Spatial and temporal patterns of nitrogen deposition in China: Synthesis of observational data

Chaoqun Lü[1,2] and Hanqin Tian[3]

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[1] Anthropogenic nitrous pollutant emissions in China significantly increased during the last decades, which contributed to the accelerated nitrogen (N) deposition. In order to characterize spatial pattern of nitrogen deposition, we employed the kriging technique to interpolate sampling data of precipitation chemistry and ambient air concentration from site-network observations over China. The estimation of wet deposition in China was limited to aqueous NO_3^- and NH_4^+, while ambient NO_2 was the only species involved in the predicted dry deposition fluxes. To obtain wet deposition fluxes, precipitation concentration was multiplied by 20-year mean precipitation amounts with a resolution of 10×10 km. Dry deposition fluxes were products of the interpolated ambient NO_2 concentration and deposition velocities modeled for the main vegetation types in China. The total deposition rates of wet and dry deposition peaked over the central south China, with maximum values of 63.53 kg N ha^{-1} yr^{-1}, and an average value of 12.89 kg N ha^{-1} yr^{-1}. With ambient NO_2 concentration data spanning from the year 1990 through 2003, we detected and evaluated trends in the time series of the annual values of atmospheric NO_2 concentration. Significant upward trends at 21 of 102 sites were exhibited, with median percent change of 61.45% over the period 1990–2003. In addition, spatially continuous patterns of dry deposition fluxes based on ambient NO_2 measurements in two 5-year phases, 9 years apart, were carried out. On average, there was a rise of 7.66% in NO_2 dry deposition during 9 years throughout China.

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1. Introduction

[2] Human activities including deforestation, the expansion of agriculture, burning of biomass, fertilizer use and industrial development, have affected the nitrogen (N) cycle [*Galloway et al.*, 2004; *Tian et al.*, 2006] or changed N deposition rate [*Holland et al.*, 2005; *Dentener et al.*, 2006a]. Anthropogenic nitrous pollutant emissions in China have significantly increased during the last decades. The total NO_x emission in China increased from 8.4 Tg/yr in 1990 to 11.3 Tg/yr in 2000, while the total NH_3 emission increased from 10.8 Tg/yr to 13.6 Tg/yr [*Wang et al.*, 1996; *Sun and Wang*, 1997; *Streets et al.*, 2003]. Increases in reactive N emissions deteriorate air quality, contribute to regional nitrogen deposition, which may lead to adverse effects on human health and ecosystem functioning, and to some extent, affect global carbon cycling [*Asner et al.*, 1997; *Matson et al.*, 2002; *Melillo et al.*, 2003; *Tian et al.*, 2003]. It is critical to estimate nitrogen deposition patterns for quantifying effects of nitrogen amendment and establish control measures to improve environmental quality [*Townsend et al.*, 1996; *Holland et al.*, 1997].

[3] In order to determine the actual nitrogen input to ecosystems, most deposition maps on country or continent scale have been based on three-dimensional chemical transport model results which need to be validated by comparison with field measurements [*Li et al.*, 2004; *Luo et al.*, 2000; *Levy and Moxim*, 1989]. Hence measurement-based maps are obviously needed to explore current deposition fluxes. However, to date, nitrogen deposition patterns are not well known yet because of nitrogen's complex reactions and involvement of various species in transportation and deposition [*Park and Lee*, 2002]. In addition, the majority of studies on acid deposition in China have just focused on the distribution of precipitation pH [*Larssen and Carmichael*, 2000]. China's acid rain is identified as sulfate-type [*Li and Gao*, 2002], and therefore field measurements on nitrous compounds deposition are not usually available.

[4] The purpose of this study is to estimate nitrogen deposition patterns in China based on field measurements, to detect trends in the time series of the annual values of atmospheric NO_2 concentration, and to reveal the anthropogenic influences on nitrogen deposition. In order to understand nitrogen deposition distribution in China, we need spatially continuous patterns from scattered monitoring

[1]Institute of Geographical Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, China.
[2]Also at School of Forestry and Wildlife Sciences, Auburn University, Auburn, Alabama, USA.
[3]School of Forestry and Wildlife Sciences, Auburn University, Auburn, Alabama, USA.

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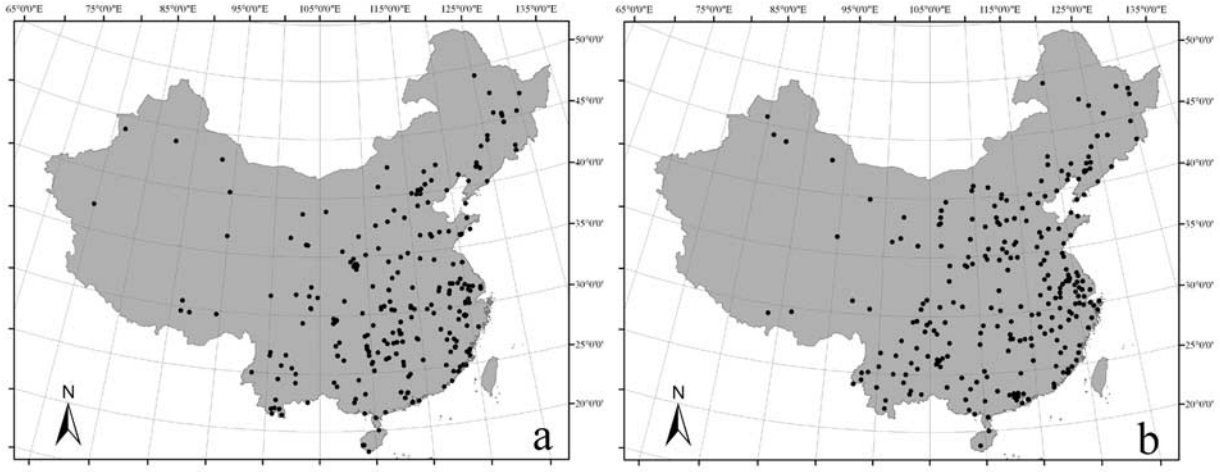

Figure 1. Monitoring stations for precipitation chemistry and ambient air NO_2 concentration over China. (a) Measurements of aqueous NO_3^- and NH_4^+ concentration with 253 sites. (b) Ambient NO_2 concentration measurements with 254 sites spanning from the year 1990 to 2003.

sites. However, the availability of sufficient sites to deduce the spatial and temporal patterns of nitrogen deposition and the improvement of extrapolation/interpolation procedures are two important determinants [*Park and Lee*, 2002; *Holland et al.*, 2005]. Because of the limit of monitoring networks in China and the errors inherent to the interpolation procedure, the associated uncertainties and incomplete estimates for nitrogen species cannot be ignored.

