Reply to interactive comments on "Imbalanced phosphorus and nitrogen deposition in China's forests" by Anonymous Referee #1

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Review:

This is a potentially publishable article about an interesting topic (N:P ratios in deposition in China), but there are a few points that need modification and/or justification before the paper can be accepted.

Reply: Thank you. We have revised the manuscript according to your suggestions.

Major point: How can you deduce dry deposition from throughfall and precipitation concentrations? This needs to be better explained or justified, and the following points are where I get confused.

Reply: Before going into the detailed questions we like to give a general overview of our assumptions, which we have now also included in the manuscript. Canopy-captured dry deposition accumulates during periods without precipitation and it is washed down during precipitation events. Here we calculated canopy-captured dry deposition as the difference between bulk deposition and the estimated total deposition. In our original manuscript, total deposition was estimated based on throughfall concentrations and total (bulk) precipitation but in the revised manuscript we now multiply it with the sum water flux of throughfall and stemflow. To estimated the sum water flux of throughfall and stemflow, we establish a new database of observed throughfall and stemflow (including data from 28 forested stands from 26 sites, see Figure R1 as below) and explored an empirical equation between *precipitation and the sum of throughfall and stemflow (TS =0.88×precipitation-64.6, R^2=0.97). The sum of throughfall and stemflow water fluxes for each forested site was then estimated from the available bulk precipitation data based on this empirical equation. We realize that our estimate of canopy-captured dry deposition is lower than total dry deposition because a proportion of dry deposition is already included in bulk deposition and our estimate of total deposition is likely underestimated due to the neglect of canopy uptake (Reddy and Majmudar, 1983; Draaijers et al., 1996; Sparks, 2009) and stemflow enrichment (N & P concentrations in stemflow are generally higher than that in throughfall). We now mention this explicitly in the discussion and we will include detailed information on the method and uncertainty in the method section in the revised manuscript.*

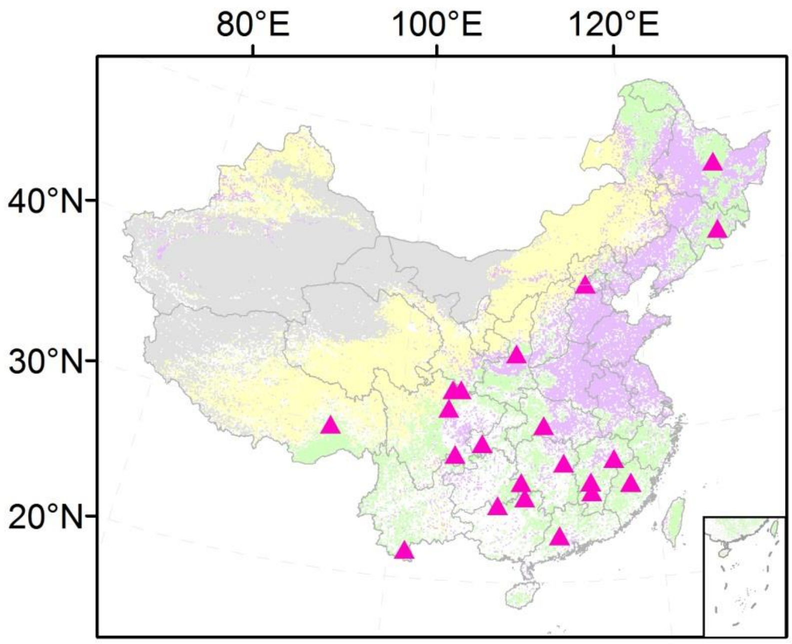

Figure R1. Distribution of 26 sites with measured data of throughfall and stemflow.

"Phosphorus and N fluxes in the bulk precipitation and throughfall were estimated according to the volume-weighted mean concentration and annual precipitation." So you are taking your measured concentrations in each precip and throughfall and multiplying by annual precip? But not all the precip comes out in throughfall does it?

Reply: This is a correct comment. Indeed not all precipitation comes out in throughfall and we now do not use total (bulk) precipitation any more but the sum of throughfall and stemflow water fluxes estimate (see above). On an annual basis, total deposition can be estimated as the sum of N/P fluxes in throughfall and stemflow as well as *canopy exchange (see Figure R2 as below). Due to a lack of measured data on canopy exchange and stemflow concentrations, we approximately estimated total deposition by multiplying the volume-weighted mean N/P concentration in throughfall with the sum of throughfall and stemflow water fluxes in the revised manuscript. Our results generally underestimate total deposition because concentrations in throughfall usually are much lower than those in stemflow and tree foliage can take up a small proportion of soluble N and P in rainwater and gaseous N (part of dry deposition) (Reddy and Majmudar, 1983; Draaijers et al., 1996; Sparks, 2009). More detailed information on the method and its uncertainty will be included in the revised manuscript.*

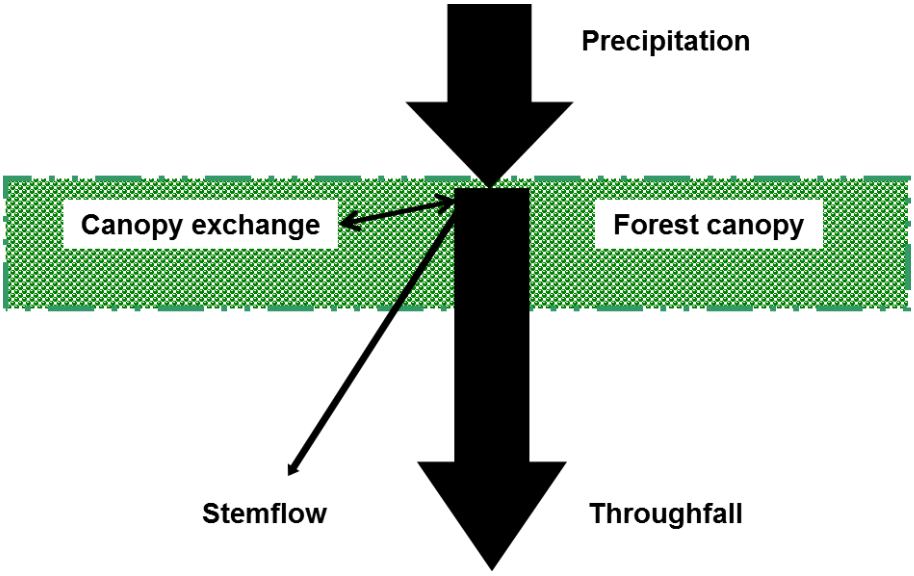

Figure R2. Partition of nitrogen or phosphorus flows when rainwater passes through forest canopy.

Canopy captured dry deposition was estimated as the difference between throughfall deposition and bulk deposition." How can you get dry deposition from the difference in two wet deposition numbers? Later on you try to use this: "Based on the P enrichment in throughfall versus bulk precipitation, the mean canopy captured dry P deposition was estimated as high as 0.46 kg P ha-1 yr-1 in China's forests, being significantly higher than bulk deposition (0.38 kg P ha-1 yr-1) (paired t-test, df = 32, $p < 0.01$)." So I think you need to be a bit clearer: maybe make a skematic of your assumptions?

