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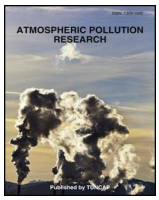


# Imbalanced nitrogen and phosphorus deposition in the urban and forest environments in southeast Tibet

Wei Wang[a,b], Xuejun Liu[b], Jin Xu[a], Anthony J. Dore[c], Wen Xu[d,e,*]

[a] Xizang Agriculture and Animal Husbandry College, Nyingchi, Tibet, 860000, China
[b] College of Resources and Environmental Sciences, China Agricultural University, Beijing, 100193, China
[c] Centre for Ecology and Hydrology, Edinburgh, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK
[d] State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
[e] College of Resources and Environment, University of Chinese Academy of Sciences, Beijing, 100049, China

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ABSTRACT

In recent decades, high levels of anthropogenic emissions in China have dramatically increased nitrogen (N) deposition and may lead to an imbalance of atmospheric N and phosphorus (P) inputs in terrestrial ecosystems. However, currently the status of N and P deposition in southeast Tibet is poorly understood. Here, we investigated spatial and monthly patterns of N and P bulk deposition based on measurements of dissolved inorganic N (DIN, including ammonium N and nitrate N) and dissolved organic N (DON) and total dissolved P (TDP) in precipitation from March to October 2017. Measurements were made at an urban site in Nyingchi city (NC) and at a forest site in Sejila Mountain (SJL). Over the study period, monthly total dissolved N (the sum of DIN and DON) deposition fluxes totalled 4.6 and 3.6 kg N $ha^{-1}$ at SJL and NC, respectively, of which dissolved organic nitrogen accounted for 35 and 38%. Monthly averages showed an increasing trend from March to June, and then a decrease during last two months (September and October). At both two sites, the ratios of ammonium to nitrate N in bulk deposition are greater than 1, indicating that reduced N mainly from agricultural sources dominated N deposition in study area. Monthly TDP deposition fluxes totalled 0.68 and 0.58 kg P $ha^{-1}$ at SJL and NC, respectively, both of which showed an increasing trend from March to May and a decreasing trend from July to October. The N/P ratio was 6.1 and 6.8 at NC and SJL, respectively.

## 1. Introduction

Nitrogen (N) and phosphorus (P) are essential nutrients for plant growth in terrestrial and marine ecosystems, but can also be considered as limiting elements when their supply does not meet demands by microbes and plants (Elser et al., 2007). Over the past few decades, reactive N (Nr) and P levels in the atmosphere have increased significantly due to the rapid development of industry and agricultural production, resulting in substantial increases in atmospheric N and P deposition to terrestrial ecosystems (Smil, 2000; Galloway et al., 2004; Liu et al., 2013a,b). It has been estimated that at a global scale, anthropogenic Nr inputs to the biosphere were between 165 and 259 M ton N $yr^{-1}$ globally, N deposition was approximately 114 M ton N $yr^{-1}$ in the year 2000 and an upward trend is expected in the future (Peñuelas et al., 2012). In contrast, anthropogenic P inputs to the biosphere were 22–26 M ton N $yr^{-1}$, and global P deposition was 3–4 M ton N $yr^{-1}$ since 1980 but had no obvious temporal trend (Peñuelas et al., 2013).

Due to the negative effects from excessive deposition on the environment, many studies have quantified the magnitudes of N and/or P deposition at a regional or national scales and determined their chemical composition, especially N deposition (Lü and Tian, 2007, 2014; Duce et al., 2008; Jia et al., 2014; Zhu et al., 2015 Liang et al., 2016). For example, based on 5-year field measurements, Xu et al. (2015) reported that total N deposition (wet and dry) ranged from 2.9 to 83.8 kg N $ha^{-1}$ $yr^{-1}$ at 43 *in situ* monitoring sites across China. However, few monitoring reports on atmospheric P deposition exist and are limited to particulate P (Luo et al., 2011; Parron et al., 2011; Hou et al., 2012; Du et al., 2016). It is well known that a complete quantification of P deposition is a big challenge, since P has no stable gaseous phase in the atmosphere and is mainly transported by wind in the form of dust (Smil, 2000; Mahowald et al., 2008). At a national scale, Zhu et al. (2016) reported that wet P deposition ranged from 0.093 to 0.63 kg P $ha^{-1}$ $yr^{-1}$ at 41 *in situ* field stations across China. Their results also

