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# Spatial and decadal variations in inorganic nitrogen wet deposition in China induced by human activity

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Atmospheric nitrogen (N) deposition, an important component in the global N cycle, has increased sharply in recent decades in China. Here, we constructed national-scale inorganic N wet deposition ( $N_{\text{dep}}$ ) patterns in China based on data from 280 observational sites and analysed the effects of anthropogenic sources and precipitation on  $N_{\text{dep}}$ . Our results showed that the mean  $N_{\text{dep}}$  over China increased approximately 25%, from 11.11 kg ha<sup>-1</sup> a<sup>-1</sup> in the 1990s to 13.87 in the 2000s.  $N_{\text{dep}}$  was highest over southern China and exhibited a decreasing gradient from southern to western and northern China. The decadal difference in  $N_{\text{dep}}$  between the 1990s and 2000s was primarily caused by increases in energy consumption and N fertiliser use. Our findings conformed that anthropogenic activities were the main reason for the  $N_{\text{dep}}$  increase and provide a scientific background for studies on ecological effects of N deposition in China.

Atmospheric nitrogen (N) deposition has dramatically increased worldwide in the past few decades<sup>1,2</sup>. Although these N inputs to ecosystems can increase food production<sup>3</sup> and stimulate plant growth<sup>4–6</sup>, particularly in N-limited regions, excessive N has caused a cascade of detrimental effects on natural ecosystems and humans, including the acidification of soils and waters<sup>7</sup>, negative impacts on the buffering capacity of soil<sup>8</sup>, a loss of biological diversity<sup>9,10</sup>, and risks to human health<sup>11</sup>. Simultaneously, N deposition can influence the balance of greenhouse gases (N oxide and ozone in addition to carbon dioxide)<sup>11,12</sup>. Therefore, an understanding of the spatio-temporal patterns and the factors controlling N deposition is essential for evaluating its ecological effects, and can provide the scientific background for research into global changes.

Both natural and anthropogenic sources contribute to atmospheric N deposition, but anthropogenic reactive N ( $N_r$ ) emissions dominate N deposition at both continental and regional scales<sup>13,14</sup>. Anthropogenic  $N_r$  is released into the atmosphere either as N oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), primarily from fossil fuel combustion, or as ammonia ( $\text{NH}_3$ ), primarily from agriculture<sup>2,13</sup>. After a series of chemical conversions and physical transport, the ultimate fate of  $\text{NO}_x$  and  $\text{NH}_3$  is removal by wet scavenging and dry deposition on terrestrial and aquatic ecosystems<sup>2,15</sup>. Although the process of N deposition is relatively clear in theory and has been applied in models, knowledge of how anthropogenic sources influence N deposition at the regional scale using observational or statistical data is lacking.

Anthropogenic  $N_r$  emissions have increased significantly in China due to rapid agricultural production and industrial development in the past three decades<sup>16</sup>, and progress has been made with regard to research into N deposition in China over the last decade, particularly wet (bulk) deposition. Three important aspects of this research are as follows. Observations of N deposition in situ have been more extensively studied across China from 1980 to the present<sup>17,18</sup>. Meta-analyses based on this massive observational dataset have been implemented in recent years to evaluate nationwide N deposition dynamics and spatial patterns<sup>19,20</sup>. Simultaneously, atmospheric chemistry transport models have also been implemented to simulate current and future N deposition in China<sup>2,21</sup>. Such studies have all indicated high N deposition in China. Nonetheless, it remains unclear how the pattern of N deposition is determined and what role anthropogenic sources play, an issue that requires further investigation.

This study established nationwide datasets of inorganic N wet deposition (abbreviated as  $N_{\text{dep}}$ ) from 280 observational sites and amassed data on N fertiliser use, energy consumption, and precipitation in China between



the 1990s and 2000s. Based on these data, this study attempts to address the following questions: (1) What are the spatial patterns of  $N_{\text{dep}}$  in the 1990s and 2000s in China? (2) How do anthropogenic sources and precipitation influence the spatial pattern of  $N_{\text{dep}}$ ? (3) Do the factors controlling the spatial pattern of  $N_{\text{dep}}$  also determine decadal variation?

## Results

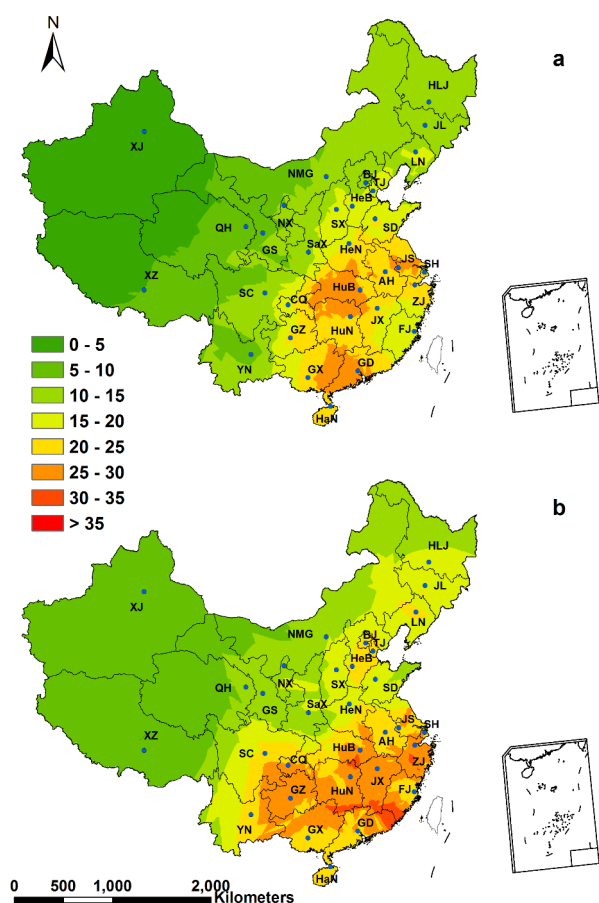
**Spatial patterns of  $N_{\text{dep}}$  in the 1990s and 2000s.** In China, the magnitude and spatial pattern of  $N_{\text{dep}}$  differed significantly according to region and decade (Fig. 1). In the 1990s,  $N_{\text{dep}}$  exhibited a decreasing gradient from southern to western and to northern China.  $N_{\text{dep}}$  was  $>30 \text{ kg ha}^{-1} \text{ a}^{-1}$  in some provinces of southern China, such as Hunan, Hubei, Guangdong, and Guangxi, whereas  $N_{\text{dep}}$  in other provinces of southern China was approximately  $20\text{--}25 \text{ kg ha}^{-1} \text{ a}^{-1}$ .  $N_{\text{dep}}$  over northern, northeastern, and northwestern China was approximately  $10\text{--}20$ ,  $5\text{--}15$ , and  $0\text{--}10 \text{ kg ha}^{-1} \text{ a}^{-1}$ , respectively (Fig. 1a).