Reply: Canopy-captured dry deposition is defined as the amounts of dry deposition captured and accumulated in forest canopy during the period without precipitation events. Therefore, we calculated the canopy-captured dry deposition as the difference between bulk deposition and the estimated total deposition (as described above). The *new result indicate that mean canopy captured dry P deposition was estimated to be 0.40 kg P ha^{-1} yr^{-1} in China's forests, being comparable to bulk deposition (0.38 kg P ha^{-1} yr^{-1}) (paired t-test, df = 32, p = 0.36). We will include more detailed information on the method in the method section and discussed uncertainties of our results in the revised manuscript.*

Again you say something here that doesn't make sense to me: "Although throughfall may still underestimate total deposition due to canopy uptake (Draaijers et al., 1996; Sparks, 2009), it is a better proxy of total N deposition than bulk deposition because bulk deposition only accounts for 63% of throughfall deposition."

Reply: The last part of this sentence may have caused confusion but our point is that even though throughfall may underestimate total deposition it is a better proxy of total N deposition than bulk deposition that makes a much larger underestimation. We now changed the sentence to: "Although our estimate based on annual sum of throughfall and stemflow water fluxes and total N concentrations in throughfall is still lower than the factual total deposition because tree foliage can take up a small proportion of gaseous N (part of dry deposition) and soluble N in rainwater (Draaijers et al., 1996; Sparks, 2009) and the stemflow N flux is likely underestimated, it is a better proxy of total N deposition than bulk deposition." In addition, the uncertainties of our estimates are also discussed in the revised Discussion section.

Are you only concerned with soluble P?

Reply: Our analysis focused on total P concentrations, which were measured after digestion and include dissolved inorganic forms, dissolved organic forms and particulate forms. This is mentioned in the text of the method section.

It is important to clarify these points. If you are going to argue that from two wet deposition numbers you can deduce dry deposition and total deposition, then maybe you want to verify at a point where you have all three numbers to show that your approach works? Your paper could be publishable with only wet deposition numbers, but I think you just need to be clear about what your results are.

Reply: Thank you for your suggestions. More detailed information on the method and uncertainty has been included in the revised manuscript (also see replies above).

Secondary points: In the comparison to the model results there are two issues:

i. "Anthropogenic sources have been traditionally thought to make only a small contribution to P deposition (Okin et al., 2004; Mahowald et al., 2008). In contrast, our results emphasize that anthropogenic sources near large cities can have significant impacts on the spatial patterns of regional P deposition. The urban hotpot of P deposition might be derived from intensive combustion-related emissions near urban areas (Wang et al., 2015) and a short-distance transfer of P-containing aerosols from P-rich farmland soils (Anderson et al., 2006)." The problem with this conclusion is that it contradicts the observations here that the highest P deposition comes from regions close to the arid sources of dust: so your gradient suggests the dominant sources are dust related. Even using the smaller anthropogenic source of Mahowald et al., 2008, anthropogenic sources should dominate near cities in China (Figure 5h: Mahowald et al., 2008). So I would actually argue that your data supports Mahowald et al., 2008's budgets quite well. In contrast, from Wang et al., 2015, you shouldn't be seeing a P deposition gradient across China (Figure 3) from the arid regions, but only the combustion hot spots. You could actually be a bit quantitative and do the comparison against the model output from these two models, to discriminate between them? See if there is a statistically significant difference in the comparison?

Reply: Our results show significantly higher P deposition nearby than far from semiarid regions and this indeed supports Mahowald et al., 2008's conclusions that large-scale gradients of P deposition are dust dominated. At regional scale, either far from or nearby the semiarid regions, our results indicate that P deposition showed a significant power-law increase with closer distance to the nearest large cities and this supports Wang et al., 2015's conclusion that anthropogenic contribution to P deposition can be substantial. Overall, our results don't contradict the conclusions either by Mahowald et al.(2008) or Wang et al. (2015). Moreover, the modelling results usually have a very coarse resolution and are not suitable for quantitative comparison with our datasets. We have revised the text to make this point more clear.

ii. Both the model of Mahowald et al., 2008 and Wang et al., 2015 only include long range transported P, so less than 10um or 20um particles. Your results, in contrast, should be including all P (unless you are only looking at soluble P, which should then not be compared to Wang et al., 2015 and only the soluble P in Mahowald et al., 2008). In forests, most of the P is in much larger mode particles, locally generated, according to previous observational synthesis (and the observational studies within them; e.g. Tipping et al., 2014). So it is likely you have a mismatch in the P deposition you are comparing (see Mahowald et al., 2008; Neff et 2009; Brahney et al., 2015 for more discussion on how to compare observational P fluxes across sizes to models or not). Notice that Wang et al., 2015 is very careful about the size of their emitted combustion P particles, but not at all careful about the size of the particles in the deposition P dataset they use (Tipping et al., 2014; which is dominated by large local generated primary biogenic particles, according to that study), compared to the particles that they are modeling (long range transported particles <20um). They actually use the mismatch in particle size and the resulting mismatch in deposition magnitude to deduce the extra-large combustion source they postulate, which makes that study problematic in its conclusions.

Reply: In the discussion section, we mostly compared our results with other assessments based on observations (e.g. Tipping et al., 2014, Vet et al., 2014). We have already recognized that different studies may focus on different components of P and therefore we are very careful when making comparison with other results.

Minor points:

Section 3.1: I am not sure what I am supposed to get out of knowing that the data follows a log-normal distribution for P or N or N:P. Isn't this what we expect? I think this would be better illustrated with a figure of the distribution, if you think it's important enough to discuss?

Reply: The description of datasets (e.g. arithmetic mean for a normal distribution and geometric mean for a log-normal distribution) should be according to their distribution. Therefore, we tested the distribution of the datasets at the beginning.

"Spatial patterns of P deposition via bulk precipitation and throughfall showed large heterogeneity" This is a factor of 4. Globally, the deposition varies by several orders of magnitude, so I'm not sure I would call this a large spatial hetereogeneity. Maybe just say the values vary by a factor of 4.

Reply: We have done so.

Some English errors, especially in the few last lines of the introduction, should be fixed.

Reply: We have checked and corrected all the linguistics errors in the manuscript.

References:

Draaijers, G. P. J., Erisman, J. W., Sprangert, T. and Wyers, G. P. 1996. The application of throughfall measurements for atmospheric deposition monitoring. Atmospheric Environment: 30(19), 3349–3361.

Reddy, S. E., Majmudar, A. M. 1983. Response of mango (Mangifera indica L.) to foliar application of phosphorus. Fertilizer Research 4(3): 281-285.

Sparks, J. P.2009. Ecological ramifications of the direct foliar uptake of nitrogen. Oecologia: 159, 1–13.

Reply to interactive comment on "Imbalanced phosphorus and nitrogen deposition in China's forests" by Anonymous Referee #2

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Review:

This is an interesting paper, discussing a previously not available dataset on phosphorus and nitrogen deposition fluxes on forests (through fall and bulk deposition). The paper is well written, and the context and relevance are well explained. The issue of increasing dis-balance of phosphorous to nitrogen ratios may further worsen, if fire from coal and biofuel use in China will be reduced, and/or particulate emissions will be better controlled. This issues could warrant some further discussion.

Reply: Thank you very much. In the revised manuscript, we will include a short discussion on future changes in the imbalance of P and N deposition in the ending paragraph.

I see some major weaknesses of this study:

1) The assumption that bulk minus through equals dry deposition is rather challenging. Throughfall measurements are easily compromised by input from the canopy, it is not clear what was done to prevent this. For N bulk deposition may not capture input potential significant input from gaseous nitric acid- and may in this sense not be a good proxy for total deposition. Some discussion on the specific situation in China is warranted. I guess the applicability of the approach to estimate phosphorus deposition is even less well known. At any rate a better quantification of errors is needed.

