

RESEARCH ARTICLE

A Review of Spatial Variation of Inorganic Nitrogen (N) Wet Deposition in China

Lei Liu¹, Xiuying Zhang^{1*}, Shanqian Wang¹, Xuehe Lu^{1,2}, Xiaoying Ouyang³

1 Jiangsu Provincial Key Laboratory of Geographic Information Science and Technology, International Institute for Earth System Science, Nanjing University, Nanjing, 210023, China, **2** Jiangsu Center for Collaborative Innovation in Geographical Information Resource Development and Application, Nanjing, 210023, China, **3** State Key Laboratory of Remote Sensing Science, Institute of Remote Sensing and Digital Earth, Chinese Academy of Sciences, Beijing, 100101, China

* lzhxy77@163.com



Abstract

Atmospheric nitrogen (N) deposition (N_{dep}), an important component of the global N cycle, has increased sharply in recent decades in China. Although there were already some studies on N_{dep} on a national scale, there were some gaps on the magnitude and the spatial patterns of N_{dep} . In this study, a national-scale N_{dep} pattern was constructed based on 139 published papers from 2003 to 2014 and the effects of precipitation (P), energy consumption (E) and N fertilizer use (F_N) on spatial patterns of N_{dep} were analyzed. The wet deposition flux of NH_4^+ -N, NO_3^- -N and total N_{dep} was 6.83, 5.35 and 12.18 $\text{kg ha}^{-1} \text{a}^{-1}$, respectively. N_{dep} exhibited a decreasing gradient from southeast to northwest of China. Through accuracy assessment of the spatial N_{dep} distribution and comparisons with other studies, the spatial N_{dep} distribution by Lu and Tian and this study both gained high accuracy. A strong exponential function was found between P and N_{dep} , F_N and N_{dep} and E and N_{dep} , and P and F_N had higher contribution than E on the spatial variation of N_{dep} . Fossil fuel combustion was the main contributor for NO_3^- -N (86.0%) and biomass burning contributed 5.4% on the deposition of NO_3^- -N. The ion of NH_4^+ was mainly from agricultural activities (85.9%) and fossil fuel combustion (6.0%). Overall, N_{dep} in China might be considerably affected by the high emissions of NO_x and NH_3 from fossil fuel combustion and agricultural activities.

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Introduction

Atmospheric nitrogen (N) deposition (N_{dep}) has dramatically increased in the past few decades owing to the rapid increases of industrialization, urbanization and intensified agricultural production in China [1–4]. Currently, the intensity of N_{dep} is equal or even exceeds that in Europe and America [5], causing general concerns of the governments and the public. Increased N_{dep} in terrestrial or aquatic ecosystems or both degrade human health [6], alter chemical components of soil and water [7], influence greenhouse gas balance [8] and reduce biological diversity [9]. Therefore, it is critical to estimate N_{dep} patterns for quantifying the effects of N amendment and establish control measures to improve environmental quality.

Some studies have reported the observed results of N_{dep} at a local scale in China [10–12]. These investigations mainly collected N deposition samples from different sampling sites in some local areas, determined the fluxes of N_{dep} , characterized the seasonal or annual variation, assessed the potential ecological risk and analyzed possible sources of N_{dep} [1, 13–19]. They have demonstrated that atmospheric N_{dep} in China increased rapidly over recent decades primarily due to increased energy consumption and N fertilizer use, and this increasing trend will continue in the future with the continuing development of China's economy. However, most of these studies did not give the magnitude and spatial pattern of N_{dep} throughout China due to the difficulty of obtaining the N fluxes on a large area of China [20–24].

There have been several studies on N_{dep} throughout China. For example, Lu and Tian [1] reported N_{dep} peaked over central south of China, with an average value of $12.89 \text{ kg ha}^{-1} \text{ a}^{-1}$ from site-network observations. Moreover, they [14] resulted in the N_{dep} was $14.05 \text{ kg ha}^{-1} \text{ a}^{-1}$ (on the assumption that wet N_{dep} contributes 70% of bulk deposition) in the recent decade, combining site-level monitoring and atmospheric transport model, and they resulted that the most rapid increase centered in southeastern China. Liu et al. [3] believed that N_{dep} increased to $21.1 \text{ kg ha}^{-1} \text{ a}^{-1}$, based on the atmospheric deposition monitoring network and the published papers, and they pointed out that the N_{dep} in the industrialized and agriculturally intensified regions of China as high as the peak levels in northwestern European in 1980s. Jia et al. [25] concluded that N_{dep} was $13.87 \text{ kg ha}^{-1} \text{ a}^{-1}$ in the 2000s, using the N fluxes at 41 stations, with an increasing rate of 25% than that in the 1990s and the highest N_{dep} occurred in southern China. Zhu et al. [4] demonstrated that N_{dep} was $13.18 \text{ kg ha}^{-1} \text{ a}^{-1}$, accounting for 73% of total N_{dep} and peaked in central and southern China.

From the above analysis, the magnitude of N_{dep} and the spatial distribution of N_{dep} were not consistent in the mentioned studies. Liu et al. [26] believed that Zhu et al. [4] might underestimate the dissolved inorganic nitrogen (DIN) due to the uncertainty resulting from the sampling, storage and analysis methods in their study [26]. Pan and Li [27] thought that Lu and Tian [14] underestimated N_{dep} based on a ratio of 0.7 and found the ratio was about 0.4 in Northern China [28]. Therefore, it is still an open question on the spatial pattern and magnitude of N_{dep} in China.

On the national scale of N_{dep} , the influencing factors on the spatial variations of N_{dep} were also studied. The spatial variations of N_{dep} had been greatly influenced by factors including N fertilizer use (F_N), energy consumption (E), and precipitation (P). Zhan et al. [29] hold that F_N , E, and P jointly explained 84.3% of the spatial pattern of N_{dep} , of which F_N (27.2%) was the most important, followed by E (24.8%) and P (9.3%). Zhu and He [4] found P and F_N can explain 80–91% of the spatial variation of N_{dep} , but E had little effect on this variation. Jia et al. [25] reported that F_N , E and P combined contributed 79% on the spatial variation of N_{dep} , while E contributed 80% of decadal variation followed by F_N , but P had little effect. These results obtained different opinions on the influences of F_N , E and P on the spatial variations of N_{dep} . The interrelationship between N_{dep} and these factors also should be further studied on a national scale.

The present study aims to (1) identify the magnitude and the spatial pattern of N_{dep} throughout China, (2) summarize how precipitation, N fertilizer use and energy consumption influencing spatial pattern of N_{dep} , quantify the correlation between factors and N_{dep} , and (3) determine the contributions of potential sources to the magnitude of N_{dep} in China.

Materials and Methods

The flowchart of this study is shown in Fig 1. Firstly, the N fluxes from the published papers throughout China were obtained, and then the Kriging interpolation technique is applied to

