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 kg ha^{-1} 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.

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<sub>dep</sub> 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<sub>dep</sub>, characterized the seasonal or annual variation, assessed the potential ecological risk and analyzed possible sources of N<sub>dep</sub> [1, 13–19]. They have demonstrated that atmospheric N<sub>dep</sub> 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<sub>dep</sub> in 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<sub>dep</sub> throughout China. For example, Lu and Tian [1] reported N<sub>dep</sub> peaked over central south of China, with an average value of 12.89 kg ha<sup>−1</sup> a<sup>−1</sup> from site-network observations. Moreover, they [14] resulted in the N<sub>dep</sub> was 14.05 kg ha<sup>−1</sup> a<sup>−1</sup> (on the assumption that wet N<sub>dep</sub> 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<sub>dep</sub> increased to 21.1 kg ha<sup>−1</sup> a<sup>−1</sup>, based on the atmospheric deposition monitoring network and the published papers, and they pointed out that the N<sub>dep</sub> in the industrialized and agriculturally intensified regions of China as high as the peak levels in northwestern Europe in 1980s. Jia et al. [25] concluded that N<sub>dep</sub> was 13.87 kg ha<sup>−1</sup> a<sup>−1</sup> 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<sub>dep</sub> occurred in southern China. Zhu et al. [4] demonstrated that N<sub>dep</sub> was 13.18 kg ha<sup>−1</sup> a<sup>−1</sup>, accounting for 73% of total N<sub>dep</sub> and peaked in central and southern China.

From the above analysis, the magnitude of N<sub>dep</sub> and the spatial distribution of N<sub>dep</sub> 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<sub>dep</sub> 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<sub>dep</sub> in China.

On the national scale of N<sub>dep</sub>, the influencing factors on the spatial variations of N<sub>dep</sub> were also studied. The spatial variations of N<sub>dep</sub> had been greatly influenced by factors including N fertilizer use (F<sub>N</sub>), energy consumption (E), and precipitation (P). Zhan et al. [29] hold that F<sub>N</sub>, E, and P jointly explained 84.3% of the spatial pattern of N<sub>dep</sub>, of which F<sub>N</sub> (27.2%) was the most important, followed by E (24.8%) and P (9.3%). Zhu and He [4] found P and F<sub>N</sub> can explain 80–91% of the spatial variation of N<sub>dep</sub>, but E had little effect on this variation. Jia et al. [25] reported that F<sub>N</sub>, E and P combined contributed 79% on the spatial variation of N<sub>dep</sub>, while E contributed 80% of decadal variation followed by F<sub>N</sub>, but P had little effect. These results obtained different opinions on the influences of F<sub>N</sub>, E and P on the spatial variations of N<sub>dep</sub>. The interrelationship between N<sub>dep</sub> 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<sub>dep</sub> throughout China, (2) summarize how precipitation, N fertilizer use and energy consumption influencing spatial pattern of N<sub>dep</sub>, quantify the correlation between factors and N<sub>dep</sub> and (3) determine the contributions of potential sources to the magnitude of N<sub>dep</sub> 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.

doi:10.1371/journal.pone.0146051.g001

Data processing

- Prior data interpolation, data distribution, outlier identification and trend analysis were conducted.
- A validation was implemented to evaluate the results of Kriging interpolation.

Data exploration

- Detailed comparison of spatial pattern of N_{dep} in China with other studies was given.
- Precipitation and N fertilizer use were found the main factors influencing spatial pattern of N_{dep}, while energy consumption accounted for little.

Source apportionment

- PMF was used to estimate the apportionment of major sources.
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 deposition of NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{3}\textsuperscript{-}-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\textsubscript{dep}.

The data on the amount of F\textsubscript{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\textsubscript{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\textsuperscript{-1} and the unit of the precipitation is mm. The units of the concentration of N species in precipitation include mg N L\textsuperscript{-1} \cite{30} and μeq L\textsuperscript{-1} \cite{31}. Both of the two units are commonly used. Thus, when the unit of the concentration of N species is mg N L\textsuperscript{-1}, the calculation formula of nitrogen deposition is:

\[
N_{\text{dep}} = \frac{C_i \times P_i}{100}
\]

where \(N_{\text{dep}}\) is the N deposition flux per year (kg ha\textsuperscript{-1} a\textsuperscript{-1}); \(C_i\) is the concentration of NH\textsubscript{4}\textsuperscript{+}-N or NO\textsubscript{3}\textsuperscript{-}-N (mg N L\textsuperscript{-1}); \(P_i\) is the annual precipitation (mm); 100 is the conversion factor.