Compared to the 1990s,  $N_{\text{dep}}$  increased across nearly all of China in the 2000s (Fig. 1b), and mean  $N_{\text{dep}}$  over China increased by approximately 25% from the 1990s ( $11.11 \text{ kg ha}^{-1} \text{ a}^{-1}$ ) to the 2000s ( $13.87 \text{ kg ha}^{-1} \text{ a}^{-1}$ ).  $N_{\text{dep}}$  over most parts of southern China reached  $30 \text{ kg ha}^{-1} \text{ a}^{-1}$  and also increased to some extent in other

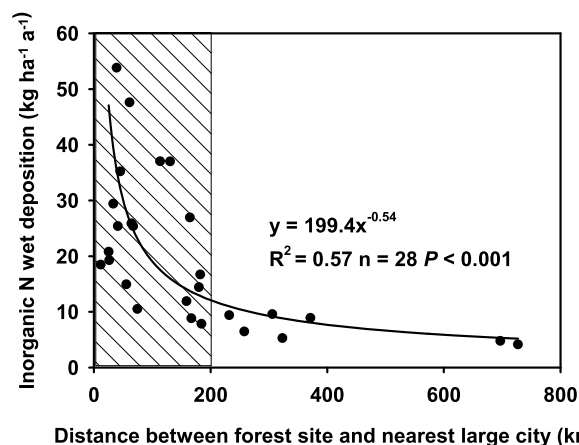
regions. It is worth noting that North China also gradually became a centre for  $N_{\text{dep}}$ , with a value of  $25 \text{ kg ha}^{-1} \text{ a}^{-1}$ .

**The effect of metropolitan areas on  $N_{\text{dep}}$  in natural forest ecosystems.** Cities are centres of human activity that emit large quantities of N pollution and can influence surrounding ecosystems through atmospheric transport. N emissions from natural forest ecosystems are mainly due to the decomposition of soil and animal excreta, although the magnitude of N deposition induced by these emissions is quite limited. We analysed the relationship between the  $N_{\text{dep}}$  of natural forest ecosystems and the distance from a forest site to the nearest large city with more than 2 million inhabitants. The results indicated that  $N_{\text{dep}}$  at a forest site was significantly related to the distance to the nearest city using a power model ( $R^2 = 0.57$ ,  $P < 0.001$ ) (Fig. 2). The distance within a city affected forest  $N_{\text{dep}}$  was approximately 200 km (shadow in Fig. 2). This result indicates that anthropogenic sources influence  $N_{\text{dep}}$  primarily at the local scale and vice versa, i.e.,  $N_{\text{dep}}$  was primarily influenced by local anthropogenic sources. This finding was the basis for studying the relationship between anthropogenic sources (N fertiliser use and energy consumption) and the spatial pattern of  $N_{\text{dep}}$  by province in the ensuing analyses.

**The effects of anthropogenic sources and precipitation on the spatial pattern of  $N_{\text{dep}}$ .** N fertiliser use, energy consumption, and precipitation were significantly correlated to  $N_{\text{dep}}$  by province in the 1990s (Fig. 3), contributing 60%, 51%, and 63%, respectively, to the spatial variation of  $N_{\text{dep}}$  ( $P < 0.001$ ).  $N_{\text{dep}}$  was strongly logarithmically related to N fertiliser use and energy consumption (Fig. 3a,b) and linearly related to precipitation (Fig. 3c). It is worth noting that there was a large dispersion of  $N_{\text{dep}}$  in provinces where N fertiliser use was approximately  $3\text{--}8 \text{ t km}^{-2} \text{ a}^{-1}$  (shadow in Fig. 3a). We found that precipitation played an important role in this dispersion; for example, given similar magnitudes of N fertiliser use in different provinces, high precipitation usually accompanied high  $N_{\text{dep}}$  (Supplementary Table S1). A similar situation was observed for the relationship between energy consumption and  $N_{\text{dep}}$ . Conversely, in the case of relatively consistent precipitation, those provinces with high  $N_{\text{dep}}$  also had high N fertiliser use or energy consumption (shadow in Fig. 3c and Supplementary Table S1). Therefore, anthropogenic sources and precipitation need be considered together when studying the factors that control the spatial patterns of  $N_{\text{dep}}$  at the regional scale.