Reply: Thanks for this useful and correct comment. Canopy-captured dry deposition accumulates during periods without precipitation and it is washed down during precipitation events. Therefore, we calculated canopy-captured dry deposition as the difference between bulk deposition and the estimated total deposition. On an annual basis, total deposition can be estimated as the sum of N/P fluxes in throughfall and stemflow as well as canopy exchange. In the revised manuscript, we approximate total deposition by multiplying the volume-weighted mean N/P concentration in throughfall with the sum of throughfall and stemflow water fluxes because of a lack of measured data on canopy exchange and stemflow concentrations. We realize that our results generally underestimate total deposition because concentrations in throughfall usually are lower than those in stemflow (underestimate of N/P fluxes in stemflow) and tree foliage can take up tree foliage can take up a small proportion of soluble N and P in rainwater and gaseous N (part of dry deposition) (Reddy and Majmudar, 1983; Draaijers et al., 1996; Sparks, 2009). We also realize that our estimate of canopy-captured dry deposition is lower than total dry deposition because a proportion of dry deposition is already included in bulk deposition and the total deposition is likely underestimated due to the neglect of canopy uptake (Reddy and Majmudar, 1983; Draaijers et al., 1996; Sparks, 2009) and the underestimate of stemflow N/P fluxes. More detailed information on the method and uncertainty will therefore be included in the revised manuscript to answer your concerns.

2) the constraint of only using bulk deposition and throughfall observations (where both are available), is providing a very limited amount of observations, and raises questions about representativity for larger regions. I understand that a wider dataset of deposition measurements are available in other ecosystems (e.g. the authors mention that N-dep

is relatively well known), and I would recommend to analyse also these in the context of this core set of depositions over forests. To what extent are the forest observation consistent with nearby depositions over other regions? Are the same urban-rural decay of depositions observable also in other datasets? What would wet-versus bulk versus throughfall tell?

Reply: Thank you very much for your suggestions. The database used in this study has included most of the forest sites where nutrient deposition has been observed. Moreover, these sites are evenly distributed in the forested areas in China (Figure S1). We believe that the datasets used in this study currently is the best to represent the observations of N and P deposition in China's forest. As indicated by the title, our analysis has been focused on China's forest ecosystems where the response of C sequestration to atmospheric nutrient deposition currently is a core topic. In addition, our estimates of total deposition are based on throughfall N/P concentrations and annual *precipitation and this method is not applicable in other types of ecosystem. Nevertheless, a previous analysis on wet N deposition across China has also indicated an urban-rural decay of N deposition (Du, E.Z. and Liu, X.J.: High rates of wet nitrogen deposition in China: A synthesis. In: Sutton, M. A., Mason, K. E., Sheppard, L. J., Sverdrup, H., Haeuber, R., Hicks W. K. (eds.) Nitrogen Deposition, Critical Loads and Biodiversity. Springer, Netherlands, pp 49–56, 2014.).*

3) As the motivation of the study is to point to a dis-balance in P:N ratios- I wonder how the numbers in this study compare to published and modeled deposition maps of N and P, used as input to vegetation models. For instance p6/l3 mentions a number of 4.6 Tg N/yr deposition on Chinese forests. In my impression this is not very different from model estimates, but this can be corroborated. How would the estimate of P deposition compare to current estimates (e.g. Wang 2015; Mahowald; 2008). Nevertheless, altogether an important dataset and analysis, which I would recommend to publish in ACP, after duly accounting for these comments.

Reply: There have been rare literatures which focus on total N and P inputs into China's forests. This hinders the comparison between our estimates with others. Nevertheless, our results in China's forests are comparable to the ranges of modelled P deposition in China (Wang et al., 2015). This is now indicated in the text. Unfortunately, the modelling results by Mahowald et al (2008) have a very coarse resolution and are not suitable for comparison with our datasets.

Minor comment:

P 3/l 9: what is taken city-centre or city-boundary? How defined?

Reply: The distance between the sampling site and the centre of the nearest large city (non-agricultural population > 0.5 million) was derived using Google Earth for Microsoft Windows. The city centre is defined as the geometric centre of the city area. We have included the information in the revised manuscript.

p. 6 l 24 were is this number coming from?

Reply: The number 63% is the percentage that bulk N deposition (16.5 kg N ha^{-1} yr^{-1}) accounts for the total N deposition (26.2 kg N ha^{-1} yr^{-1}) estimated based on annual precipitation and total N concentrations in throughfall. In the revised manuscript, we re-estimated total deposition by multiplying the volume-weighted mean N/P concentration in throughfall with the sum water flux of throughfall and stemflow (see replies above).The updated results indicate that bulk N deposition (16.5 kg N ha^{-1} yr^{-1}) accounts for 76% of the total N deposition (21.6 kg N ha^{-1} yr^{-1}).

Imbalanced phosphorus and nitrogen deposition in China's forests

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Abstract. Acceleration of anthropogenic emissions in China has substantially increased nitrogen (N) deposition during last three decades and may result in an imbalance of atmospheric N and phosphorus (P) inputs in terrestrial ecosystems. However, the status of P deposition in China is poorly understood. This study synthesized data on total P and total N concentrations in bulk precipitation and throughfall from published literature to assess the characteristics of P deposition, N deposition and N:P deposition ratio in China's forests. Our results show relatively high mean rates of bulk P deposition (0.38 kg P ha^{-1} yr^{-1}) and total P deposition (0.69 kg P ha^{-1} yr^{-1}), but they were accompanied by even much more elevated N inputs via bulk deposition (16.5 kg N ha^{-1} yr^{-1}) and total deposition (21.6 kg N ha^{-1} yr^{-1}), resulting in high N:P ratios in bulk deposition (44.4) and total deposition (32.8), respectively. Based on the difference between total deposition and bulk deposition, canopy-captured dry P and N deposition is estimated to be 0.31 kg P ha^{-1} yr^{-1} and 5.1 kg N ha^{-1} yr^{-1}, respectively. We found significantly higher P deposition and lower N:P ratios at sites nearby than those far from semiarid regions. The estimated bulk and total deposition of P and N both showed a significant power-law increase with closer distance to the nearest large cities either in the areas nearby or far from semiarid regions. Our results suggest an anthropogenic alternation of regional P and N cycling, which might shift large areas of China's forests towards human-induced P limitation especially in southern China.

1 Introduction

Nitrogen (N) and phosphorus (P) are essential macronutrients, both of which widely limit primary productivity across terrestrial ecosystems (Elser et al., 2007; Vitousek et al., 2010). New N inputs to terrestrial ecosystems are driven by biological N fixation and atmospheric deposition, the latter being increasingly important (Cleveland et al., 2013). Acceleration of anthropogenic N emissions has substantially increased N deposition in China during last three decades and aroused widespread concerns about the consequent impacts on various ecosystems (Liu et al., 2011 & 2013; Cui et al., 2013). Enhanced N deposition often stimulates forest growth and hence carbon sequestration (Högberg, 2007; De Vries et al., 2009;

Thomas et al., 2010), but the expected growth acceleration might be diminished when the accompanied P supply is deficient (Braun et al., 2010; Li et al., 2016). Soil P availability in terrestrial ecosystems is primarily driven by mineral weathering and atmospheric deposition (Vitousek et al., 2010; Cleveland et al., 2013). Newman (1995) reviewed P deposition and weathering in global terrestrial ecosystems and estimated a range of 0.07 – 1.7 kg P ha^{-1} yr^{-1} for P deposition and 0.01 – 1.0 kg P ha^{-1} yr^{-1} for P weathering, indicating that both fluxes are in the same order of magnitude. More recent assessment on observed and modelled P deposition rates on a global scale (Mahowald et al., 2008; Wang et al., 2015) show a range of 0.01 − 1.0 kg P ha^{-1} yr^{-1} on land. Despite the significant role of P deposition, its status and characteristics are poorly understood in China.