2. Data and Methods

2.1. Data Source

[5] In order to get a nitrogen deposition map of 10 × 10 km resolution, we compiled information on precipitation chemistry and air quality. The National Acid Deposition Monitoring Network (NADMN) in China was established in 1992, but mainly focused on precipitation pH and conductance. Only a few of the monitoring stations have precipitation chemistry data, such as aqueous NO_3^- and NH_4^+ concentrations [*Ding et al.*, 2004]. Since the national-scale measurement of ambient nitrous air pollutant concentration in China is restricted to NO_x and/or NO_2, to calculate dry deposition flux of gaseous HNO_3 and NH_3, and particulate NO_3^- and NH_4^+ is beyond this study. By the year 2000, the national ambient air quality standard (NAAQS) in China altered the measurement indices. Most monitoring sites then adopted ambient NO_2 concentration instead of previous NO_x concentration standards to evaluate the status of air pollution. In order to keep the consistency of measured data during the period of 1990 to 2003, we made the data conversion from NO_x concentration to NO_2, by setting the ratio of NO_2/NO_x to 0.8 [*State Environmental Protection Administration*, 1996], although it is also related to initial concentrations and reaction processes [*Stedman*, 1999].

[6] Our calculation of nitrogen deposition fluxes was performed on data of precipitation chemistry and ambient air concentration, acquired from various sources as follows. The data used to deduce wet deposition of nitrogen included 4 sources as follows:

[7] 1. Precipitation chemistry data from a nationwide monitoring network was provided by Centre for Atmosphere Watch and Services (CAWAS), China Meteorological Administration (CMA). The quarterly average values of aqueous NO_3^- and NH_4^+ concentration were collected from 81 rural and remote sites between the year 1992 and 1993. This is the only information on precipitation chemistry from background monitoring stations throughout China so far [*Ding et al.*, 2004].

[8] 2. Precipitation chemistry data of three baseline observatories in Shangdianzi (spanning the years 1984–1998), Lin'an (spanning the years 1985–1998) and Longfengshan (spanning the years 1991–1998), was offered by the Chinese Academy of Meteorological Sciences. This data includes weekly mean concentrations of aqueous NO_3^- and NH_4^+.

[9] 3. NO_3^- and NH_4^+ concentration data was measured by EANET (East Asian NET), from 9 sites in 4 cities including Chongqing, Xi'an, Xiamen and Zhuhai, between 2000 and 2004.

[10] 4. Wet deposition data or precipitation chemistry data was collected from published sources. These data were almost yearly average values of NO_3^- and NH_4^+ concentrations.

[11] As a whole, 172 out of 253 precipitation samples were collected in rural and remote locations, while the other 81 were from urban stations. The majority of ambient air NO_2 concentrations involved in the calculation of dry deposition fluxes were acquired from the China Environmental Yearbook, which presented urban air quality data collected by city-level environmental protection bureaus around China. The measurement spanned from the year 1990 to 2003 with missing values in some sites. The other database which focused on yearly average NO_2 concentrations was obtained from published literatures. However, the measurement of ambient NO_2 concentrations was concentrated in urban stations, which undoubtedly overestimated the actual state of dry deposition fluxes in China. In addition, the monitoring stations of nitrous pollutants in China were not evenly distributed. Most of them were set up in southern and eastern China, while in western China, or specifically the Tibetan plateau, there have been few stations established (Figure 1).

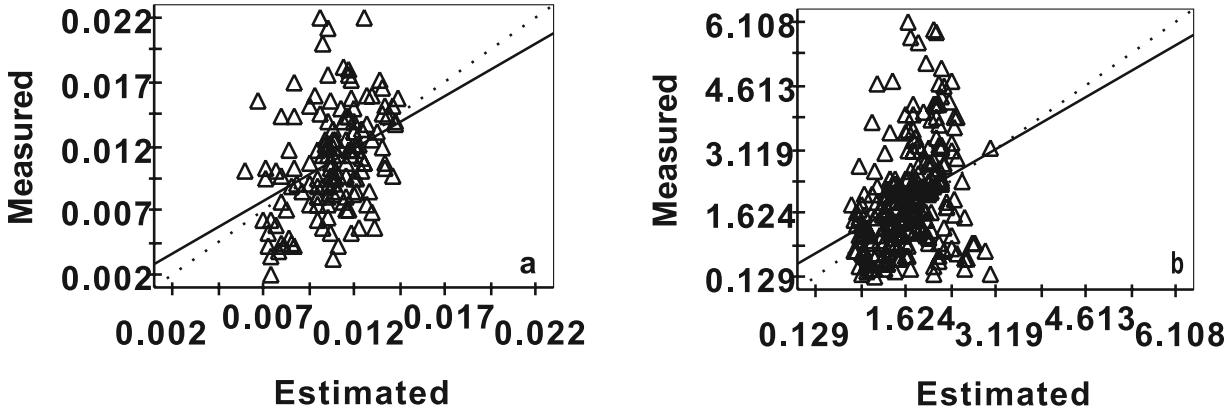

Figure 2. Cross-validation graphs constructed from kriging processes. (a) Interpolation of aqueous NO_3^- and NH_4^+ concentration over China (the units are g N m^{-3}). (b) Interpolation of ambient air NO_2 concentration (the units are mg N m^{-3}).