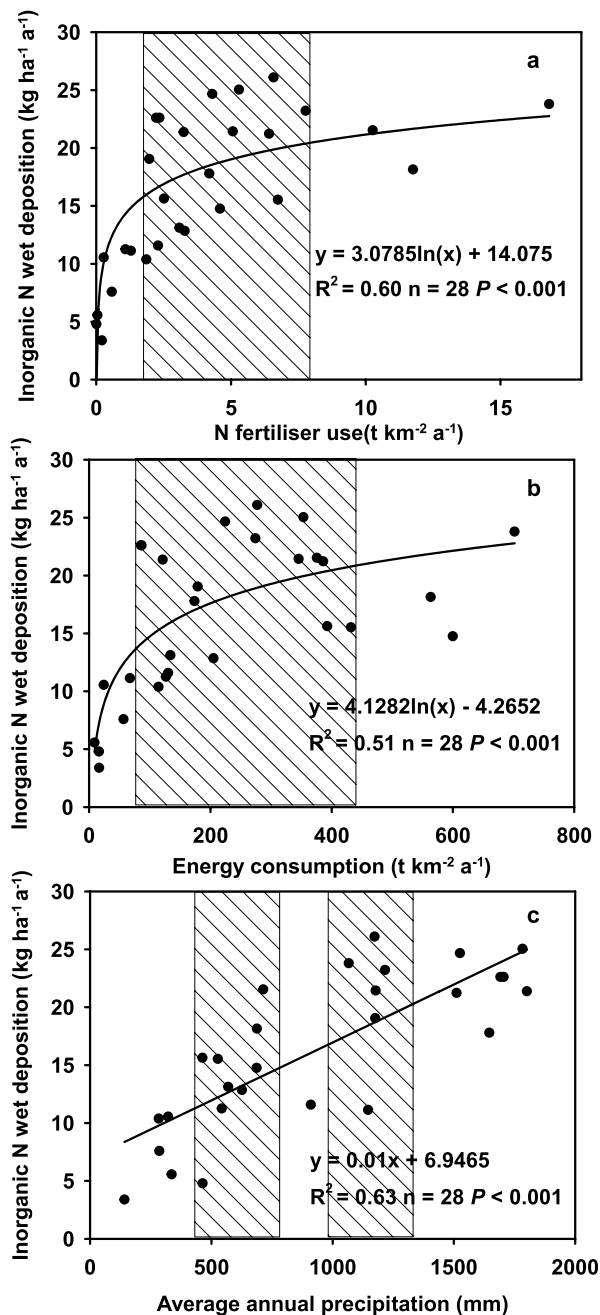
**Figure 1 | Spatial patterns of  $N_{\text{dep}}$  in China ( $\text{kg ha}^{-1} \text{ a}^{-1}$ ).** Spatial distribution maps of  $N_{\text{dep}}$  in the 1990s (a) and 2000s (b) were obtained from 136 and 144 monitoring sites, respectively, by Kriging interpolation. The letters denote the abbreviations of province names in China, and the full names of the provinces are listed in Supplementary Table S1. The dots indicate the location of the capital of each province. The distribution of monitoring sites is shown in Supplementary Figure S2. The maps were generated using ArcGIS 10.0 software.



**Figure 2 | Correlation between  $N_{\text{dep}}$  in natural forest ecosystems and the distance between the forest site and nearest large city.** All natural forest monitoring sites in the 2000s were selected from our datasets. Large cities were selected if they contained more than 2 million inhabitants. Note: the area of shadow indicates the distance to which the  $N_{\text{dep}}$  of a natural forest was strongly influenced by the nearest city.



Subsequently, we analysed the combined effect of N fertiliser use, energy consumption, and precipitation on the spatial variation of  $N_{\text{dep}}$  in China. The result showed that these three factors combined contributed 79% of the spatial variation of  $N_{\text{dep}}$  (equation (1)).



**Figure 3** | The effects of N fertiliser use, energy consumption, and precipitation on the spatial pattern of  $N_{\text{dep}}$  in the 1990s. (a) N fertiliser use (expressed as the volume of effective component). The data on N fertiliser use in provinces were obtained from the China Statistical Yearbook<sup>43</sup>. (b) Energy consumption (expressed as standard coal). The data on energy consumption in provinces were primarily from the China Energy Statistical Yearbook<sup>44</sup>. (c) Precipitation. The data on the annual amount of precipitation were obtained from the China Meteorological Administration and included 756 weather stations (Supplementary Fig. S3). The mean  $N_{\text{dep}}$  in provinces was obtained from spatial maps of  $N_{\text{dep}}$  over China using the Zonal Statistics tool of ArcGIS 10.0 software. Notes: the area of shadowing indicates the provinces with large variations in  $N_{\text{dep}}$  when the x-axis variable was relatively constant.

$$N_{\text{dep}} = 3.3366 \ln[(F_N \times 18.5\% + E \times 0.24\%) \times P] - 5.0317 \quad (R^2 = 0.79 \quad P < 0.001) \quad (1)$$

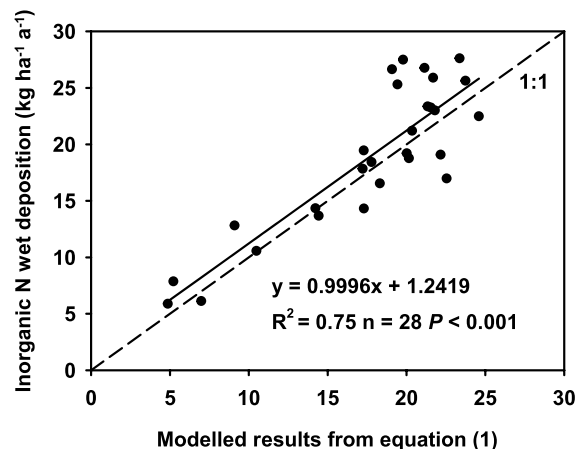
where  $N_{\text{dep}}$  is inorganic N wet deposition ( $\text{kg ha}^{-1} \text{a}^{-1}$ ),  $F_N$  is N fertiliser use (expressed as the volume of effective component) ( $\text{t km}^{-2} \text{a}^{-1}$ ),  $E$  is energy consumption (as standard coal) ( $\text{t km}^{-2} \text{a}^{-1}$ ),  $P$  is precipitation (mm), 18.5% is the average  $\text{NH}_3\text{-N}$  emission factor for N fertiliser<sup>22</sup>, and 0.24% is the average  $\text{NO}_x\text{-N}$  emission factor for energy consumption<sup>23</sup>.

We used data from the 2000s to test whether equation (1), established using data from the 1990s, can reflect the spatial variation of  $N_{\text{dep}}$  in China. The results showed that  $N_{\text{dep}}$  calculated using equation (1) was strongly related to the  $N_{\text{dep}}$  values for the 2000s interpolated by Kriging (Fig. 4), indicating that equation (1) can well describe the spatial patterns of  $N_{\text{dep}}$  in China. Assuming that the existing emission factors for N fertiliser and energy consumption do not change much, we can use N fertiliser use, energy consumption, and precipitation as the driving factors to simulate and predict future trends in  $N_{\text{dep}}$ .