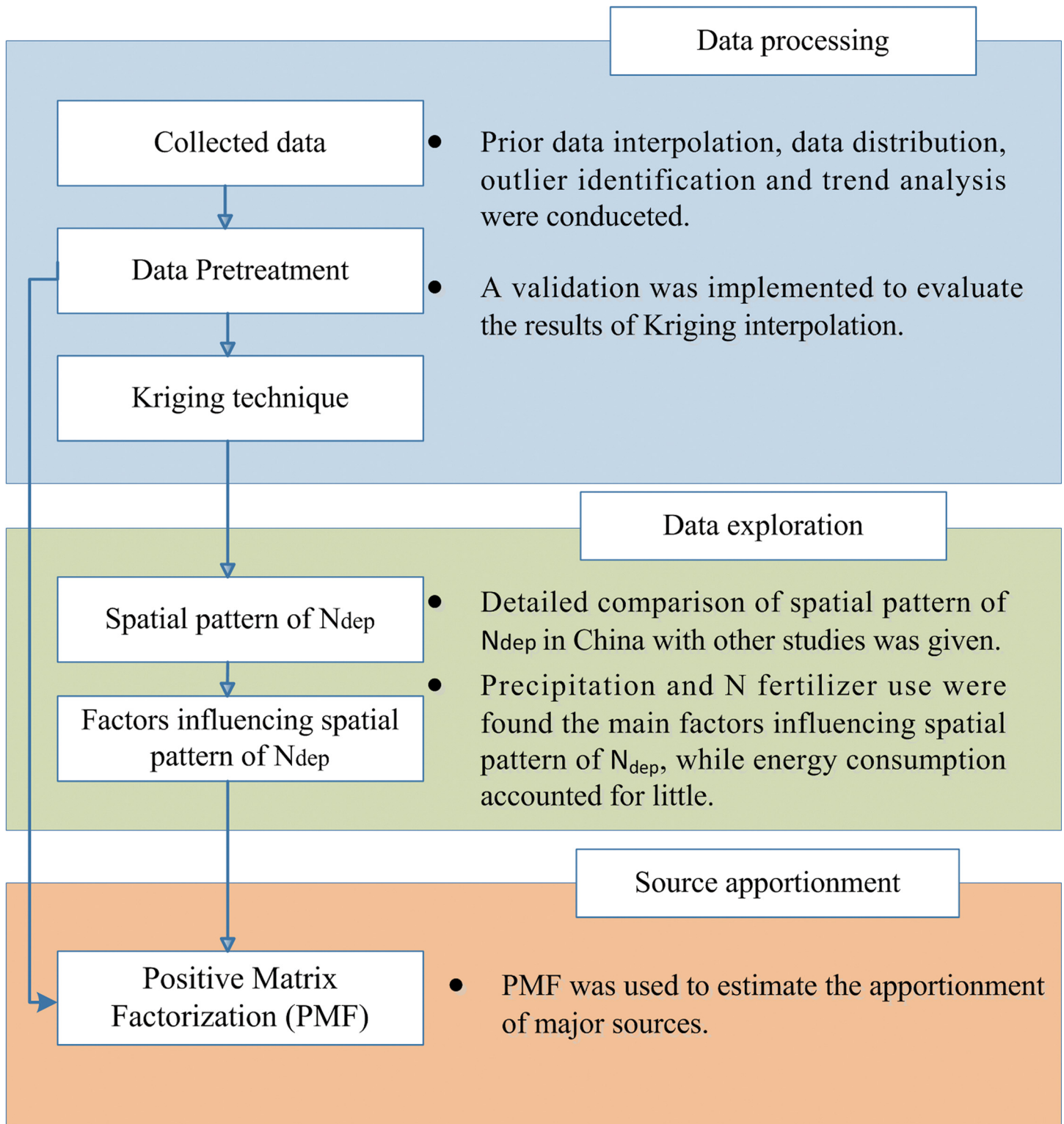


Fig 1. The flowchart of this study.

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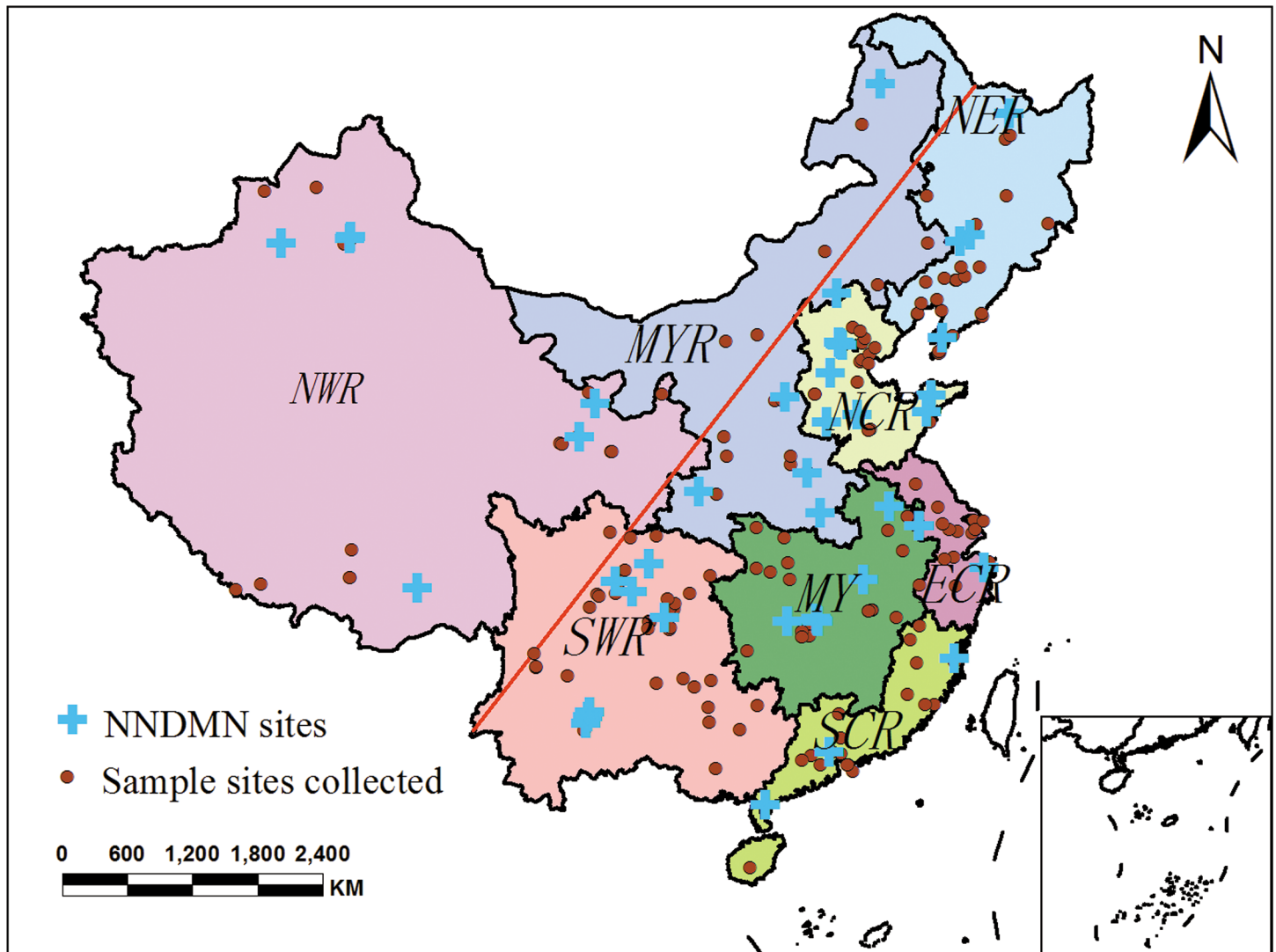


Fig 2. Spatial distribution of data points for N_{dep} in China (NER: Northeast region; NCR: North coastal region; ECR: East coastal region; SCR: South coastal region; MYR: Middle Yellow River; MY: Middle Yangtze; SWR: Southwest region; NWR: Northwest region). The red line divides China into a developed area (East) and an undeveloped area (West) in view of the levels of economic development, resource consumption, and population [5]. The NNDMN sites are from Nationwide Nitrogen Deposition Monitoring Network (NNDMN), organized by China Agricultural University [30].

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calculate N_{dep} on a national scale and compared the result with other N_{dep} maps in other studies. Then, the influence of P, F_N and E on the spatial pattern of N_{dep} is analyzed. Finally, potential sources of N_{dep} are evaluated.