[12] Although the precipitation chemistry data from the monitoring network were checked using an ion balance and/or conductivity agreement to ensure data quality, the level of quality assurance and quality control in NADMN is not yet certain [*Li and Gao*, 2002]. There is also a level of uncertainty in the measurements of ambient NO_2 concentration. However, these data provided by the monitoring network were important indices, with which the State Environmental Protection Agency (SEPA) in China annually evaluated the status of the atmospheric environment.

2.2. Methods

[13] To get a nitrogen deposition map in China, a geostatistical procedure is necessary to interpolate/extrapolate field measurements into a spatially continuous pattern. Considering the characteristics of data measured and the interpolation results expected, diversified methods have been employed with atmospheric deposition network data [*Levy and Moxim*, 1989; *Van Leeuwen et al.*, 1996; *Park and Lee*, 2002; *Holland et al.*, 2005]. We used a geostatistical analysis program of GS+ for this paper, where data were interpolated using the kriging interpolation technique [*Gamma Design Software* (*GDS*), 2004]. The first step carried out the primary data summary statistics. From this we got a descriptive report of data, including mean, maximum, minimum values and their frequency distribution, by which to determine whether or not there is a need to make a data transformation. The results of the kriging interpolation are more reliable when data are normally distributed [*Van Leeuwen et al.*, 1996]. Then the optimal variogram models were chosen to ensure the weighted residual sum of squares is minimized. A cross-validation analysis was implemented to evaluate the effective parameter of the kriging interpolation. In this analysis each measured point was individually removed, and its value estimated via kriging was compared with the original observation data. This presents the goodness of fit for the hypothetical variogram and neighborhood search parameter. A regression coefficient of 1.00 indicates a perfect 1:1 fit (GDS, 2004). Figure 2 showed a fairly good fit with the regression coefficients of 0.831 ($r^2 = 0.107$) and 0.820 ($r^2 = 0.151$) for precipitation chemistry data and ambient air NO_2 concentration, respectively. The low r^2 values reflected that the best fit line cannot fully explain the variation of measured data. Using the variogram models, estimates of concentration were made on a uniform grid of 10 × 10 km with ordinary block kriging. Because the successive monitoring of precipitation chemistry at the same station is scarce in China and the data collected from various sources are highly discrete at the temporal scale, we employed all the concentration data to produce a continuously spatial map, regardless of the time measurement. The yearly mean value was used when data from more than one year were available. Wet deposition fluxes of nitrogen can be obtained through multiplying interpolated annual mean aqueous NO_3^- and NH_4^+ concentrations on a regular grid of 10 × 10 km with annual mean precipitation amounts over 20 years. The data of ambient air NO_2 concentration from 139 monitoring stations were accessed in 2003; therefore, in order to demonstrate the current status of nitrous pollutant deposition, we performed interpolation of ambient concentration data for this single year. The dry deposition flux was calculated as the product of the deposition velocity and ambient concentration. For NO_2, the stomatal uptake mainly limits the maximum rates of deposition to canopies of vegetations [*Metcalfe et al.*, 1999]. We used the study results from *Zhang et al.* [2004], which combined the site-specific gradient meteorological data and a big-leaf model to simulate the distribution of dry deposition velocities for the main types of land use present in China.

[14] Even though a great number of studies have been conducted on the changing trends of air pollution in China [*Streets and Waldhoff*, 2000; *Liu et al.*, 2004; *Richter et al.*, 2005; *He et al.*, 2002], few studies focused on national-scale patterns of ambient nitrous pollutants based on successive monitoring in field. In order to illustrate the trends of dry deposition fluxes, some statistical techniques are required to investigate the temporal pattern of NO_2 deposition over China. First, we used a MAKESENS (Mann-Kendall test for trend and Sen's slope estimation) excel template to detect and estimate trends in the time series of the annual values of atmospheric NO_2 concentration. MAKESENS performed two types of statistical analyses: a test for the presence of a monotonic increase or decrease with the

nonparametric Mann-Kendall test, and an estimate of the slope of linear trends with the nonparametric Sen's method [*Salmi et al.*, 2002; *Nilles and Conley*, 2001]. Prior to trends analysis, the concentration data spanning from 1990 to 2003 were treated under data screening. This required the sites of measurement period longer than 4 years for Mann-Kendall test and those exhibiting significant monotonic trends and being monitored for more than 10 years to estimate trend magnitude. After data screening, 102 sites met the criteria of evaluation for trends. Second, comparison of dry deposition patterns in different periods indicated the percent changes of deposition flux with a resolution of 10×10 km over China. To avoid the possibility of extreme values in one single year, we introduced yearly average values from two 5-year phases, from 1990 to 1994 and from 1999 to 2003, which had 160 and 187 monitoring stations, respectively. The stations monitoring more than one year accounted for 67% and 73% of total stations during these two 5-year phases. We carried out the kriging interpolation based on yearly average values of ambient NO_2 concentration measured in the above period. From differences between the nitrogen deposition maps we calculated the mean percent change of dry deposition on a national scale, with the magnitude of change in every grid cell.

3. Results and Discussions

3.1. Wet- and Dry-Deposition Fluxes

[15] Nitrogen deposition maps indicated a significant gradient from industrial areas to underdeveloped regions in China. Wet deposition of nitrogen is greatest in central south China, with peak values of 62.25 kg N ha^{-1} yr^{-1}, and an average value of 9.88 kg N ha^{-1} yr^{-1} (Figure 3a). The statistical analysis of the precipitation chemistry data suggested that average deposition of NH_x_N were estimated at 7.13 kg N ha^{-1} yr^{-1}, accounting for 72.21% (SD = 16.23%) of the total wet deposition. The remainder of wet deposition was NO_y_N, with a mean deposition rate of 2.75 kg N ha^{-1} yr^{-1}(Table 1). Wet deposition fluxes totaled to 9.45 Tg N per year throughout China, including the deposition of NH_x_N with 6.82 Tg N per year and NO_y_N with 2.63 Tg N (Table 2). Furthermore, mean deposition rates of aqueous NO_3^- and NH_4^+ in China were substantially larger than those in the United States but close to those in Europe, averaged to 3.02 kg N ha^{-1} yr^{-1} and 6.76 kg N ha^{-1} yr^{-1}, respectively [*Holland et al.*, 2005]. The fact that samples in the U.S. network were only from remote areas may have contributed to the differences. It may be argued that the uncertainties associated with the representativeness of sampling sites and the uneven distribution of urban and rural monitoring stations absolutely introduced a bias to interpolated results [*Van Leeuwen et al.*, 1996]. The exact uncertainty caused by representativeness is not well known yet.