Otherwise, the formula is:

\[
N_{\text{dep}} = \frac{C_i \times P_i \times 14}{10^5}
\]

where \(N_{\text{dep}}\) is the N deposition flux per year (kg ha\textsuperscript{-1} a\textsuperscript{-1}); \(C_i\) is the concentration of NH\textsubscript{4}\textsuperscript{+}-N or NO\textsubscript{3}\textsuperscript{-}-N (μeq L\textsuperscript{-1}); \(P_i\) is the annual precipitation (mm); 14 is the atomic weight of N and 10\textsuperscript{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\textsubscript{dep} maps were constructed using the Kriging interpolation technique. An unknown value associated with a point can be estimated by Kriging as follows:

\[
Z(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i)
\]

where \(\lambda_i\) 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 \(Z(x_i)\), \(i = 1, \ldots, N\).

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:

\[
x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad i = 1, \ldots, m; j = 1, \ldots, n; k = 1, \ldots, p
\]

where \( x_{ij} \) are 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.

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

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\textsubscript{dep} distribution and comparisons with other studies

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

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

On a provincial scale, comparison of the results of N\textsubscript{dep} (kg ha\textsuperscript{-1} a\textsuperscript{-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
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 5I). 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 NH$_4^+$-N was 6.83 kg ha$^{-1}$ a$^{-1}$ with a standard deviation (STDEV) of 5.15, while the NO$_3^-$-N was 5.35 kg ha$^{-1}$ a$^{-1}$ with a STDEV of 5.71. The average of ratio of NH$_4^+$-N/NO$_3^-$-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 NH$_4^+$-N/NO$_3^-$-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 NH$_4^+$-N/NO$_3^-$-N in this study indicated both the agricultural and industrial activities collectively influence the deposition of atmosphere N.

![Comparison of $N_{dep}$ (kg ha$^{-1}$ 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.](doi:10.1371/journal.pone.0146051.g004)
Fig 5. Spatial pattern of N$_{dep}$ (kg ha$^{-1}$ 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$_3^-$-N; e, NH$_4^+$-N) by Lu and Tian [14]. The red line divides
The N$_{\text{dep}}$ was 12.18 kg ha$^{-1}$ a$^{-1}$ and the total N deposition in China would be 20.30 kg ha$^{-1}$ a$^{-1}$ assuming that the contribution of dry deposition was about 40% in China [4, 37]. The magnitude and spatial pattern of N$_{\text{dep}}$ 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$_{\text{dep}}$ exhibited a decreasing gradient from the southeast to the northwest of China. The red line (Fig 5I) indicated the significant heterogeneity in the levels of economic development for different regions, which resulted in a matching spatial heterogeneity in N$_{\text{dep}}$ across China. Similar results were also found in the study by Jia and Liu [3, 25]. The low N$_{\text{dep}}$ were in areas including Qinghai-Tibet Plateau, Inner Mongolia and northwest China, where had not well developed industrial activities [5].

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

The N$_{\text{dep}}$ on a national scale ranged from 9.88 to 21.1 kg ha$^{-1}$ a$^{-1}$ (Table 1), showing strong spatial variations. The wet deposition flux of N$_{\text{dep}}$ (12.18 kg ha$^{-1}$ a$^{-1}$) in this study was much lower than the summarized previous results (21.1 kg ha$^{-1}$ a$^{-1}$) [3].

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

| Estimation technique                        | Year         | NH$_4^+$-N | NO$_3^-$-N | N$_{\text{dep}}$ | 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|

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

$^b$The averaged value ignoring difference between regions.
than that (21.07 kg ha\(^{-1}\) a\(^{-1}\)) based on the average of those data points to represent N\(_{\text{dep}}\) 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\(_{\text{dep}}\) 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\(_{\text{dep}}\)

The process of N\(_{\text{dep}}\) 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\(_{\text{dep}}\). It is critical to understand the relationship between N\(_{\text{dep}}\) and P, F\(_N\) and E, to simulate and predict future trends in N\(_{\text{dep}}\) 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\(_{\text{dep}}\) and P, F\(_N\), E (Table 2). Jia et al. found that N\(_{\text{dep}}\) 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\(_{\text{dep}}\) on the regional scale. N\(_{\text{dep}}\) was calculated using equation $N_{\text{dep}} = a * \ln((F_N*18.5% + E*0.24%)*P) + b$. However, Zhu and He reported N\(_{\text{dep}}\) 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\(_{\text{dep}}\), whereas E did not significantly explain the variability. A multiple linear regression model (N\(_{\text{dep}}\) = a + b\(* F_N\) + c\(* P\)) was applied without E by Zhu and He.

