impacts on the large world rivers: Would the Changjiang be an illustration?, *Global Biogeochem. Cycles*, *13*, 1099–1105.

Zhao, D., and A. Wang (1994) Estimation of anthropogenic ammonia emissions in Asia, *Atmos. Env.*, *28A*, 689–694.

Zhou, Z. Y., et al. (2003), Characteristic analysis of rainwater chemistry in Chongqing city (in Chinese), *Chongqing Env. Sci.*, *25*(11), 112–114.

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