[16] The peak values of dry deposition were centered in the upper mideastern China, more than 4.93 kg N ha^{-1} yr^{-1}, and the mean deposition rate was about 3.03 kg N ha^{-1} yr^{-1}, with the total amount of NO_2 deposition fluxes up to 2.90 Tg N per year (Figure 3b). The spatial pattern of ambient air NO_2 deposition estimated in this paper was close to the distribution of tropospheric NO_2 vertical columns retrieved from satellite data, suggesting the greatest concentration of NO_2 is in east central China [*Richter et al.*, 2005], even though the estimated deposition velocity highly contributed to dry deposition fluxes. The mean deposition rates of gaseous NO_2 in China were considerably larger than that in Europe which averaged to 1.3 kg N ha^{-1} yr^{-1} [*Holland et al.*, 2005] by 2 or 3 times. The great disparity can be mostly attributed to increasing NO_x emissions in China arising from doubled vehicles and increasing industrial and domestic sources [*Richter et al.*, 2005; *Streets et al.*, 2003], while across Europe NO_x emissions began to decline after 1990 probably because of the effective environmental protocols and economic restructuring [*Metcalfe et al.*, 1999]. Furthermore, interpolation of the observation data acquired from urban monitoring sites undoubtedly overestimated current status of dry deposition fluxes in China. This may offset the lack of other chemical species than NO_2 in the national monitoring network to calculate dry deposition fluxes to some extent. The deposition velocities used in our study were parameterized by combining the in situ measurements and models [*Zhang et al.*, 2004], with 0.09–0.13 cm/s for main vegetation types and 0.01–0.07 for lakes, deserts and tundra. The V_d values were about half less than that modeled by *Holland et al.* [2005], 0.34 cm/s for the European average, while fairly close to velocities observed in the coniferous forests [*Rondón et al.*, 1993], with the range of 0.08–0.21 during the day and 0.03–0.08 at night. The simulation of deposition velocities for NO_2 emphasized canopy resistance through a big-leaf model used to capture the effect of plant physiological processes on stomatal uptake [*Zhang et al.*, 2004]. It is necessary to obtain a great number of site-specific measurements to validate model results, and thereby make the estimation of dry deposition more reliable.

[17] The total deposition rates of wet and dry deposition peaked over central southern China, with maximum values of 63.53 kg N ha^{-1} yr^{-1}, while western China was characterized by fluxes less than 14 kg N ha^{-1} yr^{-1} (Figure 3c). Spatial patterns of total nitrogen deposition by province also showed that the central southern regions, such as Jiangxi, Guangdong, Chongqing, Hubei, Hunan, Guangxi and Anhui, were among the greatest contributors to nitrogen deposition fluxes on a national scale; however, the underdeveloped area in the west and north of China, such as Xinjiang, Tibet, Qinghai, Gansu, Inner Mongolia and Ningxia, were on the contrary (Table 3). Across China the total deposition rate on average was 12.89 kg N ha^{-1} yr^{-1}, and the total deposition fluxes summed to 12.35 Tg N per year. A bottom-up inventory study estimated the emissions of NO_x and NH_3 in China in the year 2000 at 14.67 Tg N [*Streets et al.*, 2003]. The imbalance of 2.32 Tg N between emissions and deposition (Table 2) could arise from the following potential effects: First of all, the emissions and deposition were not estimated for the same time period because of difficulties in data acquiring, and the contribution of inherent yearly variability should not be ignored. Satellite retrievals indicated that NO_2 concentration in China was enhanced with a range of annual increase from 4% to 12% [*Richter et al.*, 2005]. Assuming the annual NH_3 emission increased by the same rate of NO_2, the yearly variations were far less to explain the imbalance with uncertainties resulting from the sources not yet included in emission