Data collection

To evaluate N_{dep} throughout China, it is critical to systematically collect the relevant published papers. In this study, the data pairs on precipitation sampling in China during 2003–2014 were collected. These studies were located by making a search through ISI Web of Knowledge using keywords “nitrogen deposition”, “chemical composition” or “precipitation” and “China”, and through CNKI website using the same Chinese keywords. Finally, 139 peer reviewed articles consisting 225 data records (Fig 2) on NH_4^+ -N and NO_3^- -N in precipitation throughout China

were collected (S1 Table). Basic information included the name of the monitoring sites, location, land use, rainfall, monitoring time span, annual precipitation, concentration and depositions of NH_4^+ -N and NO_3^- -N and literature source from each study. To assure the monitoring quality of rainwater components, the studies based on the technical specifications required for acid deposition monitoring in China (State Environmental Protection Administration of China, 2004) were selected to establish datasets on N_{dep} .

The data on the amount of F_N and E on provincial scales could be obtained from the China Statistical Yearbook from 2003 to 2014 (<http://www.stats.gov.cn/tjsj/>). Due to the lack of energy data in Tibet province, we assumed that the per capita energy consumption was similar between the Tibet and Xinjiang provinces, which are both located in western China, and deduced data on energy consumption in Tibet province from the Xinjiang province data.

The data on the annual precipitation were obtained from China Meteorological Administration. The mean annual precipitation in provinces was calculated based on the annual precipitation from 2003 to 2014, respectively, from the weather stations in each province.

Calculation of wet N_{dep}

Wet inorganic N deposition is calculated as the product of the precipitation amount and the concentration of N species in precipitation. The wet N deposition flux was kg N ha^{-1} and the unit of the precipitation is mm. The units of the concentration of N species in precipitation include mg N L^{-1} [30] and $\mu\text{eq L}^{-1}$ [31]. Both of the two units are commonly used. Thus, when the unit of the concentration of N species is mg N L^{-1} , the calculation formula of nitrogen deposition is:

$$N_{\text{dep}} = \frac{C_i \times P_i}{100} \quad (1)$$

where N_{dep} is the N deposition flux per year ($\text{kg ha}^{-1} \text{a}^{-1}$); C_i is the concentration of NH_4^+ -N or NO_3^- -N (mg N L^{-1}); P_i is the annual precipitation (mm); 100 is the conversion factor.

Otherwise, the formula is:

$$N_{\text{dep}} = \frac{C_i \times P_i * 14}{10^5} \quad (2)$$

where N_{dep} is the N deposition flux per year ($\text{kg ha}^{-1} \text{a}^{-1}$); C_i is the concentration of NH_4^+ -N or NO_3^- -N ($\mu\text{eq L}^{-1}$); P_i is the annual precipitation (mm); 14 is the atomic weight of N and 10^5 is the conversion factor.

Geo-statistical method

A geostatistical method was used to produce spatially continuous estimates from discrete data points. National-scale N_{dep} maps were constructed using the Kriging interpolation technique. An unknown value associated with a point can be estimated by Kriging as follows:

$$Z(x_0) = \sum_{i=1}^n \lambda_i Z(x_i) \quad (3)$$

where λ_i is the Kriging weights computed from a normal system of equations using a semivariance function, derived by minimization of the error variance; the unknown value $Z(x_0)$ is interpreted as a random variable located in x_0 , as well as the values of neighbor samples $Z(x_i)$, $i = 1, \dots, N$.

Prior to Kriging interpolation, the Explore Data tool of ArcGIS 10.0 software is applied to conduct a data analysis, including data's distributing, outlier identification, and trend analysis; the optimal variogram model and parameters are determined by GS plus.

Source apportionment of ionic species

Positive matrix factorization (PMF) developed by the U.S. Environmental Protection Agency (EPA) is a multivariate factor analysis that utilizes error estimates and produces non-negative results [32]. PMF is used to factorize a given dataset into two matrices, the source profile (F) and source contribution (G), also called factors, which is expressed by the following formula:

$$x_{ij} = \sum_{k=1}^p g_{ik}f_{kj} + e_{ij} \quad i = 1, \dots, m; j = 1, \dots, n; k = 1, \dots, p \quad (4)$$

where x_{ij} is the elements of the input data matrix, g_{ik} and f_{kj} are the elements of the factor scores and factor loading matrices, respectively; e_{ij} is the residuals (i.e. the difference between input data and predicted values) and p is the number of factors resolved [33]. The resolving algorithm computes G and F elements that minimize the so-called object function Q.

$$Q = \sum_{i=1}^m \sum_{j=1}^n \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik}f_{kj}}{S_{ij}} \right]^2 \quad (5)$$

where S_{ij} represents the elements of uncertainty matrix, and each element is the uncertainty of j th species for sample i .

Results and Discussions

Accuracy assessment of the spatial N_{dep} distribution and comparisons with other studies

Although there were several studies on the estimation of wet N_{dep} on a national scale in China, most of them showed different spatial patterns. Which map of N_{dep} could reflect the real spatial distribution of N_{dep} in China is still a question.

At a point scale, the 41 sites of N_{dep} in Zhu [4] were used to estimate the accuracy of the spatial distribution of N_{dep} by the method of Kriging. The Q-Q plot of the distribution of site-monitored N_{dep} versus that of the interpolated N_{dep} in this study is shown in Fig 3. The interpolated N_{dep} were distributed around the 1:1 line. The regression model between the original and interpolated N_{dep} had the regression coefficient (0.96) closer to 1 and a high R^2 value. This indicated that there were close distributions between interpolated N_{dep} values and true N_{dep} values for the 41 testing data. The Q-Q plot of the N_{dep} from Zhu et al. [4] and Lu and Tian [14] versus the 41 testing data were also described in Fig 3. The N_{dep} by Lu and Tian [14] also obtained high accuracy, with low RMSE and high R^2 values.

On a provincial scale, comparison of the results of N_{dep} ($\text{kg ha}^{-1} \text{a}^{-1}$) in this study with those by Jia et al. [25] and Lu and Tian [14] is shown in Fig 4. Good agreements were also found for

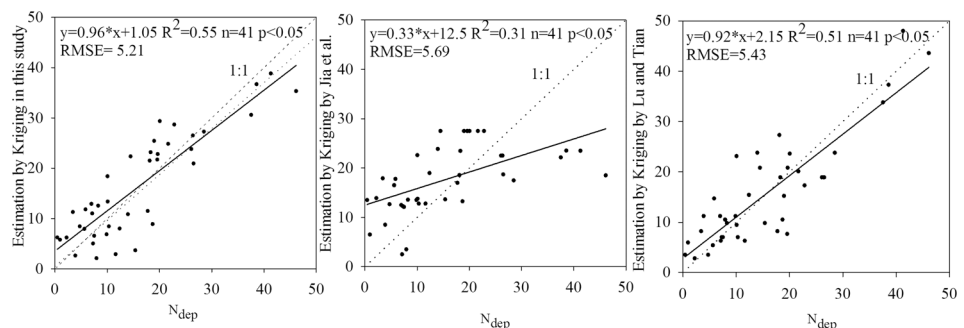


Fig 3. Comparison of N_{dep} ($\text{kg ha}^{-1} \text{a}^{-1}$) monitored in 41 sites with the estimation results in this study, by Jia et al. [25] and Lu and Tian [14] (x-axis was the testing data in the work by Zhu et al. [4], y-axis was the results estimated in this study (a), by Jia et al. [25] (b), Lu and Tian [14] (c)). Note: a regression coefficient closer to 1.00, a higher R^2 value indicate more reliable results of interpolation.

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the comparison of N_{dep} with the results by Lu and Tian [14], giving confidence in the analysis of spatial pattern of N_{dep} in China. This also confirmed that our results were more consistent with that by Lu and Tian [14] than that by Jia et al. [25].