In this study, a strong exponential correlation was found between P and N\(_{\text{dep}}\), F\(_N\) and E and N\(_{\text{dep}}\) (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\(_{\text{dep}}\) 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\(_{\text{dep}}\) (kg ha\(^{-1}\) a\(^{-1}\)). The mean N\(_{\text{dep}}\) (kg ha\(^{-1}\) a\(^{-1}\)) in provinces were obtained from spatial maps of N\(_{\text{dep}}\) (kg ha\(^{-1}\) a\(^{-1}\)) in China using Kriging.](https://doi.org/10.1371/journal.pone.0146051.g006)
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): \( N_{dep} = a \times \ln((FN \times 18.5\% + E \times 0.24\% \times P) + 1.64\) n=28 p<0.001 RMSE=6.34)

\[
y = 0.61x + 7.18, R^2 = 0.43, n=28, p<0.001, RMSE=6.34
\]

\[
N_{dep} = 4.83 \ln((FN \times 18.5\% + E \times 0.24\% \times P) + 1.64, n=28, p<0.001
\]

\[
y = 0.63x + 0.85, R^2 = 0.46, n=28, p<0.001, RMSE=6.21
\]

\[
N_{dep} = 4.47 + 1.53 \times FN + 0.0066 \times P, n=28, p<0.001
\]

\[
y = 0.92x + 0.15, R^2 = 0.68, n=28, p<0.001, RMSE=5.72
\]

\[
y = 0.95x + 0.68, R^2 = 0.86, n=28, p<0.001, RMSE=2.39
\]

\[
N_{dep} = 9.42 + 1.46 \times P^{0.33} + 7.58 \times FN^{0.47}, n=28, p<0.001
\]

\[
N_{dep} = 6.52 + 0.0065 \times P^{1.01} + 6.31 \times FN^{0.34}, n=28, p<0.001
\]

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.

doi:10.1371/journal.pone.0146051.g007
To improve this estimation of $N_{\text{dep}}$, 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 $N_{\text{dep}}$ proposed by Zhu and He [4] through our practice in this study. Thus, we adopted an equation ($N_{\text{dep}} = a + b/F_N + c/P + d$) to predict $N_{\text{dep}}$ 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 effectiveness 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 $N_{\text{dep}}$ in China in 2000s and good agreement was found for the comparison of $N_{\text{dep}}$ with prediction (Fig 7D).

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

Certainly, we had to admit that there were some uncertainties in the analysis of how $P$, $F_N$ and $E$ influencing the spatial patterns of $N_{\text{dep}}$ 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 $N_{\text{dep}}$ 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...
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 Ndep. 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 SO4\(^2-\) and NO3\(^-\) (Fig 9B), indicating a fossil fuel combustion source. The two icons were associated with NOx emitted from coal-fired power plants, residential heating and cooking, and motor vehicles [39]. The third source had a high loading of Ca\(^2+\) and Mg\(^2+\), representing a crustal or windblown dust source (Fig 9C). The profile also contained a significant SO4\(^2-\) 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 SO4\(^2-\), 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, Ndep in China may be considerably affected by the high emissions of NOx and NH\(_3\) from fossil fuel combustion and agricultural activities and relevant studies will be presented in future papers.

**Conclusion**

The Ndep throughout China was obtained by a method of Kriging, based on the N fluxes from the published papers from 2003 to 2014. The Ndep map in our study showed close spatial pattern with that by Lu and Tian (2014). There were five hotspots of Ndep 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 NH$_4^+$-N, NO$_3^-$-N and total N$_{dep}$ was 6.83, 5.35 and 12.18 kg ha$^{-1}$ 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 NO$_3^-$-N (86.0%) and biomass burning also contributed to 5.4% on the deposition of NO$_3^-$-N. NH$_4^+$-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)

Acknowledgments

This study is supported by the National Natural Science Foundation of China (No. 41471343 and 41101315) and the Open Foundation of State Key Laboratory of Remote Sensing (OFSLRSS201312).

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.