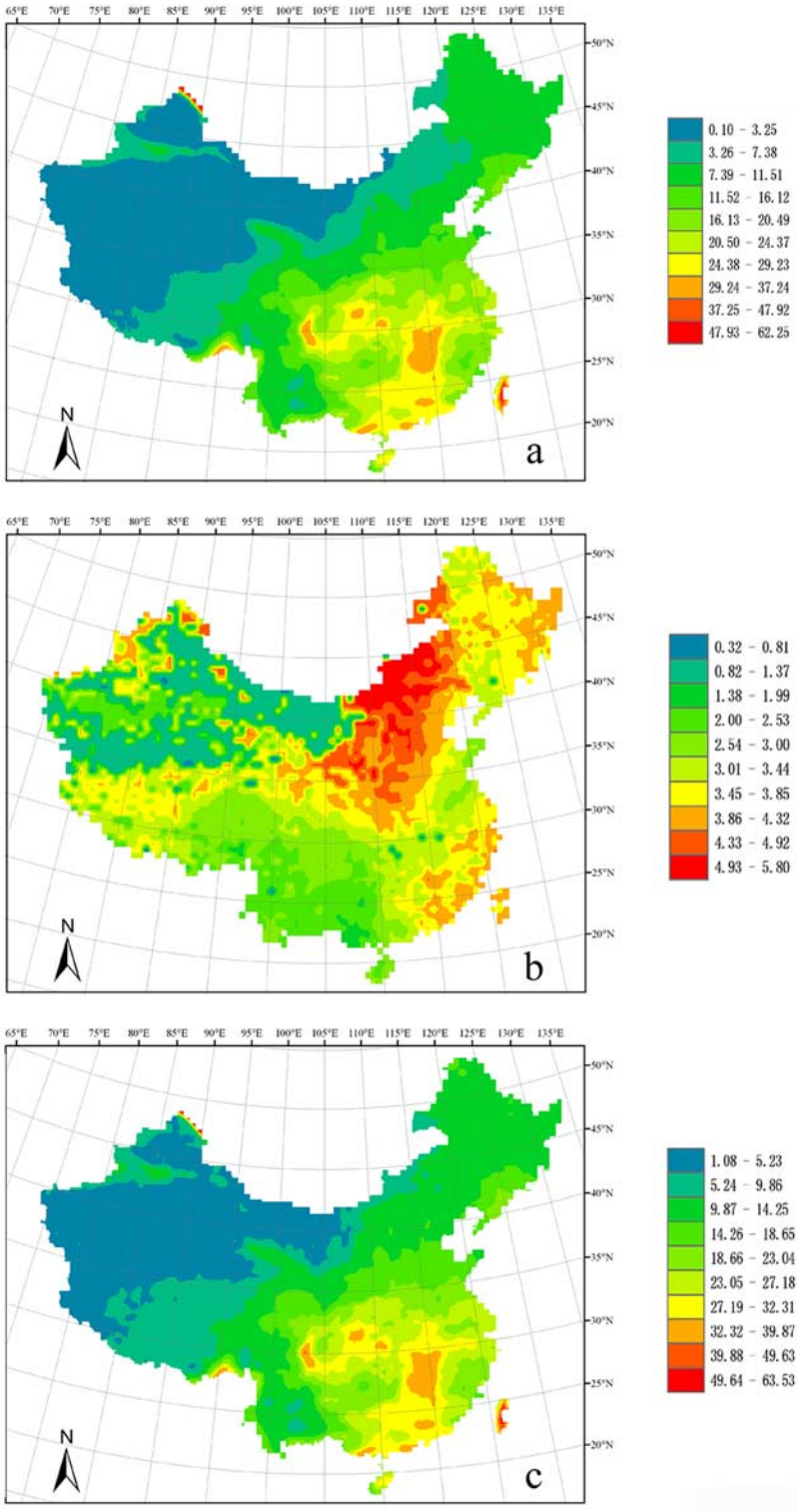

Figure 3. Spatial patterns of nitrogen deposition throughout China (the units are kg N ha^{-1} yr^{-1}). (a) Wet deposition of aqueous NO_3^- and NH_4^+. (b) Dry deposition of ambient air NO_2. (c) Total deposition rates of wet and dry deposition.

estimations and missing species in deposition measurements. Secondly, largely because of the range of the national measurements, the estimations of deposition fluxes were actually incomplete with the lack of various nitrogen species concentration measured, such as gaseous HNO_3, gaseous NH_3, particulate NO_3^-, particulate NH_4^+, and organic nitrogen as well. On the other hand, NO_x emissions were underestimated in a recent inventory because of unknown

Table 1. Comparison Between Interpolated Deposition Rates With Measurements in Field and Deposition Modeled[a]

Deposition	Year	NO_y	NH_x	Total $NO_y + NH_x$
Deposition measured				
Wet deposition	1993	2.17	9.50	11.67
Dry deposition	1993	2.70		2.70
Total wet + dry		4.87	9.50	14.37
Deposition modeled				
Wet + dry	1993	2.53	6.66	9.19

[a]Unit is kg N ha^{-1} yr^{-1}. The modeled deposition was cited from *Dentener et al.* [2006a].

biofuel consumption, unreported coal use and vehicles ownership in rural China, and so on [*Streets et al.*, 2003]. *Wang et al.* [2005] argued that regionally estimated NO_x emissions were 70% higher than the amounts calculated by *Streets et al.* [2003] because of more complete inventory of rural coal consumption and a higher NO_x emission factor for mobile sources. The negative imbalance between estimated emissions and deposition for oxidized N in Table 2 was probably related to the underestimated emissions. Then next, giving consideration to transport of air NO_x, emissions and deposition budgets were probably altered by import-export processes between neighboring countries [*Chung et al.*, 1996; *Kim and Cho*, 2003]. For instance, emissions in China were estimated to contribute 18%, 46% and 26% of fossil-fuel-derived nitric acid deposition in Japan, North Korea and South Korea, separately [*Holloway et al.*, 2002].

3.2. Model/Measurement Comparison

[18] With the present information, we compared the measured wet deposition for oxidized and reduced N in monitoring sites (offered by CAWAS, see data source 1) and the simulated values during the year 1993 [*Dentener et al.*, 2006a] and found that modeling results significantly underestimated the actual deposition rates, especially for aqueous NH_4^+ (Figures 4a and 4b). Only 44.4% of the model results for NH_4^+ deposition were accordant within ±50% with the measured values, while 71.3% of modeled NO_3^- deposition rates were within ±50% of the observation. The lower regression coefficient implied that the transport models were not fully effective in capturing the spatial variability of nitrogen deposition throughout the country. In order to further examine the capability of the air transport models in simulating nitrogen deposition fluxes, we compared the spatially interpolated deposition of reduced and oxidized N over China during the year 1993 with modeled patterns in the same grid of 10 × 10 km. The simulated deposition of N ranged from 0.71 to 33.55 kg N ha^{-1} yr^{-1}, with an average value of 9.19 kg N ha^{-1} yr^{-1}. This was much less than the measurement-based fluxes, which averaged to 14.37 kg N ha^{-1} yr^{-1} (Table 1). Separate comparison for reduced N and oxidized N also indicated that transport models had significantly underestimated the actual nitrogen deposition fluxes, especially for reduced N, the model results explained only 70% of the measured wet deposition of NH_x on country scale (Table 1). Considering the lack of measurements on gaseous HNO_3 and NH_3, and particulate NO_3^- and NH_4^+ throughout China, the model predictions would account for less. By contrast, the spatial patterns of oxidized N and reduced N simulated were in accordance with measurements, although models underestimated deposition fluxes in most areas of China.