On a national scale, to further explore the accuracy assessment of the spatial N_{dep} distribution, we compared our results with that by Lu and Tian [14] using the data of provided 74 monitored sites by Du and Liu [34] (Fig 5). There were four hotspots on the N_{dep} map in this study, namely the North China Plain or Jing-jin-ji region, the Yangtze River Delta, Sichuan Basin and the Pearl River Delta. We suspected that Lu and Tian had underestimated slightly in Jing-jin-ji region, which should have the considerable magnitude of N_{dep} with three other hotspots (Fig 5). However, Du and Liu [34] could not determine the magnitude of N_{dep} in Middle Yangtze region including Anhui province and in the south of Middle Yellow region including Henan province due to no data monitored. The work by Lu and Tian [14] reported this region also had high N_{dep} and we confirmed this hotspot in our study.

It should be noticed that this study might overestimate the N_{dep} on a national scale, since most of the monitoring sites used in these published papers in China were distributed in developed areas, which would overestimate N_{dep} on a national scale [5]. Also, there are some uncertainties in the estimation of N_{dep} in China, which resulted from different concepts, sampling procedures, analysis methods and scaling-up methods. The effects of scaling-up method on national scale results require further study and the observation network for N_{dep} needs to be strengthened to decrease the uncertainty.

Spatial pattern of N_{dep} in China

The average of wet deposition flux of $\text{NH}_4^+ \text{-N}$ was $6.83 \text{ kg ha}^{-1} \text{ a}^{-1}$ with a standard deviation (STDEV) of 5.15, while the $\text{NO}_3^- \text{-N}$ was $5.35 \text{ kg ha}^{-1} \text{ a}^{-1}$ with a STDEV of 5.71. The average of ratio of $\text{NH}_4^+ \text{-N}/\text{NO}_3^- \text{-N}$ was 1.28, which was slightly higher than the averaged ratio (1.22) in China, concluded by Zhu et al. [4]. The ratio of $\text{NH}_4^+ \text{-N}/\text{NO}_3^- \text{-N}$ was widely considered a proxy for the sources of atmospheric reactive N [4, 35, 36]. Agricultural activity is the main source of N_{dep} if the ratio is higher than 1, whereas, industrial activity is the main source if this ratio is lower than 1. The ratio of $\text{NH}_4^+ \text{-N}/\text{NO}_3^- \text{-N}$ in this study indicated both the agricultural and industrial activities collectively influence the deposition of atmosphere N.

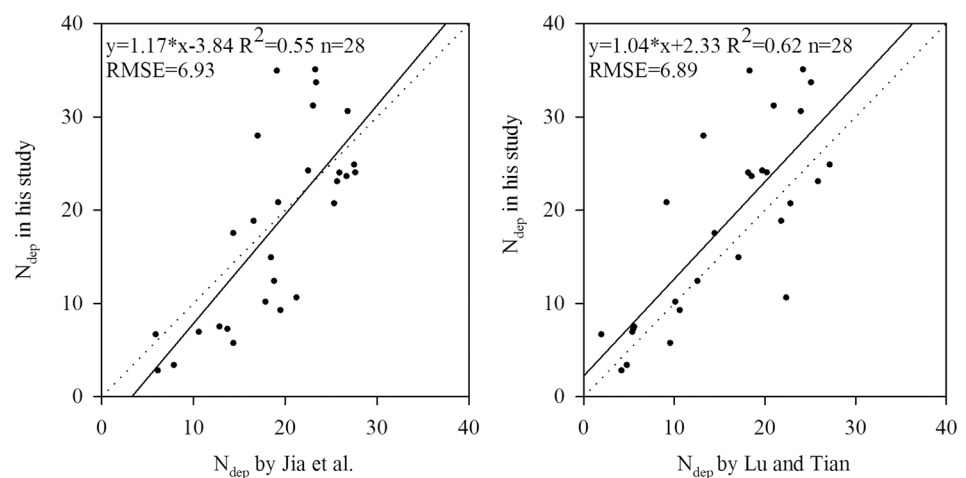


Fig 4. Comparison of N_{dep} ($\text{kg ha}^{-1} \text{ a}^{-1}$) with the results by Jia et al. [25] and Lu and Tian [14] at a provincial scale. Note: a regression coefficient closer to 1.00, higher R^2 and small RMSE values indicate more reliable results of interpolation.

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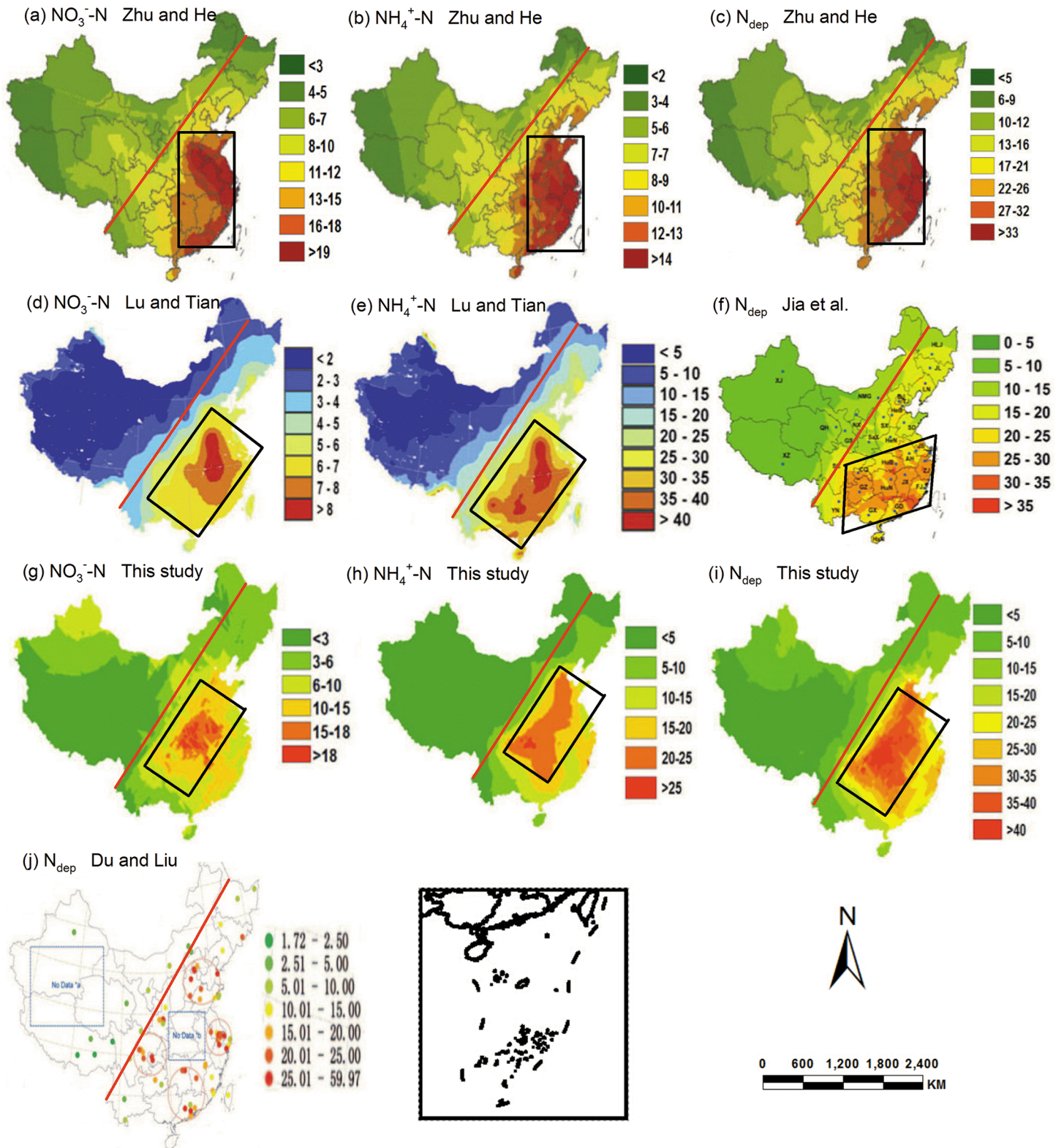


Fig 5. Spatial pattern of N_{dep} ($\text{kg ha}^{-1} \text{a}^{-1}$) in China. Spatial distribution maps of N_{dep} between 2003 and 2014 were obtained from 182 monitoring sites by Kriging interpolation (g, NO_3^- -N; h, NH_4^+ -N; i, total inorganic N) in this study, from 144 monitoring sites (f, total inorganic N) between 2000 to 2010 by Jia and Yu [25], from 41 sites (a, NO_3^- -N; b, NH_4^+ -N; c, total inorganic N) in 2013 by Zhu and He [4], from 74 sites (j, total inorganic N) between 1995 and 2007 by Du and Liu [34], combining field measurements and monitoring estimating between 2000 to 2008 (d, NO_y -N; e, NH_x -N) by Lu and Tian [14]. The red line divides

China into a developed area (East) and an undeveloped area (West) in view of the levels of economic development, resource consumption, and population [5].