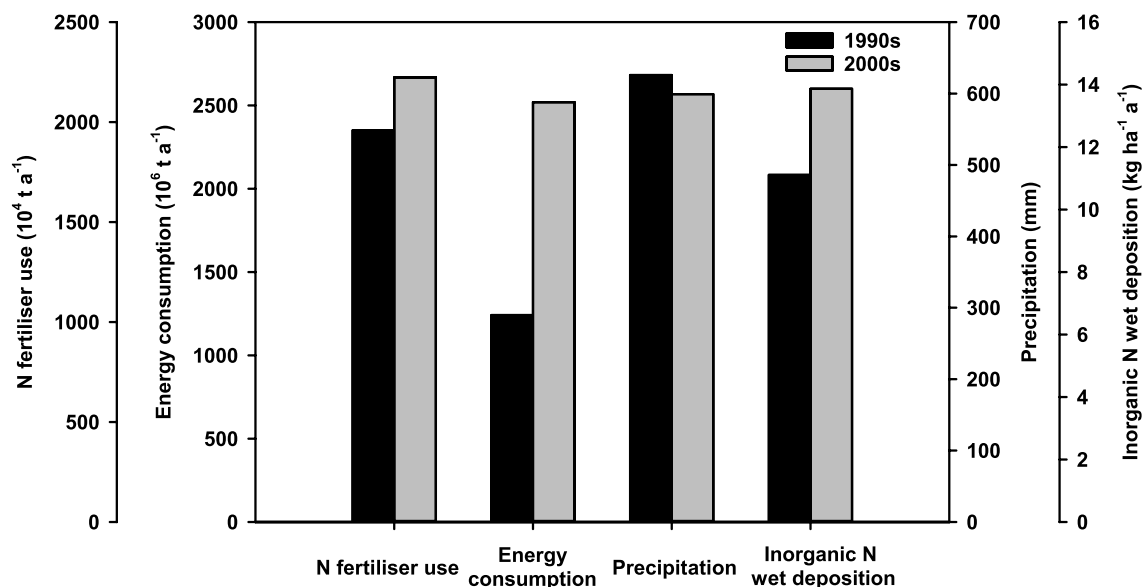
**The effects of anthropogenic sources and precipitation on the decadal variation in  $N_{\text{dep}}$ .** The changes in N fertiliser use, energy consumption, precipitation, and  $N_{\text{dep}}$  from the 1990s to the 2000s in China were quite different (Fig. 5). Compared to the 1990s, N fertiliser use increased by approximately 10%, energy consumption nearly doubled, precipitation decreased slightly, and  $N_{\text{dep}}$  increased by approximately 25% in the 2000s. We used equation (1) to calculate the individual effects of N fertiliser use, energy consumption, and precipitation on the decadal variation of  $N_{\text{dep}}$  (see Data and Methods). The results indicated that an increase in energy consumption dominated the change in  $N_{\text{dep}}$  from the 1990s to the 2000s in China, contributing approximately 80% of this decadal variation. N fertiliser use also contributed to the decadal increase in  $N_{\text{dep}}$ , but its role was relatively small. Precipitation had little effect on the decadal increase of  $N_{\text{dep}}$ , although there was an adverse effect, as shown in Fig. 6; this effect was quite small and may be produced from the deviation of equation (1).

## Discussion

Atmospheric N deposition in China has dramatically increased in recent decades. In the present study,  $N_{\text{dep}}$  averaged 11.11 and 13.87  $\text{kg ha}^{-1} \text{a}^{-1}$  in the 1990s and 2000s, respectively. Other studies



**Figure 4** | Test of equation (1) using data from the 2000s. The x-axis variable was modelled results of  $N_{\text{dep}}$  in provinces, as obtained by equation (1) and data on N fertiliser use, energy consumption, and precipitation in provinces in the 2000s. The y-axis variable was interpolated results of  $N_{\text{dep}}$ , as obtained by Kriging interpolation.



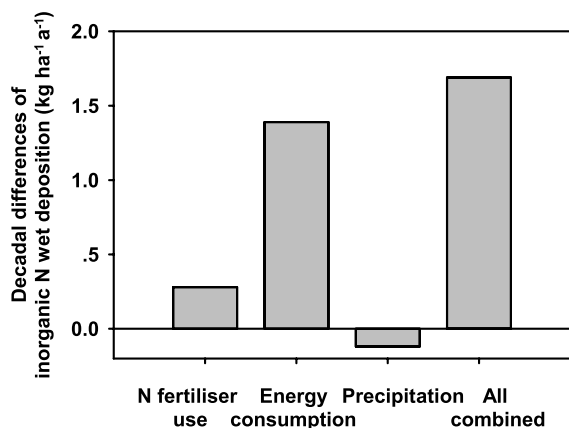
**Figure 5** | N fertiliser use, energy consumption, precipitation, and  $N_{\text{dep}}$  in China in the 1990s and 2000s. The data on N fertiliser use in provinces were obtained from the China Statistical Yearbook<sup>43</sup>. The data on energy consumption in provinces were primarily from the China Energy Statistical Yearbook<sup>44</sup>. The annual amount of precipitation was obtained from the China Meteorological Administration and included 756 weather stations (Supplementary Fig. S3).  $N_{\text{dep}}$  was obtained by Kriging interpolation.