[19] The differences between model results and actual measurements averaged to −6.97 kg N ha^{-1} yr^{-1} (SD = 8.18) for total N throughout the country. Among them, the simulated NH_x_N deposition contributed to underestimation of 4.17 kg N ha^{-1} yr^{-1}, and underestimated NO_y_N accounted for the rest. In conclusion, there were higher modeled results in the area of source emissions as indicated by *Streets et al.* [2003], which agreed well with the fact that the simulated deposition fluxes were sensitive to emission estimates [*Dentener and Crutzen*, 1993; *Holland et al.*, 1999; *Lamarque et al.*, 2005]. Likewise, the inherent uncertainty in emission estimates partially contributed to the discrepancy between model results and measurements. *Dentener et al.* [2006b] also pointed out the assumed NO_x emissions over the rapidly developing part of eastern China is unrealistically low compared with satellite observations, which is consistent with the underestimation of NO_y_N deposition in models. According to *Wang et al.* [2005], there have been great uncertainties in our emission inventory due to numerous missing sources of N in official statistics on energy use and socioeconomical activities. The fact that the IISA/EDGAR 3.2 inventory significantly underestimated the actual nitrogen emissions from eastern China, especially in wintertime [*Van Noije et al.*, 2006; *Richter et al.*, 2005], can partly account for the model underprediction of N deposition.

3.3. Trend Analysis of Ambient NO_2

[20] Trend analysis in the period 1990 through 2003 exhibited apparently upward progressions in ambient air NO_2 concentration over China. Nationwide, 21 of 102 sites indicated significant increasing trends, while 10 sites had decreasing trends. After excluding extreme values and those sampling sites with insignificant trends which accounted for nearly 70% of measurements, analysis over the whole period still exhibited statistically significant positive NO_2 concentration changes throughout the country, with a median percent change of 61.45% (Figure 5), computed from sites with a significant trend ($\alpha = 0.05$). The median trend slope of all 102 sites examined was about 1.1 $\mu g/m^3/yr$, equivalent to an annual increase of 5%. It should be noted

Table 2. Budgets of Nitrogen Deposition and Estimated Emissions in China[a]

Emissions	Year	NO_x	NH_3	Total $NO_x + NH_3$
Estimated emissions	2000	3.47	11.20	14.67
Deposition Fluxes	**Year**	**NO_y**	**NH_x**	**Total $NO_y + NH_x$**
Wet deposition	long-term mean	2.63	6.82	9.45
Dry deposition	2003	2.90		2.90
Total wet + dry		5.53	6.82	12.35
Imbalance		−2.06	4.38	2.32

[a]Unit is Tg N yr^{-1}. The estimated emissions are cited from *Streets et al.* [2003]. Wet deposition fluxes are focused on NO_3^- and NH_4^+, while dry deposition fluxes are for gaseous NO_2. The area of China is 9.5642 × 10^6 km^2.

Table 3. Summary of Nitrogen Deposition by Province in China[a]

	Wet Deposition Rate			Dry Deposition Rate			Total Deposition Rate		
Province	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean
Anhui	14.73	29.32	20.95	0.72	3.94	3.22	17.97	31.93	24.18
Beijing	8.49	10.27	9.69	4.08	4.66	4.27	12.87	14.46	13.95
Chongqing	18.42	32.01	25.09	2.51	3.89	3.01	21.08	35.58	28.05
Fujian	11.70	24.85	18.15	3.12	4.24	3.75	15.61	28.50	21.95
Gansu	0.33	18.50	5.36	0.91	5.26	2.80	1.45	22.11	8.16
Guangdong	16.37	31.95	25.84	2.43	4.17	3.46	19.75	35.87	29.42
Guangxi	10.01	36.27	22.80	1.74	3.60	2.43	12.73	38.38	25.24
Guizhou	10.28	25.67	18.53	2.00	2.99	2.46	12.87	28.27	20.96
Hainan	13.08	27.30	22.34	2.35	3.07	2.59	15.89	29.99	25.02
Hebei	5.68	13.34	9.13	3.50	5.63	4.38	9.87	17.56	13.53
Heilongjiang	7.67	11.65	9.53	3.10	4.52	3.83	11.13	15.10	13.33
Henan	11.95	27.01	18.30	3.24	4.67	4.05	16.06	30.60	22.35
Hubei	17.76	33.65	24.20	0.45	4.25	3.50	21.54	36.91	27.70
Hunan	15.65	35.47	23.95	0.50	3.89	3.13	18.23	38.88	27.06
Jiangsu	14.98	22.40	19.70	2.80	4.16	3.27	18.57	25.95	23.00
Jiangxi	17.46	36.38	27.14	1.62	4.34	3.62	21.14	39.70	30.76
Jilin	7.64	16.09	10.11	3.32	4.29	3.71	11.30	19.81	13.79
Liaoning	7.54	17.87	12.56	0.67	4.68	3.44	11.45	21.45	15.99
Neimenggu	0.49	11.97	5.57	0.34	5.78	3.57	1.31	15.07	9.24
Ningxia	3.10	9.89	5.48	1.35	4.89	3.92	4.14	14.11	9.33
Qinghai	0.10	14.36	4.76	0.44	4.36	2.82	1.08	17.81	7.55
Shandong	10.06	17.38	13.21	2.81	4.35	3.47	12.92	20.68	16.74
Shanghai	20.51	23.05	21.79	3.77	3.86	3.81	24.32	26.89	25.60
Shannxi	4.93	27.84	14.44	3.31	5.29	4.15	9.27	31.57	18.59
Shanxi	7.01	14.63	10.35	3.85	5.77	4.65	11.74	19.26	14.98
Sichuan	7.48	37.36	17.08	2.13	4.05	2.93	9.81	40.06	19.96
Taiwan	21.37	59.73	34.02	3.45	4.26	4.00	25.09	63.53	38.21
Tianjin	9.33	9.92	9.63	3.78	4.31	4.04	13.40	14.17	13.66
Xinjiang	0.14	62.25	1.94	0.38	4.51	2.06	1.09	62.54	3.84
Xizang	0.22	33.73	4.16	0.39	3.96	2.82	1.13	36.32	6.96
Yunnan	6.02	25.67	10.61	1.94	3.07	2.39	8.55	28.36	12.96
Zhejiang	15.61	24.72	20.19	3.20	4.34	3.84	19.48	28.67	24.01
China total	0.10	62.25	9.88	0.34	5.78	3.03	1.08	63.53	12.89

[a]Unit is kg N ha^{-1} yr^{-1}.

that the observation used in trend analysis were mostly located in the south and east of China, where acid pollution was more serious than in other areas of the country [*Li and Gao*, 2002], because of rapid economic development. In addition, the calculation of median percent change for individual sampling sites excluded those with insignificant trends, which accounted for large part of measurements.