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The N_{dep} was $12.18 \text{ kg ha}^{-1} \text{ a}^{-1}$ and the total N deposition in China would be $20.30 \text{ kg ha}^{-1} \text{ a}^{-1}$ assuming that the contribution of dry deposition was about 40% in China [4, 37]. The magnitude and spatial pattern of N_{dep} differed significantly in different regions in China (Fig 5I). Both NH_4^+ -N and NO_3^- -N peaked in central southern and southeastern China which are characterized by rapid industrial development and intensive N fertilizer applications [14]. N_{dep} exhibited a decreasing gradient from the southeast to the northwest of China. The red line (Fig 5) indicated the significant heterogeneity in the levels of economic development for different regions, which resulted in a matching spatial heterogeneity in N_{dep} across China. Similar results were also found in the study by Jia and Liu [3, 25]. The low N_{dep} were in areas including Qinghai-Tibet Plateau, Inner Mongolia and northwest China, where had not well developed industrial activities [5].

High N_{dep} occurred across the south of Middle Yellow region, the North Coastal region and the middle and lower reaches of Yangtze River Basin (Fig 5G, 5H and 5I), which was in good agreement with the results by Lu and Tian (Fig 5D and 5E), but much different with that by Jia et al. (Fig 5F) [14, 25]. Jia et al. [32] did not found the hotspots of N_{dep} in the south of Middle Yellow region including Henan and Shaanxi provinces and in the North Coastal region including Beijing, Tianjin, Hebei and Shandong provinces. Du and Liu [34] also concluded high N_{dep} in the North Coastal region including Beijing, Tianjin, Hebei and Shandong provinces (Fig 5I) [34] in good agreement with our findings. Jia et al. [25] maybe have underestimated N_{dep} in the North Coastal region due to the uncertainty resulting from the limited number of data and analysis method in this area. Liu et al. [26] believed that Zhu et al. [4] (Fig 5A, 5B and 5C) might underestimate the dissolved N deposition throughout China due to the uncertainty from limited number of samples (41 sites), and the storage in their studies [26]. This study also confirmed that Zhu et al. underestimated N_{dep} in the Southwest region including Chongqing and Guizhou provinces and the results by Du and Liu, Lu and Tian confirmed this suspect.

In summary, there were five hotspots of N_{dep} in China, including the North Coastal region, East Coastal region, Southwest region and South Coastal region, and Middle Yangtze. N_{dep} exhibited a decreasing gradient from southern to western and to northern China. N_{dep} was $> 35 \text{ kg ha}^{-1} \text{ a}^{-1}$ in some provinces of southern China, such as Chongqing, Hunan, Hubei and Henan, whereas N_{dep} in other provinces of southern China was about $20\text{--}35 \text{ kg ha}^{-1} \text{ a}^{-1}$. N_{dep} over northern, northeastern and northwestern China was about $10\text{--}20$, $5\text{--}15$, $0\text{--}10 \text{ kg ha}^{-1} \text{ a}^{-1}$.

The N_{dep} on a national scale ranged from 9.88 to $21.1 \text{ kg ha}^{-1} \text{ a}^{-1}$ (Table 1), showing strong spatial variations. The wet deposition flux of N_{dep} ($12.18 \text{ kg ha}^{-1} \text{ a}^{-1}$) in this study was much lower

Table 1. Atmospheric N deposition ($\text{kg ha}^{-1} \text{ a}^{-1}$) on the bias of different methods and temporal scales.

Estimation technique	Year	NH_4^+ -N	NO_3^- -N	N_{dep}	Reference
Summarized previous results	2000–2010	-	-	21.1 ^b	[3]
Data collection	2000–2010	-	-	13.87	[25]
Combining measurements and estimating	2000–2008	-	-	14.05 ^a	[14]
Measurements	2013	7.25	5.93	13.18	[4]
Measurements	1995–2007	10.66 ^b	6.57 ^b	17.36 ^b	[34]
Measurements	1990–2003	-	-	9.88	[1]
Summarized previous results	2003–2014	6.83	5.35	12.18	This study

^aGiven the ratio of wet to bulk N deposition (20.07) as 0.7, the wet N deposition was 14.05.

^bThe averaged value ignoring difference between regions.

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Table 2. Comparison of different models used to simulate P, F_N and E influencing spatial patterns of N_{dep}

N _{dep} and P, F _N and E	N _{dep} and P	N _{dep} and F _N	N _{dep} and E	Reference
$N_{dep} = a \cdot \ln((F_N \cdot 18.5\% + E \cdot 0.24\%) \cdot P) + b$	$y = a \cdot P + b$	$y = a + b \cdot \ln(F_N)$	$y = a + b \cdot \ln(E)$	[25]
$N_{dep} = a + b \cdot F_N + c \cdot P$	$y = a \cdot P^b$	$y = a \cdot F_N + b$	$y = a \cdot E^b$	[4]
-	$y = a \cdot P + b$	$y = a + b \cdot \ln(F_N)$	$y = a + b \cdot \ln(E)$	[38]
$N_{dep} = a + b \cdot F_N^c + d \cdot P^e$	$y = a \cdot P^b$	$y = a \cdot F_N^b$	$y = a \cdot E^b$	This study

a, b, c, d, e are regression coefficients; N_{dep} represents N deposition; P represents precipitation (mm); F_N represents fertilizer N use (t km⁻² a⁻¹); E represents energy consumption (t km⁻² a⁻¹).

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than that (21.07 kg ha⁻¹ a⁻¹) based on the average of those data points to represent N_{dep} status across the whole China [3]. It was a bit higher than that (9.88 kg ha⁻¹ a⁻¹) by Lu and Tian (2007) calculated from at 253 sites from 1990 to 2003, and it was close to the results by Jia et al. (13.87 kg ha⁻¹ a⁻¹), Lu and Tian (14.05 kg ha⁻¹ a⁻¹) and Zhu (13.18 kg ha⁻¹ a⁻¹). These similar studies all considered spatial variability and area-weighted contribution from high- and low-N deposited regions, which was critically important to generate estimation of N_{dep} on a national scale [6, 14].

Influencing factors of Precipitation (P), N fertilizer use (F_N) and energy consumption (E) on the spatial patterns of N_{dep}

The process of N_{dep} is relatively clear in theory and has been applied in models, however, no agreement was reached upon how P, F_N and E influenced N_{dep}. It is critical to understand the relationship between N_{dep} and P, F_N and E, to simulate and predict future trends in N_{dep} assuming that the existing emission factors for F_N and E don't change much.