Considering the importance of atmospheric deposition for N and P availability, the variation in N and P deposition may make a difference in N or P-limited ecosystems (Peñuelas et al., 2013). Spatial patterns and temporal trends of N deposition have recently been well characterized in China (Liu et al., 2013; Du and Liu, 2014; Lu and Tian, 2014; Jia et al., 2014; Du et al., 2014; Xu et al., 2015; Zhu et al., 2015). However, most assessments on N deposition in China have been based on measurements of bulk deposition (Liu et al., 2013), which substantially underestimates the levels of total deposition because it consists mainly of wet deposition (Kulshrestha et al., 1995; Staelens et al., 2005; Chantara and Chunsuk, 2008). The N flux in throughfall has been used as a more precise estimate of total deposition (Du et al., 2014 & 2015), although it is still an underestimate due to neglect of N input by stemflow and the occurrence of canopy N uptake, especially at lower N deposition levels (Draaijers et al., 1996; Sparks, 2009). Unlike N, there is a lack of evaluation on P deposition across China. In the context of low soil P contents in terrestrial ecosystems across most areas of China (Jiang et al., 1986; Han et al., 2005), the role of P deposition is relevant because high-level N deposition, initially stimulating forest growth, is likely shifting large areas of China's forests towards P limitation.

Previous studies have indicated that large cities in China are hotspots of N deposition (Du et al., 2014 & 2015) because the enhancement of N deposition is primarily driven by anthropogenic emissions from power generation, motor traffic and agricultural activities near urban areas (Liu et al., 2013; Jia et al., 2014). Unlike reactive N which can form stable gaseous compounds (e.g. NO_x and NH_3), atmospheric P occurs primarily in the form of coarse particles and is dominantly derived from mineral dust in natural conditions (Mahowald et al. 2008; Vet et al., 2014). Higher P deposition is thus expected nearby the semiarid regions, where receive large amounts of P-containing particulates transported from neighbouring deserts or barren lands due to the effect of wind erosion (Okin et al., 2004; Mahowald et al. 2008). Based on measurements of P content in various fuels and estimates of the P partitioning during combustion processes, a recent assessment indicates that anthropogenic sources, such as combustion-related emissions, can contribute to over 50% of the global atmospheric P and make a substantial contribution to global P deposition (Wang et al., 2015). We can thus expect higher P deposition nearby large cities with intensive anthropogenic P emissions, although the transportation of P-containing dust may lead to distinct urban hotspots of P deposition nearby and far from the semiarid regions. Here we synthesized data on total P and total N concentrations in bulk precipitation and throughfall from published literature to assess the status and characteristics of P deposition, N deposition and N:P deposition ratios in China's forests. Moreover, we also tested whether spatial patterns of P deposition showed an increase with closer distance to large cities.

2. Data and methods

2.1 Data sets

We collected data from published literatures on total P and total N concentrations in bulk precipitation and throughfall for typical forests in China, as well as information on site location (latitude and longitude) and annual precipitation. Total P and total N concentrations were assessed after digestion and include dissolved inorganic forms, dissolved organic forms and particulate forms. Observational data were selected only when P and/or N concentrations in precipitation and throughfall were measured simultaneously. Data on P and N concentrations for each sampling period were either taken directly from tables or digitized from figures using a GetData Graph Digitizer (Version 2.25, http://www.getdata-graph-digitizer.com). If concentration data at one site were measured for more than one forest stand or available for more than one year, a volume-weighted mean was calculated and used for further analysis. The distance between the sampling site and the geometric centre of the nearest large city (non-agricultural population > 0.5 million) was derived using Google Earth for Microsoft Windows (Version 7.1.5.1557, Google Inc., USA).

Our database consisted of 33 sites which were distributed across main forest biomes in China (see Fig. S1 and Table S1 for detailed information). Annual precipitation ranged from 500 mm to 2900 mm. The distance from the sampling sites to the nearest large cities ranged from 5 km to 465 km. Using a criteria of a distance of 400 km to the semiarid regions (e.g. grassland), we grouped our datasets into sites nearby semiarid regions (n= 11) and sites far from the semiarid regions (n=22) (Fig. S1).

2.2 Calculation of bulk deposition, total deposition and canopy-captured dry deposition

Bulk deposition of total P and total N was calculated by multiplying the volume-weighted mean concentration in bulk precipitation with annual precipitation. Canopy-captured dry deposition accumulates during periods without precipitation and it is washed down during precipitation events. On an annual basis, total deposition can be estimated as the sum of N or P fluxes in throughfall, stemflow and canopy exchange (Fig. S2). Due to a lack of measured data on canopy exchange and stemflow concentrations, we approximate total deposition by multiplying the volume-weighted mean concentration in throughfall with the sum water fluxes of throughfall and stemflow. To estimate the sum water flux of throughfall and stemflow, we establish a database of observed throughfall and stemflow (including data from 28 forested stands from 26 sites, Fig. S3) and explored an empirical equation between precipitation and the sum water flux of throughfall and stemflow (Fig. S4). The sum of throughfall and stemflow water fluxes for each forested site was then estimated from the available bulk precipitation data based on this empirical equation. This method generally underestimates the factual total deposition. First, tree foliage can take up a small proportion of soluble N and P in rainwater and gaseous N (part of dry deposition) (Reddy and Majmudar, 1983; Draaijers et al., 1996; Sparks, 2009). Moreover, P and N fluxes in stemflow were underestimated because throughfall concentrations of N or P generally were lower than those in stemflow. However, the total element input by stemflow is mostly less than 5% of that by throughfall (e.g. Talkner et al., 2010) and thus it only introduces a small error of the overall estimate.

Canopy-captured dry deposition, defined as the amounts of dry deposition captured and accumulated in forest canopy during the period without precipitation events, was calculated as the difference between the estimated total deposition and bulk deposition. Our estimate of canopy-captured dry deposition is lower than total dry deposition because a proportion of dry deposition is already included in bulk deposition and the total deposition is likely underestimated.

2.3 Statistical analysis

A Shapiro-Wilk normality test was used to test whether data were normally distributed. Data ranges were indicated by the first and third quantile. We used a paired sample t-test to test the differences of concentrations and N:P ratios between bulk precipitation and throughfall. A Student's t-test was used to test the difference of N deposition levels between sites nearby the semiarid regions (n=11) and far from the semiarid regions (n=22).

Previous studies have indicated that N deposition shows a power-law increase with closer distance to the nearest large cities (Du et al., 2014 & 2015). To test the urban hotspot hypothesis of P deposition, we also used a power-law model to explore changes in concentrations and fluxes of total P with the distance between the sampling site and the nearest large city. The analysis was conducted separately for sites nearby the semiarid regions (n=11) and far from the semiarid regions (n=22). Spatial patterns of P deposition, N deposition and N:P ratios were illustrated using ArcGIS Desktop (version 9.3, ESRI, USA). All statistical analysis was performed using R software (version 3.1.0; R Development Core Team, 2014, http://www.r-project.org/) with a significance level of $p < 0.05$.