[21] To illustrate the extent and spatial pattern of ambient NO_2 change, comparison between deposition maps based on annual mean values of NO_2 concentration measured

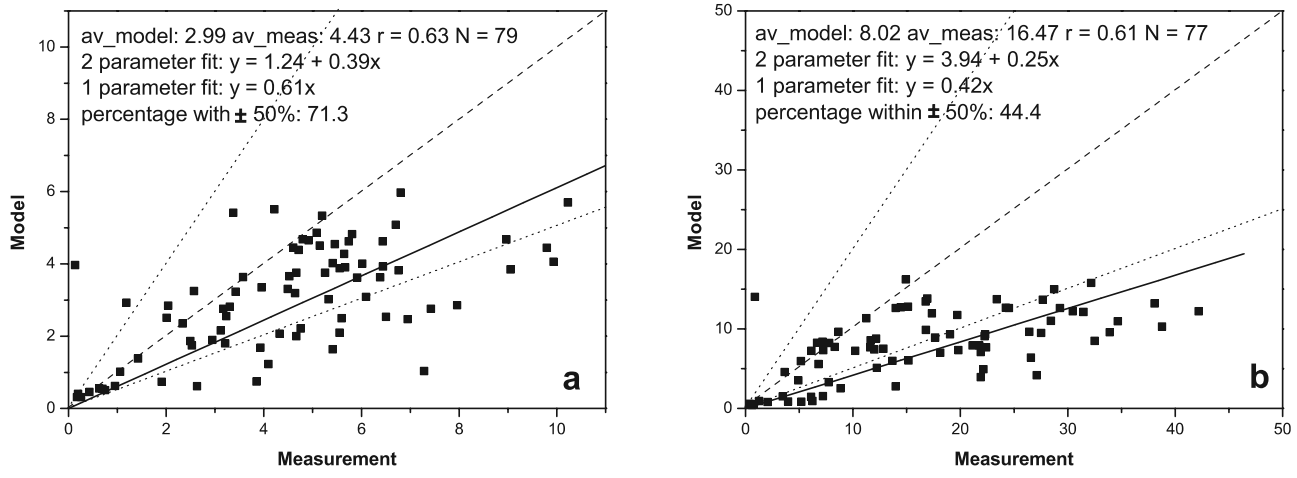

Figure 4. Comparison of simulated deposition rates with measured data (units are kg N ha^{-1} yr^{-1}). (a) Comparison of simulated wet deposition rates of NO_x_N with measured deposition for NO_3^- in the year 1993. (b) Comparison of modeled wet deposition of NH_4^+ with our measured deposition for NH_4^+ in the year 1993. The dotted lines are 1:2 and 2:1 fit line, and the dashed line is 1:1 fit. The black solid line is a linear fit of modeled and measured deposition through zero.

Median Change	61.40%
sites with positive trend	21
sites with negative trend	10
sites with no trend	71

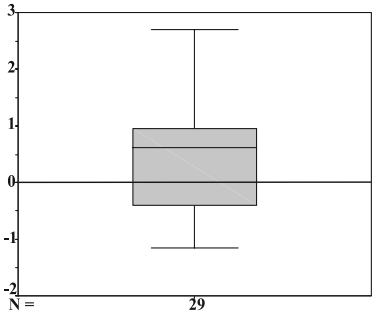

Figure 5. Percent change of ambient air NO_2 concentration from the year 1990 to 2003.

from the year 1990 to 1994 and the year 1999 to 2003, was carried out. Regionally, levels of NO_2 concentration had increased in the southeast and southwest of China and decreased in the northwest and central parts (Figure 6). On average, there was a rise of 7.66% in NO_2 dry deposition during the 9 year period throughout China. This increase is partly associated with the fact that measurements employed in spatial pattern extrapolation were confined in urban sites and subject to gradual reductions in NO_2 concentrations for the effective environmental agreements. This in turn overestimated declines of ambient NO_2 across China. Still, it should be recognized that major sources of NO_x emissions over China consisted of industry, electric power and transportation sectors, which were centralized in urban sites [*Tian et al.*, 2001]. As a result, the relatively short NO_2 chemical lifetime also proved the data presented here may reveal the actual changes. Considering the selection of representative samples and uncertainties of the kriging technique, we can still conclude that ambient NO_2 concentration throughout China has been raised gradually.

3.4. Uncertainty and Future Research Needs

[22] Two major sources of uncertainties led to the bias in the maps of N deposition: (1) uncertainty from status of measurement data and (2) uncertainty related to computation methods and interpolation procedure. Although some of them cannot be exactly quantified, uncertainty has been addressed as a key issue to present the current confidence level and to propose future perspectives.

[23] As we have seen, there still exist large uncertainties in the extrapolation of the nitrogen deposition pattern arising from the shortcoming of network measurements on national scale. To some extent, the incomplete and incontinuous measurements limit the comparability of deposition maps with the emissions and modeling results. Despite we made use of the yearly average values and adopted comparable species and time periods to weaken the uncertainties, we were not able to figure out the accurate magnitude of errors. The work presented here gave prominence to the establishment of well developed large-scale monitoring network. In the first place, with the focus of acid pollution research shifted from sulfuric to nitrous compounds, more nitrous species should be included in the range of measurements, especially those important to nitrogen deposition budgets, such as gaseous NH_3 and organic nitrogen. Secondly, a series of uniform monitoring methods should be set down and implemented in order to keep the measured data uniform and therefore comparable. Last but not least, the sampling sites should be located with principle of extensive even distribution, increasing the number of observatories in the west of China, and intensifying the monitoring of rural and remote areas.