Several models have been developed to simulate the correlation of N_{dep} and P, F_N, E (Table 2). Jia et al. found that N_{dep} was linearly related to P and logarithmically to F_N and E [25]. They believed that E, F_N and P should be considered together when studying the factors that control the spatial pattern of N_{dep} on the regional scale. N_{dep} was calculated using equation $N_{dep} = a \cdot \ln((F_N \cdot 18.5\% + E \cdot 0.24\%) \cdot P) + b$. However, Zhu and He reported N_{dep} was exponentially related to P and E and linearly related to F_N [4]. They thought that P and F_N explain 80%-91% of the spatial variation of N_{dep}, whereas E did not significantly explain the variability. A multiple linear regression model ($N_{dep} = a + b \cdot F_N + c \cdot P$) was applied without E by Zhu and He.

In this study, a strong exponential correlation was found between P and N_{dep}, F_N and N_{dep}, E and N_{dep} (Fig 6), which was in good agreement with that conducted by Zhu and He [4]. The models by Jia et al. (Fig 7A) and Zhu and He (Fig 7B) were applied to predict N_{dep} in China in

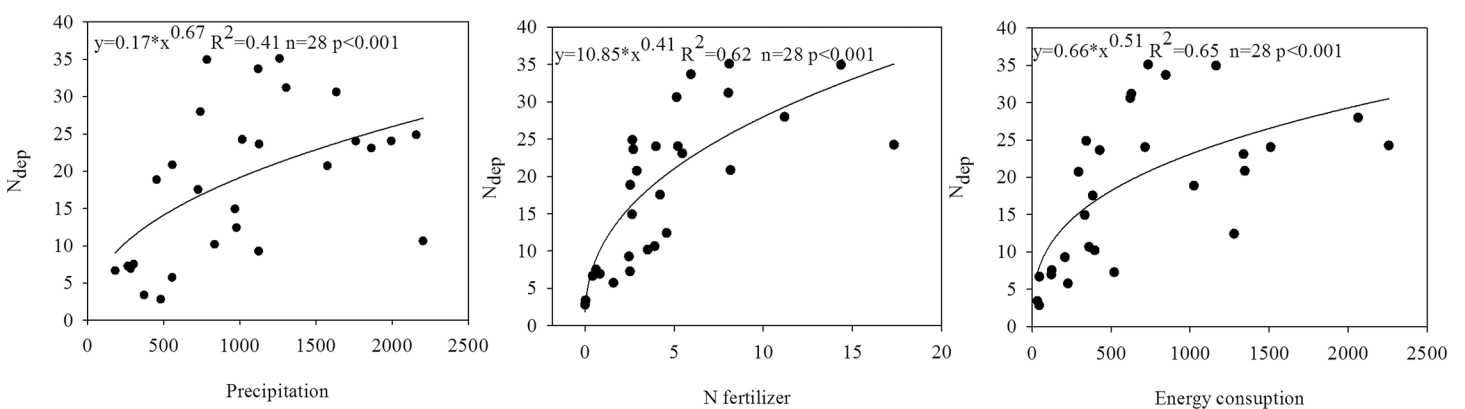


Fig 6. The effects of precipitation (mm), N fertilizer (t km⁻² a⁻¹) and energy consumption (t km⁻² a⁻¹) on the spatial pattern of N_{dep} (kg ha⁻¹ a⁻¹). The mean N_{dep} (kg ha⁻¹ a⁻¹) in provinces were obtained from spatial maps of N_{dep} (kg ha⁻¹ a⁻¹) in China using Kriging.

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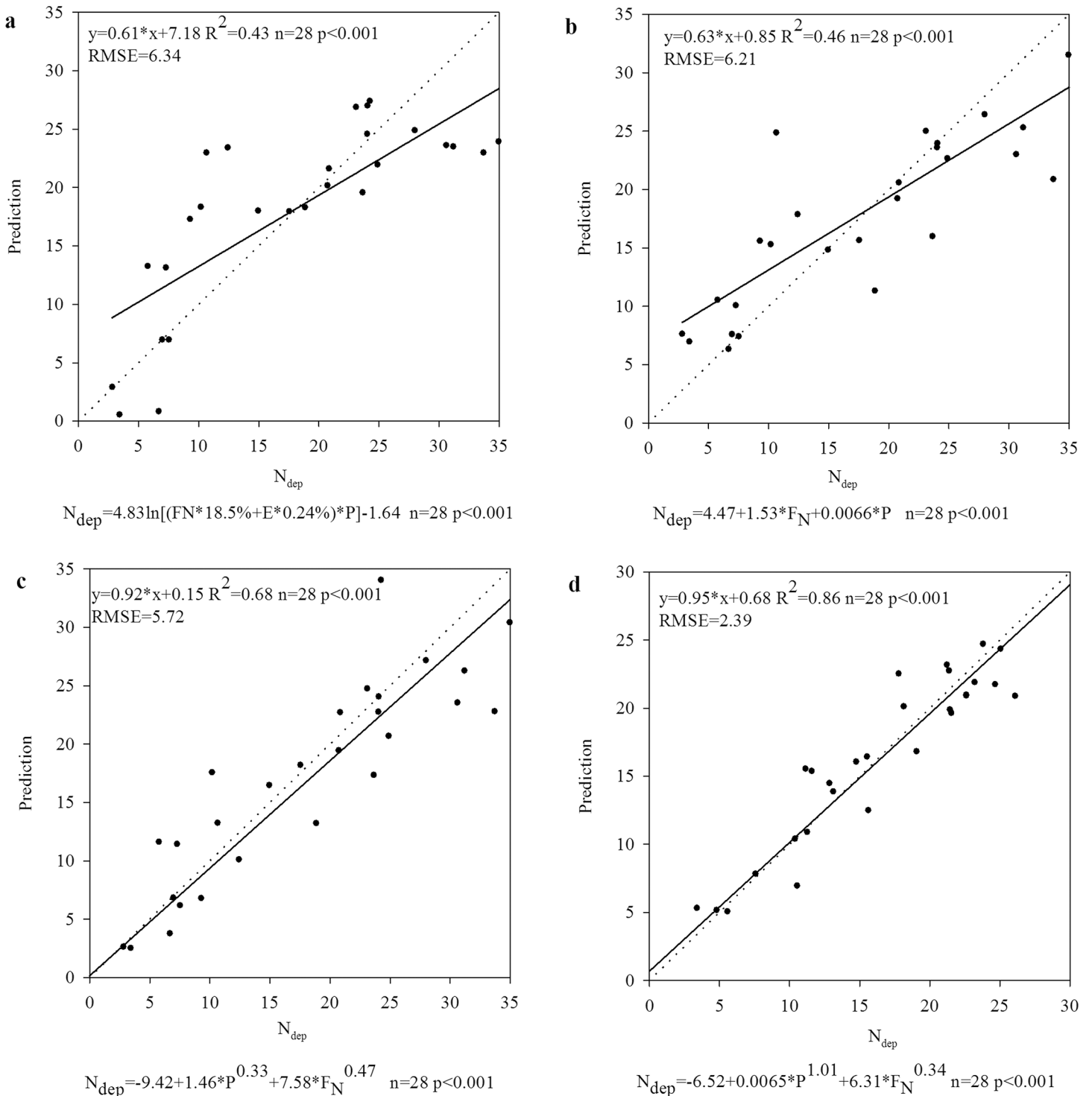


Fig 7. Test of equations using data from 2003 to 2014. The x-axis variable (this study: a, b, c; Jia et al. [25]: d) was the modeled results of N_{dep} ($kg\ ha^{-1}\ a^{-1}$) in provinces as obtained by Kriging method and data on precipitation (mm), N fertilizer ($t\ km^{-2}\ a^{-1}$) and energy consumption ($t\ km^{-2}\ a^{-1}$) in provinces excluding Beijing, Shanghai and Tianjin. The y-axis variable was calculated by different prediction model equations (Jia et al. [25] (a): $N_{dep} = a*\ln((F_N*18.5\%+E*0.24\%)*P)+b$; Zhu and He [4] (b): $N_{dep} = a+b*F_N+c*P$; this study (c, d): $N_{dep} = a+b*F_N^c+d*P^e$). **Note:** a regression coefficient closer to 1.00 and higher R^2 and small RMSE values indicate more reliable results. The regression coefficient reached approximately 0.92 and R^2 were about 0.58 in this study.