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* Corresponding author. State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China.
*E-mail addresses:* wenxu@rcees.ac.cn, hi.xuwen@163.com (W. Xu).

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show that the ration of N to P in wet deposition was 77 (by mass), much higher than that in continents deposition value (47, based on molar ratio) or terrestrial plants (22–30, based on molar ratio) (Peñuelas et al., 2013).

The Qinghai-Tibet plateau, occupying about one-fourth of the land area of China (Zhang et al., 2002), is sensitive to global climate change (Liu et al., 2013a,b; Xu et al., 2014). Long-term N addition can decrease the species richness of both vegetation and soil seed banks in alpine meadow ecosystems (Ma et al., 2014). At present, little is known about the magnitude of N deposition in the Qinghai-Tibet plateau (Liu et al., 2015; Zhu et al., 2015). In addition, atmospheric P deposition in the Qinghai-Tibet plateau remains unclear, especially in southeast Tibet, which accounted for 80% of the total forest area ($1.47 \times 10^7$ ha) in Tibet Province. In this paper, we presented estimates of bulk N and P deposition at two field monitoring sites in Nyingchi city (NC) and Sejila mountain (SJL) during the main rain season from March to October 2017, with the purposes being to quantify fluxes, forms and monthly variations of N and P deposition (sampling with continuously-open precipitation collectors) to better understand the current status of N and P deposition and impacts in a remote region of China.

## 2. Materials and methods

### 2.1. Site description

For bulk N and P deposition measurements, the monitoring site in NC city was located at Xizang Agriculture and Animal Husbandry College (29°66′N 94°34′E 2990 m a.g.l.), southeast of the city, whereas that at SJL mountain was established at the National Field Scientific Observation Station of Alpine Forest Ecosystem (29°65′N 94°72′E 3950 m a.g.l.), on the edge of NC city (Fig. 1). Nyingchi City is located beside the Niyang River, which was one of the main tributaries of the Brahmaputra. The climate is mainly dominated by warm air currents in the Indian Ocean, with an annual average temperature of 8.7 °C and an annual average precipitation of 650 mm. Tourism is a major local economic industry. At the NC site, there was no heavy industry nearby, and potential emission sources were a small village and agricultural fields. The SJL site was surrounded by natural fir forest, in which undergrowth vegetation were mainly *Sorbus*, *Rosa*, and *Lonicera as well as*other herbaceous plants. At this site, there were no anthropogenic Nr emission sources except for a state road (#318). The annual average temperature was −0.73 °C and the annual average precipitation was approximately 1000 mm.

### 2.2. Sampling and chemical analysis

The rainwater samples were collected using continuously-open rain gauges, and therefore contained mainly wet deposition with unquantifiable fractions from gaseous and particulate Nr from the dry-deposited process. Effectively, wet deposition measured in the present work was therefore bulk deposition. The rain gauge consisted of a stainless steel funnel and glass bottle and was installed 1.2 m above the ground. After each precipitation event, the rainwater samples were thoroughly stirred and immediately transferred to clean polyethylene bottles (50 ml) for storage. The rainwater-collecting bottle was then rinsed with deionized water to eliminate cross contamination. All samples were filtered with a 0.45 mm syringe filter (Tengda Inc., Tianjin, China), then filtrates were frozen in a refrigerator at −20 °C prior to analysis in the laboratory.