[24] In addition, limited to the difficulties in data sharing, most concentration data we got are annual average values. The measurement sites with quarterly mean values are not sufficient to extrapolate concentration nationwide. However, it is quite important to demonstrate the seasonal variations of N deposition due to the large divergency of nitrous

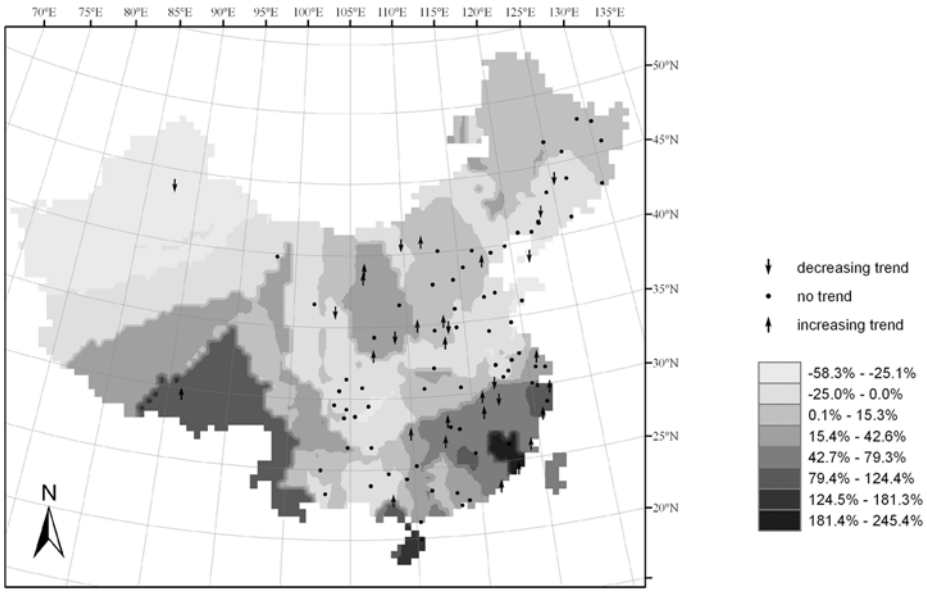

Figure 6. Distribution of NO_2 percent changes and trends at monitoring sites (arrows).

pollutants concentrations among seasons. In order to estimate the errors from spatial patterns without consideration of seasonal or monthly variation, the available quarterly measurements were compiled and the deviations between the concentrations of annual mean and those of seasonal means were calculated. For nitrate, the relative errors varied from 9.1% to 173% with a mean value of 70% when not considering the seasonal variation. While for ammonium, they varied from 9.1% to 222%, average to 67.8%. It can be concluded that the monthly or quarterly information on N deposition is more crucial than yearly one in demonstrating the current deposition status and evaluate the following effects of N deposition amendment. Future measurement work should focus on the fluctuations of monthly deposition fluxes, especially those on growing season of local plants.

[25] Interpolation uncertainty comes from the number and distribution of neighboring samples used to estimate the unknown values. Under given confidence levels, uncertainty associated with interpolation procedure can be quantified using the well-known Central Limit Theorem based on the interpolation variance, which is more reliable than kriging variance [*Yamamoto*, 1999]. We calculated the relative interpolation error with 95% confidence intervals for wet and dry deposition fluxes. For wet deposition, the interpolation uncertainties ranged from 8.84% in central and eastern China to 56% in western China, and from 2.75% to 12% with the same spatial trends for dry deposition. The large uncertainties in wet deposition may be caused by two facts: (1) Significant variations of concentration even in a small area made the estimation extremely variable, which can be improved by choosing optimal variogram models in smaller regions rather than throughout nation if sampling sites in such regions are enough for semivariance analysis and the calculation speed permits, and (2) lack of uniform measurement methods and consistent measurement period for wet deposition amplifies the discrepancy of values among neighboring sites.

4. Conclusions

[26] Our study has concluded that total N deposition rate in China in the past decade has increased significantly, with the greatest increase in central-south China. China's nitrogen deposition rate shows a higher mean value than those in the United States and Europe. The nitrogen budget in China implied that most of NO_x and NH_3 emitted were deposited in aqueous NO_3^-, NH_4^+ and gaseous NO_2 within China. The total wet and dry deposition accounted for 84.2% of the emissions. Transboundary effects within the neighboring countries were among the leading contributors to the imbalance between emissions and deposition. During the period 1990 to 2003, ambient air NO_2 concentrations were significantly enhanced in urban observatories as a result of anthropogenic influences. While dry deposition fluxes during 9 years throughout China were slightly raised on average, with an apparent increase centered in the southeast and southwest of China, declines were also marked in the northeast and parts of midland.

[27] A great number of studies on critical loads of nutrient nitrogen have indicated that most types of landscape except croplands are sensitive with critical loads of less than 40 kg N ha^{-1} yr^{-1}. This is especially true for coniferous forests, grasslands and deserts, which were more sensitive with critical loads of less than 20 kg N ha^{-1} yr^{-1} [*Duan et al.*, 2001, 2002; *Hao et al.*, 2003]. The average deposition rates in China suggest large areas are subject to the risk of nitrogen saturation, even acidification due to the considerable exceedance, if the emissions and deposition keep increasing by the current rates.

[28] This estimation of deposition patterns in China is the first to quantify the current status of nitrogen deposition with monitoring data on national scale. Interpolation from measurements in the field is among the most convincing way to explore nitrogen budget, even though the accuracy is limited by the characteristics of measured data and uncertainties associated with the interpolation technique. The establishment of an extensive long-range monitoring network over China is in urgent need for estimating nitrogen deposition fluxes and distribution, along with the evaluation of the impacts of nitrogen deposition on carbon cycling with anthropogenic influences. The measurement based maps are also required for comparison with three-dimensional transport models in the validation and calibration of models.

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C. Lü, Institute of Geographical Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China.

H. Tian, School of Forestry and Wildlife Sciences, Auburn University, Auburn, AL 36849, USA. (tianhan@auburn.edu)