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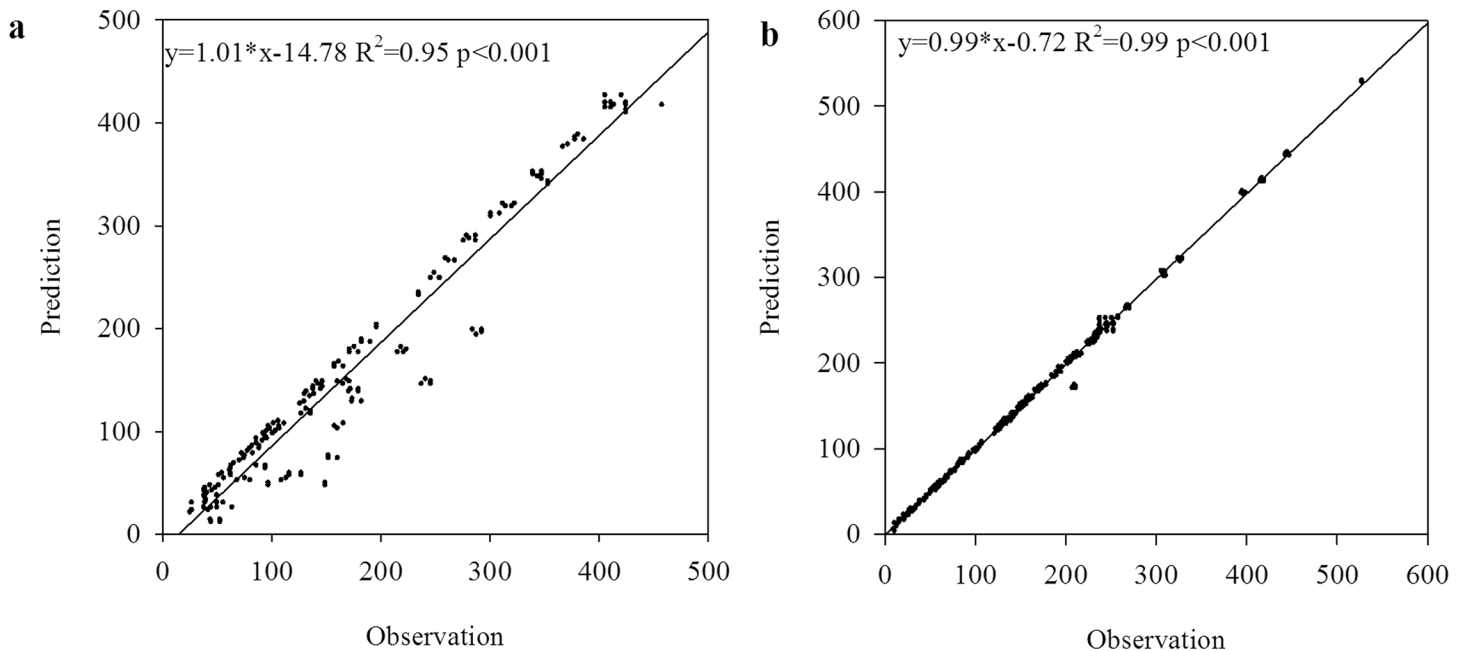


Fig 8. Comparison of PMF predictions with observations for NO_3^- (a) and NH_4^+ (b) concentrations (μeqL^{-1}) in the wet deposition samples from 2003 to 2014 in China.

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this study. To improve this estimation of N_{dep} , we established a new model to simulate this correlation based on a strong exponential correlation found (Fig 6). We agreed that E had little effect on the spatial pattern of N_{dep} proposed by Zhu and He [4] through our practice in this study. Thus, we adopted an equation ($N_{\text{dep}} = a + b * F_N^c + d * P^e$) to predict N_{dep} and found a higher R^2 (Fig 7C) compared with the results by Jia et al. (Fig 7A) and Zhu and He (Fig 7B). To confirm the effective of this new model, we used the data published by Jia et al. [25] to test whether this equation can reflect the spatial variation of N_{dep} in China in 2000s and good agreement was found for the comparison of N_{dep} with prediction (Fig 7D).

It should be noted that we agree with E contributing much to the magnitude of decadal N_{dep} in China [25], but had little effect on the spatial variation of N_{dep} [4]. In summary, P, F_N and E were all significantly correlated with the magnitude of N_{dep} , P and F_N contributed more than E to the spatial variation of N_{dep} . It was critically essential to reduce E and F_N to control reactive N emissions from fossil fuel combustion using maximum fessible reduction [4, 22].

Ceratianly, we had to admit that there were some uncertainties in the analysis of how P, F_N and E influencing the spatial patterns of N_{dep} , which resulted from the limited statistical data obtained. The constructed analytical relationship was based on a provincial statistical data, and we believe that more data, such as municipal or county-level data, will obtain more reliable statistical models. However, it was too difficult to obtain such municipal or county-level data on both F_N and E from the statistical yearbooks in China. The data on energy consumption (expressed as standard coal) on a municipal or county-level scale were not included in municipal or county-level statistical yearbook and only the total energy consumption on a provincial scale could be obtained. Thus, we have to use the provincial statistical data to explore the correlation.

Anthropogenic sources of N_{dep} in China

Detailed source contributions data are critical for policy makers to develop effective policies to protect Chinese terrestrial ecosystems [3]. Fossil fuel combustion and agricultural activities