have also assessed wet deposition (the same N deposition species as in this study, including  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) in China using different approaches. Lü and Tian employed the Kriging technique to characterise spatial pattern of wet deposition, arriving at an average of  $9.88 \text{ kg ha}^{-1} \text{ a}^{-1}$  during 1980–2005 throughout China<sup>20</sup>, a value that is slightly lower than the results of our study. One possible reason for this discrepancy is the different time scales used in the two studies. Ti et al. noted that annual wet deposition averaged  $5.37\text{--}9.1 \text{ kg ha}^{-1} \text{ a}^{-1}$  over China during 1985–2007 (ref. 3), which was based on the relationship between wet deposition from monitoring and N emissions, with a resolution of  $0.5^\circ \times 0.5^\circ$ ; however, as the gridded emissions were obtained based on regional emission data and population data<sup>24</sup>, that estimate of wet deposition may have a large uncertainty. By summarising monitoring data from publications and measurements, Liu et al. reported that annual bulk deposition (wet deposition) averaged  $13.2$  and  $21.1 \text{ kg ha}^{-1} \text{ a}^{-1}$  in the 1980s and 2000s, respectively, over China<sup>19</sup>. Their results were considerably higher

than those of other studies, and a possible reason for this being that the mean wet deposition over China reported by Liu et al. was obtained directly from the arithmetic average of monitoring data, which did not consider the spatial differences in wet deposition in China. In summary, due to the lack of an extensive long-term monitoring network, the assessment of N deposition in China still has a large uncertainty. Nonetheless, the results from geostatistical methods considering spatial differences may be reliable<sup>20,25</sup>.

Although the values of critical loads in different ecosystems have a given amount of uncertainty, it is currently believed that the values of terrestrial ecosystems are approximately  $10\text{--}20 \text{ kg N ha}^{-1} \text{ a}^{-1}$  (ref. 10,25–27). Considering only  $N_{\text{dep}}$  in this study (Fig. 1), we evaluated the possible regions where N deposition exceeded the critical loads (Supplementary Fig. S1). Based on our results, 53% and 16% of land in China received N deposition exceeding 10 and  $20 \text{ kg N ha}^{-1} \text{ a}^{-1}$  in the 1990s, and these proportions reached 61% and 24%, respectively, in the 2000s. However, according to the results from their models, Dentener et al. reported that 11% of the world's natural vegetation received N deposition exceeding the critical load of  $10 \text{ kg N ha}^{-1} \text{ a}^{-1}$  (ref. 2), and Zhang et al. noted that 35% of US land received N deposition exceeding this load<sup>14</sup>. These results indicated that the potential risk of N saturation may be higher in China than in other regions, which may cause a cascade of detrimental effects on natural ecosystems and humans, such as the acidification of soils and waters<sup>7</sup>, a negative impact on the soil's buffering capacity<sup>8</sup>, the loss of biological diversity<sup>9,10</sup>, and human health risks<sup>11</sup>. Consequently, it is important and urgent to study the impact of N saturation on terrestrial ecosystems in China.

Previous studies have suggested that anthropogenic activities are the main cause of atmospheric N deposition<sup>2,13,14,19,28,29</sup> and that the pattern of wet deposition depends on precipitation and N emissions<sup>14,15</sup>; however, these results were obtained primarily from model simulations and isotope techniques. For example, Zhang et al. used the GEOS-Chem global chemical transport model to separate the contributions to N deposition from anthropogenic and natural sources<sup>14</sup>; the results showed that anthropogenic and natural sources account for 84% and 16%, respectively, of N deposition in the US. Russell et al. combined back trajectories and isotope techniques to reveal that the dominant sources of N deposition were most likely



**Figure 6** | The effects of N fertiliser use, energy consumption, and precipitation on the decadal variation in  $N_{\text{dep}}$ . The individual effects of these three factors on the decadal variation of  $N_{\text{dep}}$  was obtained by equation (1) and data on N fertiliser use, energy consumption, and precipitation in provinces in the 1990s and 2000s (see Data and Methods).



fertilisers, soil, animal excreta, and fossil fuel combustion<sup>28</sup>. Based on isotope techniques, Hastings et al. distinguished nitrate from anthropogenic emissions and from lightning in different seasons<sup>29</sup>.

In the present study, we used monitoring data and statistical information to demonstrate how anthropogenic sources and precipitation influence the spatial pattern and decadal variation of  $N_{\text{dep}}$  in China (Fig. 3, 4, and 6). The combination of anthropogenic sources (N fertiliser use and energy consumption) and precipitation contributed 79% of the spatial variation of  $N_{\text{dep}}$  (equation (1)), and energy consumption contributed approximately 80% of the decadal variation in  $N_{\text{dep}}$  (Fig. 6). The findings further demonstrated in a new way that anthropogenic sources have played an important role in the increase of  $N_{\text{dep}}$  and that  $N_{\text{dep}}$  is primarily influenced by regional human activities. These findings suggest that it is possible for regions to control their N deposition by decreasing their emissions.

Currently, it is generally considered that forest ecosystems have the greatest carbon uptake potential under increasing N deposition<sup>4</sup>. Based on the interpolated results of this study, we evaluated the possible contribution of  $N_{\text{dep}}$  to forest carbon sequestration in China. For this, we assumed the following: the forest average of  $N_{\text{dep}}$  was equivalent to the national average over China (11.11 and 13.87 kg ha<sup>-1</sup> a<sup>-1</sup> in the 1990s and 2000s); the net ecosystem production (NEP) response to N deposition would be approximately 45 kg C per kg N in forest ecosystems<sup>30–37</sup> (Supplementary Table S2); and the area of forests in China were 146 and 185 million ha (ref. 38) and that these forests may take up an additional 72 and 115 Tg C each year owing to  $N_{\text{dep}}$ , respectively, in the 1990s and 2000s. According to the results of Gregg et al., CO<sub>2</sub> emissions from fossil fuel combustion and cement manufacturing reached approximately 1500 Tg C a<sup>-1</sup> in 2006 in China<sup>39</sup>, suggesting that forests may have absorbed approximately an additional 7% of anthropogenic CO<sub>2</sub> emissions owing to  $N_{\text{dep}}$  in the 2000s in China. Because there was no consideration of some factors, such as forest type, forest age, and N saturation, that can influence the response of forest carbon sequestration to N deposition, the above assessment has a large uncertainty. Nonetheless, this preliminary assessment does suggest that anthropogenic N emissions can offset anthropogenic CO<sub>2</sub> emissions to some extent, particularly in China, which has a large forest area and high N deposition.