3. Results

3.1 Concentrations and deposition of total phosphorus

Phosphorus concentrations in bulk precipitation and throughfall were characterized by a log-normal distribution (Shapiro-Wilk normality test, $p > 0.10$). The geometric mean of P concentration in throughfall (0.068, ranging 0.041 – 0.138 mg P L^{-1}) was significantly higher (paired sample t-test, $df = 32$, $p < 0.01$), on average being 2.18 (1.40 – 3.11) times of that in bulk precipitation (0.031, ranging 0.017 – 0.050 mg P L^{-1}). Similarly, bulk P deposition and total P deposition were also characterized by a log-normal distribution (Shapiro-Wilk normality test, $p > 0.10$), showing geometric means at 0.38 (0.21 – 0.57) and 0.69 (0.40 – 1.20) kg P ha^{-1} yr^{-1}, respectively. The canopy-captured dry P deposition, calculated as the difference between total deposition and bulk deposition, was estimated at 0.31 kg P ha^{-1} yr^{-1}, being comparable to bulk P deposition (paired sample t-test, $df = 32$, $p = 0.36$).

Spatial patterns of bulk P deposition and total P deposition showed remarkable heterogeneity, varying by a factor exceeding four (Fig. 1a and 1b). Specifically, geometric means of bulk P deposition and total P deposition were estimated to be 0.54 (0.39 – 0.98) and 0.97 (0.74 – 1.27) kg P ha^{-1} yr^{-1} at the 11 sites nearby the semiarid regions. At the other 22 sites far from the semiarid regions, geometric means of bulk P deposition and total P deposition were significantly lower (Student's t-test, $df = 31$, $p < 0.01$), being 0.31 (0.20 – 0.50) and 0.57 (0.26 – 1.05) kg P ha^{-1} yr^{-1}, respectively.

3.2 Concentrations and deposition of total nitrogen

Concentrations and fluxes of total N were also log-normally distributed (Shapiro-Wilk normality test, $p > 0.10$). The geometric mean of total N concentration in bulk precipitation were 1.34 (0.88 – 2.19) mg N L^{-1} and increased significantly (paired sample t-test, $df = 31$, $p < 0.01$) to 2.13 (1.23 – 3.87) mg N L^{-1} in throughfall. Geometric means of bulk N deposition and total N deposition were 16.5 (9.9 – 24.2) and 21.6 (15.0 – 31.2) kg N ha^{-1} yr^{-1}, leading to an estimate of canopy-captured dry N deposition of 5.1 kg N ha^{-1} yr^{-1}. The ratio of total deposition versus bulk deposition was 1.31 (0.98 – 1.60) for N, which was significantly lower than that (1.80, 1.19 – 2.56) for P (paired sample t-test, $df = 31$, $p < 0.01$). Spatial patterns of bulk N deposition and total N deposition showed several regional hotspots near large city clusters in central, eastern and southern China (Fig. 2a and 2b).

3.3 Ratios of nitrogen deposition versus phosphorus deposition

The N:P ratios in bulk precipitation and throughfall were also characterized by a log-normal distribution (Shapiro-Wilk normality test, $p > 0.10$). The geometric mean of N:P ratio was 44.4 (23.1 – 97.6) in bulk precipitation and decreased to 32.8 (18.7 – 63.6) in throughfall. At the 11 sites nearby the semiarid regions, the geometric mean of N:P ratio in bulk precipitation and throughfall were estimated at 19.3 (9.1 – 39.9) and 16.2 (10.9 – 28.6), respectively. However, the N:P ratios in bulk precipitation (geometric mean = 64.0, ranging 40.9 – 116.7) and throughfall (geometric mean =45.3, ranging 25.8 – 74.6) were significantly higher (Student's t-test, $df = 31$, $p < 0.01$) at the other 22 sites far from the semiarid regions, most of which were located in southern China (Figs. 3a and 3b).

3.4 Urban hotspots of phosphorus and nitrogen deposition

Bulk P deposition and total P deposition both showed a significant power-law increase with closer distance to the nearest large cities, either nearby or far from the semiarid regions (Figs. 4a, 4d, 5a & 5d). In line with the urban hotspot hypothesis, bulk N deposition and total N deposition also showed a significant power-law increase with closer distance to the nearest large cities (Figs. 4b, 4e, 5b & 5e). At sites far from semiarid regions, N:P ratios in bulk precipitation and throughfall both showed no significant trend with changing distance to the nearest large cities (Figs. 4c & 4f). However, the N:P ratios in throughfall at sites nearby semiarid regions showed a significant power-law increase with closer distance to the nearest large cities, while no such trend was found for N:P ratios in bulk precipitation (Figs. 5c & 5f).

4. Discussion

4.1 Phosphorus deposition in China's forests

Atmospheric P-containing aerosols are either scavenged by precipitation or gravitationally deposited to the ground surface during dry weather. Based on very limited measurements of wet deposition around the world, Vet et al. (2014) summarized that total P fluxes in wet deposition range from 0.04 to 0.32 kg P ha^{-1} yr^{-1}. However, most reported measurements are based on bulk deposition, which includes wet deposition plus a fraction of dry deposition. A recent synthesis of global datasets with 246 sites indicates that bulk deposition of total P is log-normally distributed and showed a geometric mean of 0.27 kg P ha^{-1} yr^{-1} (Tipping et al., 2014). However, large uncertainties remain in regional estimates due to the scarcity of observational data and unevenness of site distribution. For instance, mean bulk deposition of total P was estimated at 0.12 kg P ha^{-1} yr^{-1} in Asia based on measurements from only 7 sites (Tipping et al., 2014). Using observed data from 33 sites in China's forests, here we show much higher bulk deposition of total P with a geometric mean of 0.38 kg P ha^{-1} yr^{-1}. Overall, our estimate of bulk P deposition in China is higher than the estimates for Europe (0.22 kg P ha^{-1} yr^{-1}), Oceania (0.24 kg P ha^{-1} yr^{-1}) and North America (0.29 kg P ha^{-1} yr^{-1}) by Tipping et al. (2014), while it is lower than those in South America (0.43 kg P ha^{-1} yr^{-1}) and Africa (0.62 kg P ha^{-1} yr^{-1}).

Measurements of dry P deposition are rather scarce. Based on limited data of aerosol concentrations and the referential dry deposition velocity, Vet et al. (2014) estimated that annual dry deposition of total P on land ranges from 0.01 to 0.62 kg P ha^{-1} yr^{-1}. Based on the difference between total deposition and bulk deposition, here we estimated that the mean canopy-captured dry P deposition was as high as 0.31 kg P ha^{-1} yr^{-1} in China's forests. Although canopy-captured dry P deposition underestimates dry deposition because a proportion of dry deposition is already included in bulk deposition and the total N deposition was likely underestimated in this study, it was comparable to bulk deposition (0.38 kg P ha^{-1} yr^{-1}) (paired t-test, $df = 32$, $p = 0.36$). This result implies that dry deposition is an important pathway of atmospheric P deposition.

Our assessment shows that the geometric mean of total P deposition in China's forests was 0.69 (0.40 – 1.20) kg P ha^{-1} yr^{-1}, being comparable to the modelling results ranging from 0.4 − 1.0 kg P ha^{-1} yr^{-1} in the forested areas in China (Wang et al., 2015). Using the mean total deposition of 0.69 kg P ha^{-1} yr^{-1} and a forested area of 1.76 $\times 10^{8}$ ha (Zhang et al., 2010), we further estimated a total atmospheric P input of 0.12 Tg P yr^{-1} in China's forests.