References

1. Lü C, Tian H. Spatial and temporal patterns of nitrogen deposition in China: synthesis of observational data. Journal of Geophysical Research: Atmospheres (1984–2012). 2007; 112(D22).
2. Zhang Y, Song L, Liu XJ, Li WQ, Lü SH, Zheng LX, et al. Atmospheric organic nitrogen deposition in China. Atmospheric Environment. 2012; 46(0):195–204. Available: doi:http://dx.doi.org/10.1016/j.atmosenv.2011.09.080.
3. Liu X, Zhang Y, Han W, Tang A, Shen J, Cui Z, et al. Enhanced nitrogen deposition over China. Nature. 2013; 494(7438):459–62. doi: 10.1038/nature11917 PMID: 23426264
4. Zhu J, He N, Wang Q, Yuan G, Wen D, Yu G, et al. The composition, spatial patterns, and influencing factors of atmospheric wet nitrogen deposition in Chinese terrestrial ecosystems. Science of the Total Environment. 2015; 511:777–85. doi: 10.1016/j.scitotenv.2014.12.038 PMID: 25617702
5. He N, Zhu J, Wang Q. Uncertainty and perspectives in studies of atmospheric nitrogen deposition in China: A response to Liu et al.(2015). Science of The Total Environment. 2015; 520:302–4. doi: 10.1016/j.scitotenv.2015.03.063 PMID: 25818390
6. Richter A, Burrows JP, Nüß H, Granier C, Niemeier U. Increase in tropospheric nitrogen dioxide over China observed from space. Nature. 2005; 437(7055):129–32. PMID: 16136141
7. Vitousek PM, Aber JD, Howarth RW, Likens GE, Matson PA, Schindler DW, et al. Human alteration of the global nitrogen cycle: sources and consequences. Ecological applications. 1997; 7(3):737–50.
8. Matson P, Lohse KA, Hall SJ. The globalization of nitrogen deposition: consequences for terrestrial ecosystems. AMBIO: A Journal of the Human Environment. 2002; 31(2):113–9.
9. Clark CM, Tilman D. Loss of plant species after chronic low-level nitrogen deposition to prairie grasslands. Nature. 2008; 451(7179):712–5. doi: 10.1038/nature06503 PMID: 18258670
10. Zhao X, Yan X, Xiong Z, Xie Y, Xing G, Shi S, et al. Spatial and temporal variation of inorganic nitrogen wet deposition to the Yangtze River Delta Region, China. Water, air, and soil pollution. 2009; 203(1–4):277–89.

11. Larssen T, Duan L, Mulder J. Deposition and leaching of sulfur, nitrogen and calcium in four forested catchments in China: implications for acidification. Environmental science & technology. 2011; 45(4):1192–8.

12. Pan Y, Wang Y, Tang G, Wu D. Wet and dry deposition of atmospheric nitrogen at ten sites in Northern China. Atmospheric Chemistry and Physics. 2012; 12(14):6515–35.

13. Huang D-Y, Xu Y-G, Zhou B, Zhang H-H, Lan J-B. Wet deposition of nitrogen and sulfur in Guangzhou, a subtropical area in South China. Environmental monitoring and assessment. 2010; 171(1–4):429–39. doi: 10.1007/s10661-009-1289-7 PMID: 20052612

14. Lu C, Tian H. Half-century nitrogen deposition increase across China: A gridded time-series data set for regional environmental assessments. Atmospheric Environment. 2014; 97:68–74.

15. Cao Y-Z, Wang S, Zhang G, Luo J, Lu S. Wet and dry deposition of atmospheric nitrogen at ten sites in Northern China. Atmospheric Chemistry and Physics. 2012; 12(14):6515–35.

16. Huang D-Y, Xu Y-G, Zhou B, Zhang H-H, Lan J-B. Wet deposition of nitrogen and sulfur in Guangzhou, a subtropical area in South China. Environmental monitoring and assessment. 2010; 171(1–4):429–39. doi: 10.1007/s10661-009-1289-7 PMID: 20052612

17. Lu C, Tian H. Half-century nitrogen deposition increase across China: A gridded time-series data set for regional environmental assessments. Atmospheric Environment. 2014; 97:68–74.

18. Pan Y, Wang Y, Tang G, Wu D. Spatial distribution and temporal variations of atmospheric sulfur deposition in Northern China: insights into the potential acidification risks. Atmospheric Chemistry and Physics. 2013; 13(3):1675–88.

19. Jia Y, Yu G, He N, Zhan X, Fang H, Sheng W, et al. Spatial and decadal variations in inorganic nitrogen wet deposition in China induced by human activity. Scientific Reports. 2014; 4.