Our findings are still uncertain to some extent due to the use of derived data, although we conducted rigorous data screening and quality control. There were four plausible contributors to the uncertainty. First, error is involved in the preservation of samples and in measuring instruments. The samples of inorganic wet deposition were obtained from precipitation collected in open rain collectors by different researchers, and some errors were introduced by the researchers using different methods of sample preservation and different measuring instruments. Second, errors may be contributed by the number and distribution of monitoring sites. Due to the lack of an extensive long-term monitoring network, the temporary monitoring sites were limited and distributed unevenly; therefore, uncertainty from the interpolated results was induced by the limited amount and uneven distribution of the monitoring sites. Third, only N fertiliser use and energy consumption were considered as anthropogenic sources. In China, the largest sources of NH<sub>3</sub> and NO<sub>x</sub> are due to N fertiliser use and energy consumption<sup>40–42</sup>, respectively, which is why we selected these two human activities as anthropogenic sources; however, other N sources, such as livestock and biomass burning, may impact the study results because of regional differences in these sources. Furthermore, some uncertainties are attributed to the data from governmental statistical yearbooks. The data from governmental statistical yearbooks were collected not only from professional statistical departments but also from competent departments of various industries, which may affect the neutrality of data for some subjective needs. Therefore, it is necessary and urgent to establish an extensive long-term monitoring network with consistent

quality control in China to reduce the uncertainty associated with N deposition estimates and evaluation of the ecological effects of N deposition.

## Methods

**Data sources.** Datasets on  $N_{\text{dep}}$  were summarised from published sources for the 1980–2010 period (see Supplementary Information for a complete reference list) and the National Acid Deposition Monitoring Network (NADMN) established by the China Meteorological Administration. After rigorous data screening and quality control, we obtained a total of 620 site-year data for  $N_{\text{dep}}$ . The contents of our datasets included the following: the name of the monitoring site, location of the monitoring site, monitoring period, monitoring method, ecosystem type, annual precipitation, concentration and deposition of NH<sub>4</sub><sup>+</sup>-N, and NO<sub>3</sub><sup>-</sup>-N, total inorganic N wet deposition, and the literature source. To study the spatio-temporal pattern of  $N_{\text{dep}}$ , we divided the datasets into three sections according to decade (1980s, 1990s, and 2000s). The mean  $N_{\text{dep}}$  was calculated per site and decade, which represented the regular status of  $N_{\text{dep}}$  at the site for the period. After the above integration, the monitoring sites distributed in China numbered 25, 136, and 144 for the 1980s, 1990s, and 2000s, respectively. The number of monitoring sites in the 1980s was insufficient to study the spatial pattern of  $N_{\text{dep}}$  by geostatistical methods; therefore, we focused on the  $N_{\text{dep}}$  occurring in the 1990s and 2000s. The monitoring sites were distributed throughout China (Supplementary Fig. S2) and were used to produce maps of  $N_{\text{dep}}$  for China in the 1990s and 2000s using a geostatistical method.

The data on N fertiliser use (expressed as the volume of effective component) in provinces were obtained from the China Statistical Yearbook<sup>43</sup>. The data on energy consumption (expressed as standard coal) in provinces were predominantly from the China Energy Statistical Yearbook<sup>44</sup>, which primarily consists of the consumption of coal, crude oil and their products, and natural gas. Nevertheless, as there were no energy data for 1991–1994 in the national yearbooks, we obtained the energy data for those years from provincial yearbooks. 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 populations in these two provinces were known). The mean annual N fertiliser use in provinces in the 1990s and 2000s was calculated from annual data for 1990–1999 and 2000–2009, respectively. The mean annual energy consumption in provinces was treated in the same way.

Data on the annual amount of precipitation were obtained from the China Meteorological Administration, comprising 756 weather stations (Supplementary Fig. S3). The mean annual precipitation in provinces in the 1990s and 2000s was calculated based on the annual precipitation between 1990–1999 and 2000–2009, respectively, from the weather stations in each province.

**Geostatistical method and cross-validation.** A geostatistical method was used to produce spatially continuous estimates from discrete field measurements. For this study, we constructed national-scale  $N_{\text{dep}}$  maps for the 1990s and 2000s using the Kriging interpolation technique. Kriging is a statistical method of providing unbiased estimates of variables in regions where the available data exhibit spatial autocorrelation, and “Kriging estimates” are obtained in such a way that they have minimum variance<sup>25</sup>. Prior to Kriging interpolation, the Explore Data tool of ArcGIS 10.0 software was employed to conduct a data analysis, including the data’s distribution, outlier identification, and trend analyses; the optimal variogram model and parameters were then determined. Because the original data did not follow a normal distribution, we transformed the data through Box-Cox transformation ( $\lambda = 0.6$ ) using the transformation tool in ArcGIS 10.0 software. The normal distribution plots and normal distribution tests are shown in Supplementary Figure S4 and Table S3. Subsequently, the transformed data were used for Kriging interpolation, and the data are back-transformed before the final map was created. Additionally, a cross-validation analysis was implemented to evaluate the results of the Kriging interpolation. In this analysis, every monitoring site was individually removed, and its value estimated via Kriging based on the other surrounding sites was compared to the original observed value. The results of the cross-validation analysis and prediction errors are shown in Supplementary Table S4 and Figure S5, including the mean prediction error, root-mean-square standardised error, root-mean-square error, average standard error, R<sup>2</sup>, and regression coefficient. From these parameters, we found that the Kriging method worked well to predict the spatial patterns of  $N_{\text{dep}}$  in China although the predicted values for some sites were not perfect due to relatively higher root-mean-square error and low R<sup>2</sup>. These results indicated that the results of interpolation can express the trend of spatial patterns of  $N_{\text{dep}}$  in the 1990s and 2000s in China.