Previous assessments have suggested that large-scale gradients of P deposition is dust dominated because mineral dust from neighbouring deserts contributes substantially to atmospheric P deposition in semiarid regions (Okin et al., 2004; Mahowald et al., 2008). Accordingly, our results also show that P deposition tended to be higher nearby the semiarid regions (Fig. 1a & 1b). Geometric means of bulk P deposition and total P deposition were estimated to be as high as 0.54 (0.39 – 0.98) and 0.97 (0.74 – 1.27) kg P ha^{-1} yr^{-1} nearby the semiarid regions, while the values were significantly lower (Student's t-test, $df = 31$, $p < 0.01$) far from the semiarid regions, being 0.31 (0.20 – 0.50) and 0.57 (0.26 – 1.05) kg P ha^{-1} yr^{-1}, respectively. This indicates a significant contribution of dust-borne sources to atmospheric P deposition in forest ecosystems nearby the semiarid regions.

4.2 Nitrogen deposition in China's forests

Our results show high levels of bulk N deposition and total N deposition in China's forests, on average being 16.5 kg N ha^{-1} yr^{-1} and 21.6 kg N ha^{-1} yr^{-1}, respectively. Most previous assessments on N deposition in China were either based on bulk deposition or wet deposition (Liu et al., 2013; Du and Liu, 2014; Jia et al., 2014; Du et al., 2014; Zhu et al., 2015; Xu et al., 2015), showing similar values (13.7 to 19.3 kg N ha^{-1} yr^{-1}) as our estimates based on bulk deposition in China's forests. Although our estimate based on total N concentrations in throughfall and annual sum of throughfall and stemflow water fluxes is still lower than the factual total deposition because tree foliage can take up a small proportion of gaseous N (part of dry deposition) and soluble N in rainwater (Draaijers et al., 1996; Sparks, 2009) and the stemflow N flux is likely underestimated, it is a better proxy of total N deposition than bulk deposition. Bulk deposition (16.5 kg N ha^{-1} yr^{-1}) only accounts for 76% of our estimate of total deposition (21.6 kg N ha^{-1} yr^{-1}) in China's forests. This difference leads to an estimate of canopy-captured dry N deposition of at least 5.1 kg ha^{-1} yr^{-1}, which is equivalent to 31 % of bulk deposition. The likely underestimation of this value is confirmed by a recent estimate based on airborne concentration measurements via a nationwide N deposition monitoring network and modelling inferential dry deposition velocity, which indicated that on average dry N deposition even exceeded wet/bulk deposition across China (Xu et al., 2015). Based on the mean total N deposition of 21.6 kg N ha^{-1} yr^{-1} and a forested area of 1.76×10^8 ha (Zhang et al., 2010), total N inputs via atmospheric deposition was thus estimated to be 3.8 Tg N yr^{-1} in China's forests.

4.3 Urban hotspots of phosphorus and nitrogen deposition

Bulk P deposition and total P deposition both showed a significant power-law increase with closer distance to the nearest large cities, either far from (Figs. 4a, 4d) or nearby (Figs. 5a & 5d) the semiarid regions. Anthropogenic sources have been traditionally thought to make only a small contribution to P deposition (Okin et al., 2004; Mahowald et al., 2008). In contrast, our results emphasize that anthropogenic sources near large cities can have significant impacts on the spatial patterns of regional P deposition. The urban hotpot of P deposition might be derived from intensive combustion-related emissions near urban areas (Wang et al., 2015) and a short-distance transfer of P-containing aerosols from P-rich farmland soils (Anderson et al., 2006).

Spatial patterns of bulk N deposition and total N deposition showed several regional hotspots near large city clusters in central, eastern and southern China (Fig. 2a and 2b). In line with our previous assessments on inorganic N deposition (Du et al., 2014 & 2015), bulk N deposition and total N deposition were also in accordance to the urban hotspot hypothesis (Figs. 4b, 4e, 5b & 5e). This spatial pattern has been attributed to intensive motor traffic, energy production, waste treatment and agricultural activities (mainly N-fertilizer application and livestock breeding) near urban areas (Du et al., 2014 & 2015). Overall, our results suggest that rapid urbanization in China may have exerted significant alternation of regional P and N cycling by enlarging anthropogenic emissions and deposition. In addition, the urban hotspot model is an important approach to describe the way in which large cities shape the spatial pattern of P and N deposition. Therefore, it should be incorporated in modelling of P and N deposition at regional scales.

At sites far from semiarid regions, N:P ratios in bulk precipitation and throughfall both showed no significant trend with changing distance to the nearest large cities (Figs. 4c & 4f), indicating an synchronous changes in P and N deposition around these urban hotspots. However, N:P ratios in throughfall at sites nearby semiarid regions showed a significant power-law increase with closer distance to the nearest large cities, while no such trend was found for N:P ratio in bulk precipitation (Figs. 5c & 5f). This distinct trend of N:P ratios in bulk precipitation and throughfall suggest a more rapid increase in dry N deposition than in dry P deposition with closer distance to the nearest large cities.

4.4 Implications of imbalanced phosphorus and nitrogen deposition

Our results indicated an imbalance of N and P supply by atmospheric nutrient deposition in China's forests. The N:P ratio generally showed high values (geometric mean = 44.4) in bulk precipitation in China's forests. Although the N:P ratio decreased in the throughfall, the geometric mean (32.8) was still more than twice of that in tree leaves (geometric mean N:P ratio = 15) (Han et al., 2005) and three times of that in current-year twigs (geometric mean N:P ratio = 10.6) (Yao et al., 2015). It is also much higher than critical N:P ratios related to relative P limitation in view of forest growth, which are near 15 for coniferous forests and near 25 for deciduous forests (after Mellert and Göttlein, 2012). Compared to the sites nearby semiarid regions, the imbalance of P and N deposition was more intense in forests of southern China, showing significantly higher N:P ratios in bulk precipitation (geometric mean = 64.0, ranging 40.9 – 116.7) and throughfall (geometric mean =45.3, ranging 25.8 – 74.6) (Figs. 3a & 3b). Moreover, the ratio of total N versus total P may overestimate the relative P supply versus N because a fraction of atmospheric N deposition is most likely already taken up by the canopy (Draaijers et al., 1996; Sparks, 2009) and a fraction of atmospheric P usually is not bioavailable (Mahowald et al., 2008; Tipping et al., 2014).

The imbalance of N and P deposition may lead to an increase in the N:P ratio of soils and plant tissues and hence a shift towards human-induced P limitation (Peñuelas et al., 2013). Accordingly, a recent assessment has shown that foliar N concentration of woody plants in China's non-agricultural ecosystems increased significantly between the 1980s and the 2000s, while leaf P concentration did not change significantly over the same period (Liu et al., 2013). In addition, mean leaf P concentrations of China's plants were found to be significantly lower than the global averages, most likely due to lower soil P content (Han et al., 2005). Lower leaf P may constrain the response of photosynthetic capacity to leaf N as P-deficient plants have limited ribulose-1,5-bisphosphate regeneration (Reich et al., 2009). Although enhanced N deposition often stimulates forest growth and carbon sequestration (Högberg, 2007; De Vries et al., 2009; Thomas et al., 2010), the expected growth acceleration can be diminished in P-limited forest ecosystems (Braun et al., 2010; Crowley et al., 2012; Li et al., 2016). Phosphorus limitation may not only constrain future forest growth in response to N deposition but also lower the projected CO_2 fertilization effects on primary productivity (Wieder et al., 2015). Modelling results have also indicated that terrestrial carbon sequestration in China showed a lower response to per unit N deposition in recent years (Tian et al., 2011).