20. Liu X, Xu W, Pan Y, Du E. Liu et al. suspect that Zhu et al.(2015) may have underestimated dissolved organic nitrogen (N) but overestimated total particulate N in wet deposition in China. Science of The Total Environment. 2015; 520:300–1. doi: 10.1016/j.scitotenv.2015.03.004 PMID: 25759249

21. Pan Y, Li Y, Wang Y. Comments on'Half-century nitrogen deposition increase across China: A gridded time-series dataset for regional environmental assessments' by Chaoqun Lu and Hanqin Tian. Atmospheric Environment (2014), 97: 68–74. doi:10.1016/j.atmosenv.2014.10.016.

22. Stevens CJ, Dise NB, Gowing DJ. Regional trends in soil acidification and exchangeable metal concentrations in relation to acid deposition rates. Environmental Pollution. 2009; 157(1):313–9. doi: 10.1016/j.envpol.2008.06.033 PMID: 18674853

23. Zhang X, Jiang H, Zhang Q, Zhang X. Chemical characteristics of rainwater in northeast China, a case study of Dalian. Atmospheric Research. 2012; 116:151–60.

24. Xiao H-Y, Liu C-Q. Sources of nitrogen and sulfur in wet deposition at Guiyang, southwest China. Atmospheric Environment. 2002; 36(33):5121–30.

25. Pan Y, Wang Y, Tang G, Wu D. Spatial distribution and temporal variations of atmospheric sulfur deposition in Northern China: insights into the potential acidification risks. Atmospheric Chemistry and Physics. 2013; 13(3):1675–88.

26. Jia Y, Yu G, He N, Zhan X, Fang H, Sheng W, et al. Spatial and decadal variations in inorganic nitrogen wet deposition in China induced by human activity. Scientific Reports. 2014; 4.

27. Shi Y, Cui S, Ju X, Cai Z, Zhu Y-G. Impacts of reactive nitrogen on climate change in China. Scientific Reports. 2015; 5.

28. Zhan X, Yu G, He N, Jia B, Zhou M, Wang C, et al. Inorganic nitrogen wet deposition: Evidence from the North-South Transect of Eastern China. Environmental Pollution. 2015; 204:1–8. doi: 10.1016/j.envpol.2015.03.016 PMID: 25898231

29. Xu W, Luo X, Pan Y, Zhang L, Tang A, Shen J, et al. Quantifying atmospheric nitrogen deposition through a nationwide monitoring network across China. Atmospheric Chemistry and Physics Discussions. 2015; 15(13):18365–403.

30. Zhang N, He Y, Cao J, Ho K, Shen Z. Long-term trends in chemical composition of precipitation at Lijiang, southeast Tibetan Plateau, southwestern China. Atmospheric Research. 2012; 106:50–60.
32. Huang K, Zhuang G, Xu C, Wang Y, Tang A. The chemistry of the severe acidic precipitation in Shanghai, China. Atmospheric Research. 2008; 89(1):149–60.

33. Comero S, Vaccaro S, Locoro G, De Capitani L, Gawlik BM. Characterization of the Danube River sediments using the PMF multivariate approach. Chemosphere. 2014; 95(0):329–35. Available: doi:http://dx.doi.org/10.1016/j.chemosphere.2013.09.028 PMID: 24120015

34. Du E, Liu X. High rates of wet nitrogen deposition in China: a synthesis. Nitrogen Deposition, Critical Loads and Biodiversity: Springer; 2014. p. 49–56.

35. Huang Y, Lu X, Chen K. Wet atmospheric deposition of nitrogen: 20 years measurement in Shenzhen City, China. Environmental Monitoring and Assessment. 2013; 185(1):113–22. doi: 10.1007/s10661-012-2537-9 PMID: 22362555

36. Xie Y, Xiong Z, Xing G, Yan X, Shi S, Sun G, et al. Source of nitrogen in wet deposition to a rice agroecosystem at Tai lake region. Atmospheric Environment. 2008; 42(21):5182–92.

37. Qi JH, Shi JH, Gao HW, Sun Z. Atmospheric dry and wet deposition of nitrogen species and its implication for primary productivity in coastal region of the Yellow Sea, China. Atmospheric Environment. 2013; 81(0):600–8. Available: doi:http://dx.doi.org/10.1016/j.atmosenv.2013.08.022.

38. She W. Huanyong Hu: Father of China’s population geography. China Population Today. 1998; 15(4):20.

39. Li Y, Wang Y, Ding A, Liu X, Guo J, Li P, et al. Impact of long-range transport and under-cloud scavenging on precipitation chemistry in East China. Environmental Science and Pollution Research. 2011; 18(9):1544–54. doi: 10.1007/s11356-011-0516-2 PMID: 21567155