**The effect of metropolitan area on  $N_{\text{dep}}$  in natural forest ecosystems.** We selected all of the natural forest monitoring sites in the 2000s from our datasets and used the Near tool in ArcGIS 10.0 software to calculate and record the distance between each forest site and the nearest large city with more than 2 million inhabitants. These distances were fitted to the  $N_{\text{dep}}$  of natural forests by a power model that depended on the distribution of the scatter diagram and the correlation coefficient and *P* value. These data were analysed using SPSS (Statistical Package for the Social Sciences) 11.0 statistical software. Through the above analysis, we determined the maximum possible distance at which anthropogenic sources influence atmospheric N deposition, which was the basis for studying the relationship between anthropogenic



sources (N fertiliser use and energy consumption) and the spatial pattern of  $N_{\text{dep}}$  by province in the analyses described below.

**The effects of anthropogenic sources and precipitation on the spatial pattern of  $N_{\text{dep}}$ .** Based on our Kriging interpolation, we obtained maps of  $N_{\text{dep}}$  over China in the 1990s and 2000s with a resolution of  $10 \times 10$  km. The Zonal Statistics tool of ArcGIS 10.0 software was employed to obtain the mean  $N_{\text{dep}}$  by province. N fertiliser use, energy consumption, and precipitation in provinces were fitted with the mean  $N_{\text{dep}}$  using a linear or nonlinear regression model. Subsequently, we analysed the combined effect of these three factors on the spatial variation of  $N_{\text{dep}}$  in China (equation (1)). It should be noted that Beijing, Tianjin, and Shanghai are three economically developed municipalities with a total area of 34,400 km<sup>2</sup>, less than 0.4% of the national area, but their energy consumption is significantly higher than the other provinces (Supplementary Table S1). Therefore, these three municipalities did not follow the same relationship between energy consumption and  $N_{\text{dep}}$  (Supplementary Fig. S6) and were excluded when we explored the effects of anthropogenic sources and precipitation on the spatial pattern of  $N_{\text{dep}}$ . Moreover, due to a lack of data from Taiwan, Hong Kong, and Macao, these three provinces were also not considered. A total of 28 provinces were considered in the analysis; aside from Hainan province, with an area of 34,000 km<sup>2</sup>, the area of every other 27 province is more than 60,000 km<sup>2</sup> (Supplementary Table S1).

**The effects of anthropogenic sources and precipitation on the decadal variation in  $N_{\text{dep}}$ .** We used equation (1) to calculate the individual effects of N fertiliser use, energy consumption, and precipitation on the decadal variation in  $N_{\text{dep}}$ . Specifically, we quantified the individual effects of a given factor by applying three factors in different decades (1990s or 2000s) as input data for equation (1). The specific method was as follows (using N fertiliser use as an example). First, data on N fertiliser use in provinces in the 1990s and energy consumption and precipitation in the 2000s were input to equation (1), and the mean  $N_{\text{dep}}$  over China (N1) was then calculated for these parameters; i.e., N fertiliser data were held constant in the 1990s, and data for energy consumption and precipitation taken from the 2000s. Second, data on N fertiliser use, energy consumption, and precipitation in provinces in the 2000s were input into equation (1), and the mean  $N_{\text{dep}}$  over China (N2) was calculated for these parameters. Third, the difference between N2 and N1 was the individual effect of N fertiliser use on the decadal change (1990s–2000s) in  $N_{\text{dep}}$  over China because this difference was obtained for conditions in which only N fertiliser use was varied.