Unless efficient measures are taken to reduce anthropogenic N emissions in China, the threats of human-induced nutrient imbalance to the health and function of forest ecosystems may keep increasing in the next decades.

5. Conclusions

Our results show elevated atmospheric P deposition in China's forests, but they are accompanied by even much more elevated N deposition. High N:P ratios in bulk precipitation and throughfall suggest an imbalance of P and N deposition, which is likely resulting in a shift towards P limitation in forests especially in southern China. Moreover, spatial patterns of P and N deposition both showed a strong power-law increase with closer distance to the nearest large cities, implying a significant alternation of regional P and N cycling by rapid urbanization in China.

China has started to cut down NO_x emissions since early 2010s (Twelfth Five-year Plan, A full version of the plan is available at http://news.xinhuanet.com/politics/2011-03/16/c_121193916.htm) and a stricter national control of air pollution is expected to reduce emissions of NOx from combustion of fossil fuels and biofuels in the future (http://www.mep.gov.cn/ztbd/rdzl/dqst/201307/t20130709_255093.htm). This will consequently lead to a substantial decrease in anthropogenic deposition of oxidized N (e.g. nitrate). However, the absence of NH_3 regulation policy and an increase in meat and dairy consumption may further enhance emissions and deposition of reduced N (e.g. ammonium) in the future. Overall, the issue of increasing imbalance of P and N deposition may further worsen because high levels of N deposition are expected to continue in the next decades. In order to gain a better understanding of the sources, composition and rates of P deposition as well as its ecological effects, monitoring networks of atmospheric deposition (e.g. Nationwide Nitrogen Deposition Monitoring Network, NNDMN, Xu et al., 2015; Chinese Ecosystem Research Network, CERN, Zhu et al., 2015) are encouraged to include measurements of P deposition across the country based on standardized sampling protocols and analytical methods. Field observations and manipulated experiments should be conducted to assess the impacts of nutrient imbalance on the health and function of China's forest ecosystems. Moreover, better forest management strategies should be adopted to avoid loss of forestry production from the human-induced P and N imbalance.

Author contribution

E. Du. and W. de Vries conceived the idea. E. Du. conducted data analysis and prepared the manuscript. W. de Vries, Y. Jiang, W. Han, X. Liu and Z. Yan reviewed and edited the manuscript.

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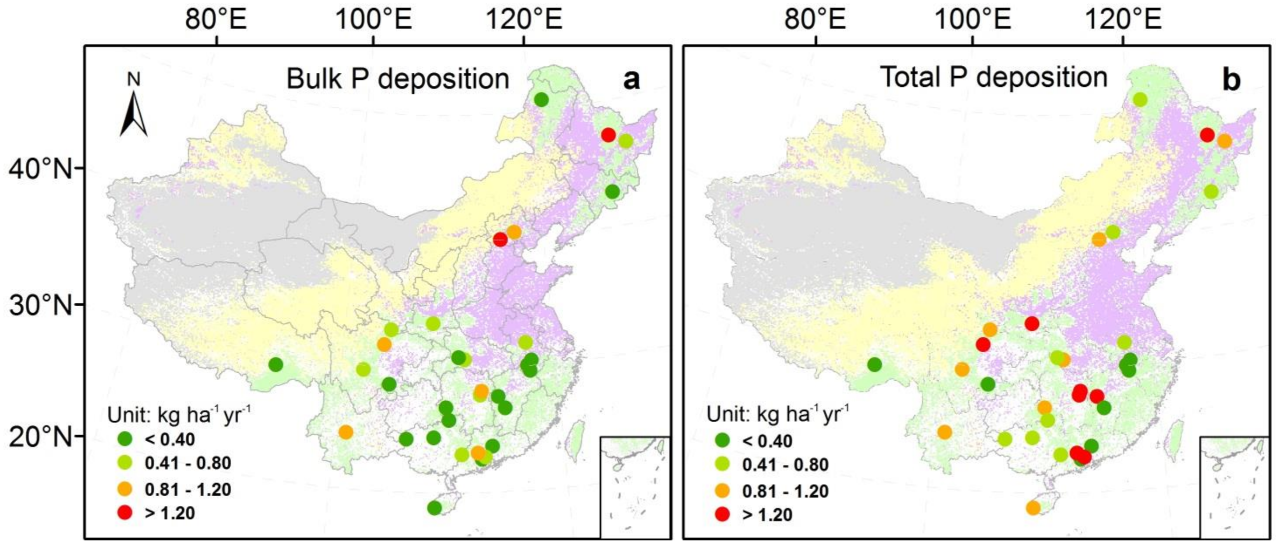

Figure 1. Spatial patterns of a) bulk P deposition (kg ha^{-1} yr^{-1}) and b) total P deposition (kg ha^{-1} yr^{-1}) in China's forests. The background shadows in light green, light yellow, light purple and light grey indicate the distributions of forest, grassland (semiarid region), cropland and non-vegetated land, respectively.

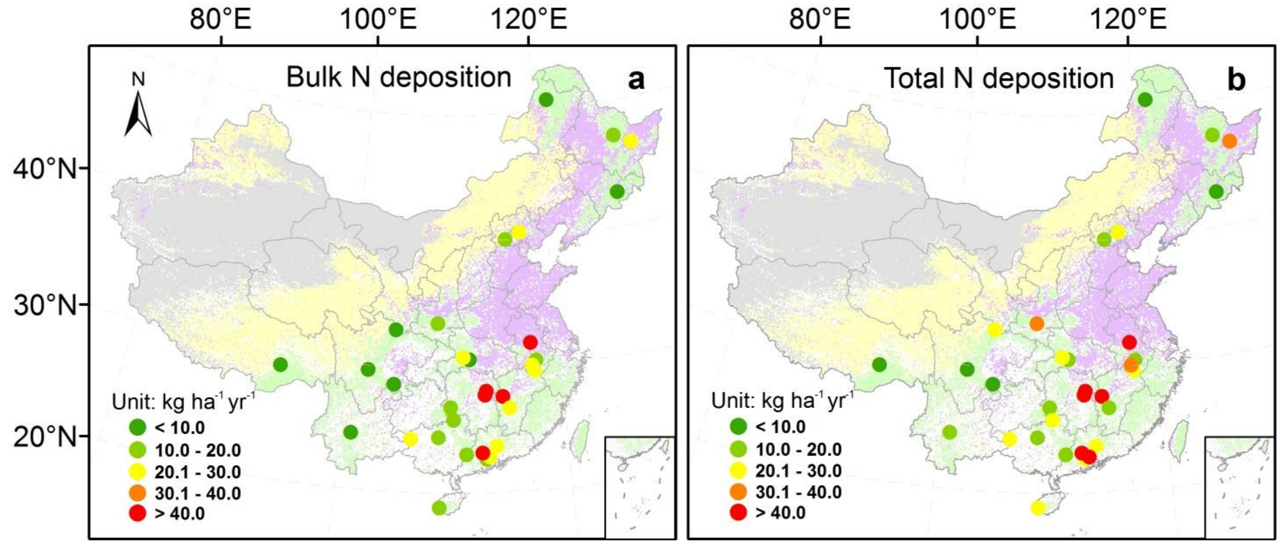

Figure 2. Spatial patterns of a) bulk N deposition (kg ha^{-1} yr^{-1}) and b) total N deposition (kg ha^{-1} yr^{-1}) in China's forests. The background shadows in light green, light yellow, light purple and light grey indicate the distributions of forest, grassland (semiarid region), cropland and non-vegetated land, respectively.