The laboratory analysis was performed according to Chinese standard methods. Total dissolved nitrogen (TDN) was measured by the alkaline potassium persulfate digestion-UV spectrophotometric method (GB11894-89); Nitrate nitrogen ($NO_3^-$-N) was measured by the UV spectrophotometric Method; ammonium nitrogen ($NH_4^+$-N) was measured by the reagent colorimetric method (GB7479-87); Total dissolved phosphorus (TDP) was measured by the ammonium molybdate spectrophotometric method (GB11893-89); Rainwater was digested using an intelligent multiparameter digestion meter (LH-25A, Lianhua, China). $NO_3^-$-N, $NH_4^+$-N, and TDP were measured using ultraviolet and visible spectrophotometry (DR6000,HACH, America). The DON concentration was defined as the difference between the TDN and inorganic N ($NH_4^+$-N and $NO_3^-$-N) concentrations (Zhang et al., 2012). During each analysis, rainwater samples were analyzed in duplicate with each analysis run consisting of 8 samples, one blank and a set of standard concentrations of $NH_4^+$-N, $NO_3^-$-N and TDN. Standard solutions were prepared in deionized water with concentrations ranges of 0–1 mg $L^{-1}$ for both $NH_4^+$-N and $NO_3^-$-N, and 0–2 mg $L^{-1}$ for TDN. TDP contains phosphate and dissolved organic P. Duplicate blank and standard reference materials (monopotassium phosphate, $KH_2PO_4$) methods were used for quality assurance.

### 2.3. Data calculation and analysis

Monthly Nr (TDN, $NH_4^+$-N, $NO_3^-$-N, DON) bulk deposition fluxes were calculated as follows:

$$N = \sum_{i=1}^{n} Ni*Pi/100$$

Monthly dissolved phosphorus deposition fluxes were calculated as follows:

$$D = \sum_{i=1}^{n} Di*Pi\ /100$$

where P is the precipitation per month(mm); N is the bulk deposition flux of the measured Nr species (TDN, $NH_4^+$-N, $NO_3^-$-N) (kg $ha^{-1}$ $month^{-1}$); D is the total dissolved phosphorus deposition flux (kg $ha^{-1}$ $month^{-1}$); *i* is the number of precipitations per month; *Pi* is the precipitation volume in *i* precipitation events; *Ni* is the volume-weighted mean concentration of measured Nr (TDN, $NH_4^+$-N, $NO_3^-$-N) components in *i* precipitation events; *Di* is the is the volume-weighted mean concentration of TDP in *i* precipitation events; 100 is the unit conversion factor of $mgm^{-2}$ to $kgha^{-1}$.

### 2.4. Statistical analysis

The Pearson correlation and regression analyses were conducted using the SPSS software package, version 20.0 (SPSS Inc., Chicago, IL), and significance was tested using a significance level (*P*) of 0.05.

### 2.5. Backward trajectory analysis

To recognize the potential sources and transport routes of air pollutants and precipitation concentration, air mass backward trajectory analysis was performed using the Hybrid-Single Particle Integrated Trajectory Model (HYSPLIT 4) (Xu et al., 2017a), provided by the Air Resource Laboratory of the National Oceanic and Atmospheric Administration (NOAA) (Stein et al., 2015; Roy et al., 2016). Meteorological data were input from the Global Data Assimilation System (GDAS) meteorological data archives of the Air Resource Laboratory, (NOAA). Three-day backward trajectories were calculated at 6 h intervals (00:00, 06:00, 12:00, 18:00 UTC) on sampling days at both study sites, with an arrival height of 500 m above ground level. Then, cluster analysis was performed using the trajectories based on the total spatial variance (TSV) method (Draxler et al., 2012).

## 3. Results

### 3.1. Concentrations of Nr species and TDP in precipitation

Total rainfall amounts during March–October, the main rain season were 625 mm at NC and 839 mm at SJL. Monthly precipitation amounts