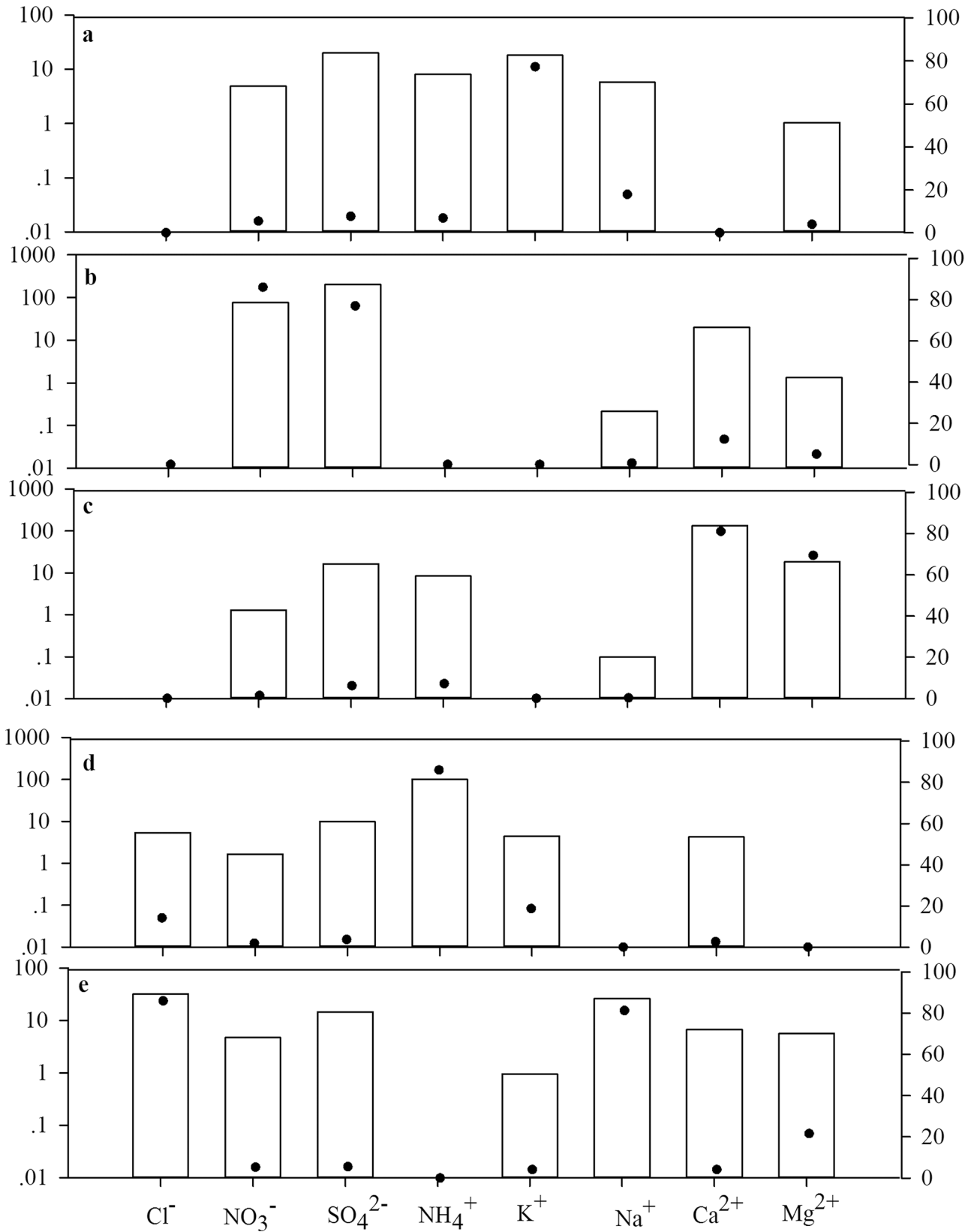


Fig 9. Predicted source profiles of PMF for wet deposition data collected in China. The bars indicate source profiles (left y-axis), and the filled dots indicate percentage of species (right y-axis) attributed to that source. (Biomass burning (a), Fossil fuel combustion (b), Crust (c), Agriculture (d), Aged sea salt (e)).

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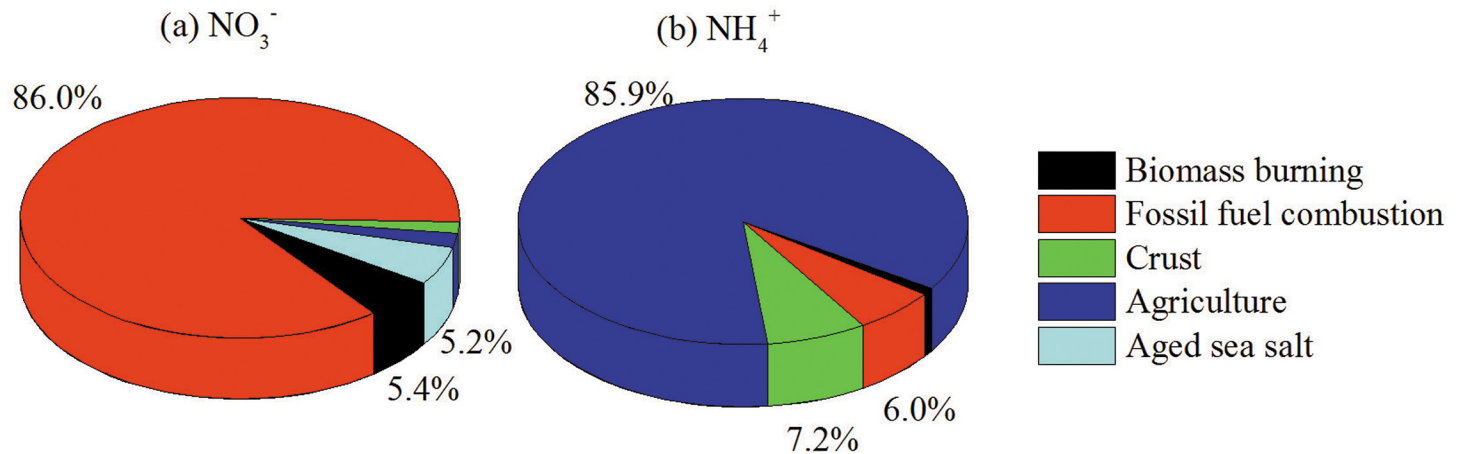


Fig 10. Percentage contributions of aged sea salt, crust, agriculture, fossil fuel combustion, and biomass burning to annual wet deposition flux of NH₄⁺-N, NO₃⁻-N in China between 2003 and 2014.

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were likely the main anthropogenic sources for NH₄⁺-N and NO₃⁻-N depositions, but their relative contributions in China cannot be determined in previous studies. In this study, a PMF source apportionment analysis was used to further explore the main source of N_{dep}. Fig 8 shows a comparison of the observed and PMF predicted concentration of NO₃⁻ and NH₄⁺ for each sample. Excellent agreement was found, giving confidence that the PMF model captured the major sources and correctly quantified their contributions.

The PMF model resolved five distinct sources (Fig 9). The first source had high K⁺, indicating a biomass burning (Fig 9A). The second source was enriched with SO₄²⁻ and NO₃⁻ (Fig 9B), indicating a fossil fuel combustion source. The two icons were associated with NO_x emitted from coal-fired power plants, residential heating and cooking, and motor vehicles [39]. The third source had a high loading of Ca²⁺ and Mg²⁺, representing a crustal or windblown dust source (Fig 9C). The profile also contained a significant SO₄²⁻ indicating a great effect of neutralizing the acid [39]. The fourth source was dominated by NH₄⁺ suggesting an agricultural source (Fig 9D). The fifth source had high loading of Na⁺ and Cl⁻, a clear signal of sea salt impact (Fig 9E). However, the profile also contained a significant SO₄²⁻, a typical characteristic of aged sea salt.

The percentage contributions of each source to NH₄⁺-N and NO₃⁻-N are shown in Fig 10. Fossil fuel combustion was the main contributor to NO₃⁻-N (86.0%). Biomass burning also contributed to 5.4% on the deposition of NO₃⁻-N. NH₄⁺-N was mainly from agricultural activities (85.9%), fossil fuel combustion (6.0%) and Crust (7.2%). Overall, N_{dep} in China may be considerably affected by the high emissions of NO_x and NH₃ from fossil fuel combustion and agricultural activities and relevant studies will be presented in future papers.

Conclusion

The N_{dep} throughout China was obtained by a method of Kriging, based on the N fluxes from the published papers from 2003 to 2014. The N_{dep} map in our study showed close spatial pattern with that by Lu and Tian (2014). There were five hotspots of N_{dep} across the North Coastal

region, East Coastal region, Southwest region and South Coastal region, and Middle Yangtze, and exhibited a decreasing gradient from southeast to northwest of China. The wet deposition flux of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and total N_{dep} was 6.83, 5.35 and 12.18 $\text{kg ha}^{-1} \text{a}^{-1}$, respectively. A strong exponential correlation was found between P and N_{dep} , F_{N} and N_{dep} and E and N_{dep} , P and F_{N} (80–91%) contributed more than E to the spatial variation of N_{dep} . Fossil fuel combustion was the main contributor to $\text{NO}_3^-\text{-N}$ (86.0%) and biomass burning also contributed to 5.4% on the deposition of $\text{NO}_3^-\text{-N}$. $\text{NH}_4^+\text{-N}$ was mainly from agriculture (85.9%), fossil fuel combustion (6.0%). Our findings confirmed that the anthropogenic activities were the main reason for N_{dep} increase and provided a scientific background for studies on ecological effects of N_{dep} in China.

Supporting Information

S1 PRISMA Checklist. The PRISMA 2009 Checklist
(DOC)

S1 Table. The information of the collected data records in this study.
(XLSX)

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Author Contributions

Conceived and designed the experiments: LL XZ. Performed the experiments: LL SW. Analyzed the data: LL XL SW. Contributed reagents/materials/analysis tools: LL SW. Wrote the paper: LL XZ XO.

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