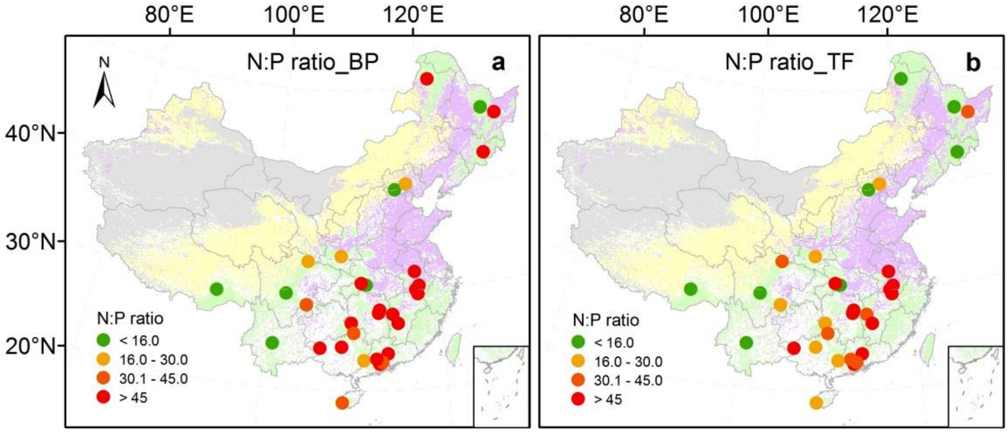

Figure 3. Spatial patterns of N:P ratios in a) bulk precipitation (BP) and b) throughfall (TF) in China's forests. The background shadows in light green, light yellow, light purple and light grey indicate the distributions of forest, grassland (semiarid region), cropland and non-vegetated land, respectively.

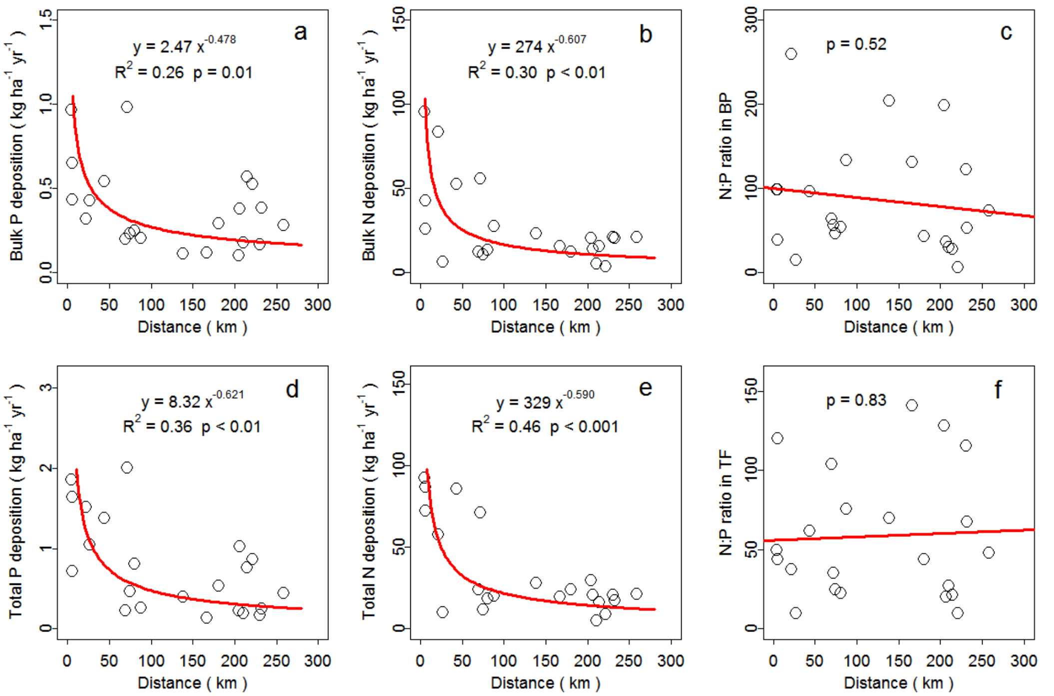

Figure 4. Changes in bulk deposition of P and N (kg ha^{-1} yr^{-1}), total deposition of P and N (kg ha^{-1} yr^{-1}), and N:P ratios in bulk precipitation (BP) and throughfall (TF) with the distance to the nearest large cities based on datasets of forested sites far from semiarid regions in China.

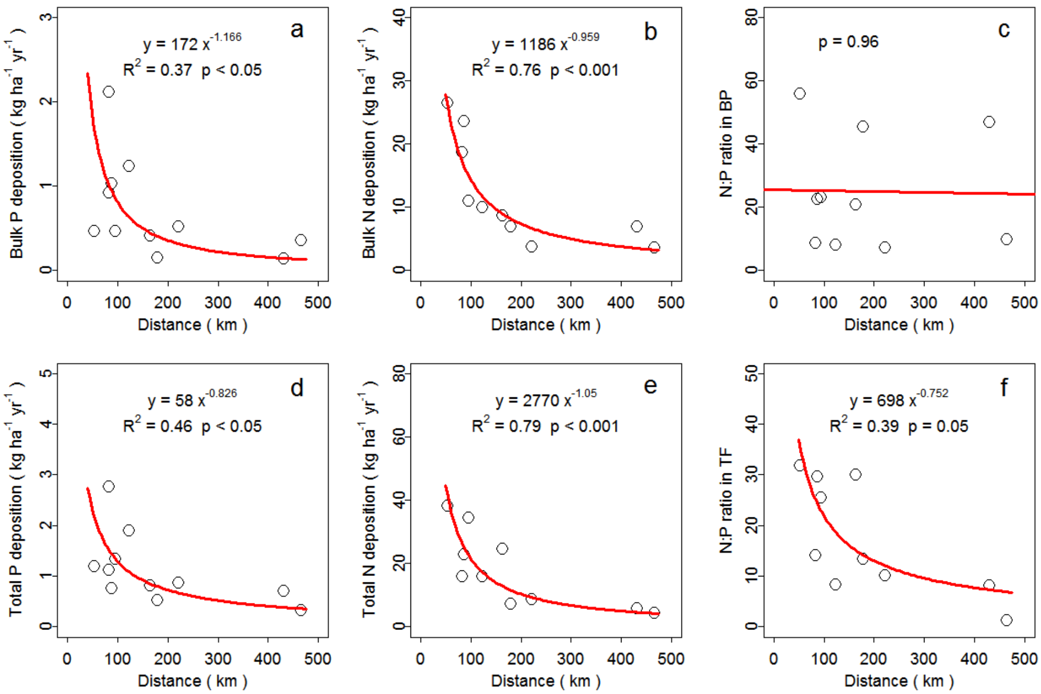

Figure 5. Changes in bulk deposition of P and N (kg ha^{-1} yr^{-1}), total deposition of P and N (kg ha^{-1} yr^{-1}), and N:P ratios in bulk precipitation (BP) and throughfall (TF) with the distance to the nearest large cities based on datasets of forested sites nearby semiarid regions in China.