- Hall, S. J. & Matson, P. A. Nitrogen oxide emissions after nitrogen additions in tropical forests. *Nature* **400**, 152–155 (1999).
- Dentener, F. *et al.* Nitrogen and sulfur deposition on regional and global scales: A multimodel evaluation. *Glob. Biogeochem. Cycles* **20**, doi: 10.1029/2005GB002672 (2006).
- Ti, C., Pan, J., Xia, Y. & Yan, X. A nitrogen budget of mainland China with spatial and temporal variation. *Biogeochemistry* **108**, 381–394 (2011).
- Reay, D. S., Dentener, F., Smith, P., Grace, J. & Feely, R. A. Global nitrogen deposition and carbon sinks. *Nature Geosci.* **1**, 430–437 (2008).
- Fleischer, K. *et al.* The contribution of nitrogen deposition to the photosynthetic capacity of forests. *Glob. Biogeochem. Cycles* **27**, 1–13 (2013).
- Thomas, R. Q., Canham, C. D., Weathers, K. C. & Goodale, C. L. Increased tree carbon storage in response to nitrogen deposition in the US. *Nature Geosci.* **3**, 13–17 (2010).
- Vitousek, P. M. *et al.* Human alteration of the global nitrogen cycles: sources and consequences. *Ecol. Appl.* **7**, 737–750 (1997).
- Bowman, W. D., Cleveland, C. C., Halada, L., Hreško, J. & Baron, J. S. Negative impact of nitrogen deposition on soil buffering capacity. *Nature Geosci.* **1**, 767–770 (2008).
- Stevens, C. J., Dise, N. B., Mountford, J. O. & Gowing, D. J. Impact of nitrogen deposition on the species richness of grasslands. *Science* **303**, 1876–1879 (2004).
- Bobbink, R. *et al.* Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecol. Appl.* **20**, 30–59 (2010).
- Richter, A., Burrows, J. P., Nuss, H., Granier, C. & Niemeier, U. Increase in tropospheric nitrogen dioxide over China observed from space. *Nature* **437**, 129–132 (2005).
- Templer, P. H., Pinder, R. W. & Goodale, C. L. Effects of nitrogen deposition on greenhouse-gas fluxes for forests and grasslands of North America. *Front. Ecol. Environ.* **10**, 547–553 (2012).
- Paulot, F., Jacob, D. J. & Henze, D. K. Sources and processes contributing to nitrogen deposition: an adjoint model analysis applied to biodiversity hotspots worldwide. *Environ. Sci. Technol.* **47**, 3226–3233 (2013).
- Zhang, L. *et al.* Nitrogen deposition to the United States: distribution, sources, and processes. *Atmos. Chem. Phys.* **12**, 4539–4554 (2012).
- Dentener, F. J. & Crutzen, P. J. A three-dimensional model of the global ammonia cycle. *J. Atmos. Chem.* **19**, 331–369 (1994).
- Liu, X. *et al.* Nitrogen deposition and its ecological impact in China: an overview. *Environ. Pollut.* **159**, 2251–2264 (2011).
- Ding, G., Xu, X., Wang, S., Yu, X. & Cheng, H. Database from the acid rain network of China Meteorological Administration and its preliminary analysis. *J. Applied Meteorological Sci.* **15**, 85–94 (2004).
- Sheng, W. *et al.* Monitoring nitrogen deposition in typical forest ecosystems along a large transect in China. *Environ. Monit. Assess.* **185**, 833–844 (2013).
- Liu, X. *et al.* Enhanced nitrogen deposition over China. *Nature* **494**, 459–462 (2013).
- Lü, C. & Tian, H. Spatial and temporal patterns of nitrogen deposition in China: Synthesis of observational data. *J. Geophys. Res.* **112**, doi: 10.1029/2006JD007990 (2007).
- Zhao, Y. *et al.* Soil acidification in China: Is controlling SO<sub>2</sub> emissions enough? *Environ. Sci. Technol.* **43**, 8021–8026 (2009).
- Yin, S. Study on anthropogenic ammonia emission inventory in the Pearl River Delta and effects on source contribution to particulate matter formation. *PhD thesis, South China University of Technology* (2011).
- Zhang, Q. *et al.* NO<sub>x</sub> emission trends for China, 1995–2004: The view from the ground and the view from space. *J. Geophys. Res.* **112**, doi: 10.1029/2007JD008684 (2007).
- Ohara, T. *et al.* An Asian emission inventory of anthropogenic emission sources for the period 1980–2020. *Atmos. Chem. Phys.* **7**, 4419–4444 (2007).
- Holland, E. A., Braswell, B. H., Sulzman, J. & Lamarque, J. F. Nitrogen deposition onto the United States and Western Europe: synthesis of observations and models. *Ecol. Appl.* **15**, 38–57 (2005).
- Duan, L., Xie, S. D., Zhou, Z. P., Ye, X. M. & Hao, J. M. Calculation and mapping of critical loads for S, N and acidity in China. *Water, Air, Soil Pollut.* **130**, 1199–1204 (2001).
- Bouwman, A. F., Van Vuuren, D. P., Derwent, R. G. & Posch, M. A global analysis of acidification and eutrophication of terrestrial ecosystems. *Water, Air, Soil Pollut.* **141**, 349–382 (2002).
- Russell, K. M., Galloway, J. N., Macko, S. A., Moody, J. L. & Scudlark, J. R. Sources of nitrogen in wet deposition to the Chesapeake Bay region. *Atmos. Environ.* **32**, 2453–2465 (1998).
- Hastings, M. G., Sigman, D. M. & Lipschultz, F. Isotopic evidence for source changes of nitrate in rain at Bermuda. *J. Geophys. Res.* **108**, doi: 10.1029/2003JD003789 (2003).
- Zhan, X. Variations in nitrogen deposition and nitrogen use efficiency of forest ecosystems along the North-South Transect of Eastern China. *PhD thesis, University of Chinese Academy of Sciences* (2013).
- De Vries, W., Reinds, G. J., Gundersen, P. & Sterba, H. The impact of nitrogen deposition on carbon sequestration in European forests and forest soils. *Glob. Change Biol.* **12**, 1151–1173 (2006).
- Hyvönen, R. *et al.* Impact of long-term nitrogen addition on carbon stocks in trees and soils in northern Europe. *Biogeochemistry* **89**, 121–137 (2007).
- Sutton, M. A. *et al.* Uncertainties in the relationship between atmospheric nitrogen deposition and forest carbon sequestration. *Glob. Change Biol.* **14**, 2057–2063 (2008).
- Nadelhoffer, K. *et al.* Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. *Nature* **398**, 145–148 (1999).
- Pregitzer, K. S., Burton, A. J., Zak, D. R. & Talhelm, A. F. Simulated chronic nitrogen deposition increases carbon storage in Northern Temperate forests. *Glob. Change Biol.* **14**, 142–153 (2007).
- De Vries, W. *et al.* Ecologically implausible carbon response? *Nature* **451**, E1–E3 (2008).
- Dezi, S., Medlyn, B. E., Tonon, G. & Magnani, F. The effect of nitrogen deposition on forest carbon sequestration: a model-based analysis. *Glob. Change Biol.* **16**, 1470–1486 (2010).
- State Forestry Administration. The seventh national forest resources inventory and the status of forest resources. *Forest Resources Man.* **1**, 1–8 (2010).
- Gregg, J. S., Andres, R. J. & Marland, G. China: Emissions pattern of the world leader in CO<sub>2</sub> emissions from fossil fuel consumption and cement production. *Geophys. Res. Lett.* **35**, doi: 10.1029/2007GL032887 (2008).
- Zhang, Y. *et al.* Agricultural ammonia emissions inventory and spatial distribution in the North China Plain. *Environ. Pollut.* **158**, 490–501 (2010).
- Dong, W., Xing, J. & Wang, S. Temporal and spatial distribution of anthropogenic ammonia emissions in China: 1994–2006. *Environ. Sci.* **31**, 1457–1463 (2010).
- Tian, H., Hao, J., Lu, Y. & Zhu, T. Inventories and distribution characteristics of NO<sub>x</sub> emissions in China. *China Environ. Sci.* **21**, 493–497 (2001).
- National Bureau of Statistics of China. *China Statistical Yearbook* (China Statistics Press, 1991–2010).
- Department of Energy Statistics, National Bureau of Statistics of China. *China Energy Statistics Yearbook* (China Statistical Press, 1995–2010).

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## Author contributions

Y.J. analysed the data and wrote the manuscript. G.Y. and N.H. supervised the project and commented on the contents of the manuscript. X.Z., H.F., W.S., Y.Z. and Y.J. collected the datasets and conducted the data pre-processing. D.Z. and Q.W. revised and edited the manuscript.



## Additional information

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