



Atmospheric deposition of inorganic nitrogen in a semi-arid grassland of Inner Mongolia, China

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Abstract: Due to increasing global demand for crop production and energy use, more and more reactive nitrogen (Nr) has been generated and emitted to the environment. As a result, global atmospheric nitrogen (N) deposition has tripled since the industrial revolution and the ecological environment and human health have been harmed. In this study, we measured dry and wet/bulk N deposition from July 2013 to December 2015 in a semi-arid grassland of Duolun County, Inner Mongolia, China. The samples of dry and wet/bulk N deposition were collected monthly with a DELTA (DENuder for Long Term Atmospheric sampling) system and with Gradko passive samplers and a precipitation gauge. The measured results show that the annual mean concentrations of NH₃, NO₂, HNO₃, particulate NH₄⁺ (pNH₄⁺) and particulate NO₃⁻ (pNO₃⁻) in atmosphere were 2.33, 1.90, 0.18, 1.42 and 0.42 μg N/m³, respectively, and that the annual mean volume-weighted concentrations of NH₄⁺-N and NO₃⁻-N in precipitation were 2.71 and 1.99 mg N/L, respectively. The concentrations of Nr components (including NH₃, NO₂, HNO₃, pNH₄⁺, pNO₃⁻, NH₄⁺-N and NO₃⁻-N) exhibited different seasonal variations. Specifically, NO₂ and HNO₃ exhibited higher concentrations in autumn than in summer, while the other Nr components (NH₃, pNH₄⁺, pNO₃⁻, NH₄⁺-N and NO₃⁻-N) showed the highest values in summer. Based on measured concentrations of Nr components and their deposition velocities estimated using the GEOS-Chem global atmospheric chemical transport model, the calculated annual mean dry deposition fluxes were 3.17, 1.13, 0.63, 0.91 and 0.36 kg N/(hm²·a) for NH₃, NO₂, HNO₃, pNH₄⁺ and pNO₃⁻, respectively, and the calculated annual mean wet/bulk deposition fluxes were 5.37 and 3.15 kg N/(hm²·a) for NH₄⁺-N and NO₃⁻-N, respectively. The estimated annual N deposition (including dry N deposition and wet/bulk N deposition) reached 14.7 kg N/(hm²·a) in grassland of Duolun County, approaching to the upper limit of the N critical load (10–15 kg N/(hm²·a)). Dry and wet/bulk deposition fluxes of all Nr components (with an exception of HNO₃) showed similar seasonal variations with the maximum deposition flux in summer and the minimum in winter. Reduced Nr components (e.g., gaseous NH₃ and pNH₄⁺ in atmosphere and NH₄⁺-N in precipitation) dominated the total N deposition at the sampling site (accounted for 64% of the total N deposition), suggesting that the deposited atmospheric Nr mainly originated from agricultural activities. Considering the projected future increases in crop and livestock production in Inner Mongolia, the ecological and human risks to the negative effects of increased N deposition could be increased if no mitigation measures are taken.

Keywords: atmospheric reactive nitrogen; dry deposition; wet/bulk deposition; reduced nitrogen; grassland ecosystem; Inner Mongolia

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1 Introduction

Nitrogen (N) is a primary controlling factor for the net primary productivity of many ecological ecosystems, especially in regions with low levels of N supplies (Wedin and Tilman, 1996; Liu et al., 2011). It plays a significant role in increasing food production and stimulating plant growth (Gruber and Galloway, 2008; He et al., 2016). With increasing human activity, a large amount of reactive nitrogen (Nr) was generated and emitted to the environment, thus influencing the N balance in ecosystems. Specifically, large consumption of fossil fuels, heavy application of chemical N fertilizers, excessive population growth, and intensive livestock production all resulted in a dramatic increase in Nr emissions in recent decades (Galloway et al., 2004; Fowler et al., 2013). As a result, atmospheric N emission increased from 34 Tg N in 1860 to 109 Tg N in 2010, and the value is projected to reach 270 Tg N in 2050 (Galloway et al., 2004; Fowler et al., 2013). After the release of Nr compounds into the atmosphere, they normally experience a variety of physical and chemical transformation processes before undergoing wet or dry depositions, leading to adverse impacts on the ecological environment and human health.

In China, rapid economic development including agricultural and industrial expansions has resulted in a sharp increase in the N deposition (Duan et al., 2016). Based on an integrated analysis of historical data and the monitoring data, Liu et al. (2013) showed that annual bulk N deposition had increased by approximately 8 kg N/hm² in the 2000s compared with that in the 1980s and that this growth trend will persist in the future. Jia et al. (2016) evaluated the present dry N deposition rate in China using the results from satellite observations and found that the present dry N deposition rate had reached up to 7.5 Tg N/a. This estimation was more or less consistent with the recent model findings of Zhao et al. (2017), who reported that the dry deposition rate was 6.4 Tg N/a. Generally speaking, excessive N deposition can negatively cause a wide range of environmental issues, such as soil acidification, lake eutrophication, biodiversity loss, and N₂O emission increases (Bobbink et al., 2010; Duprè et al., 2010; Song et al., 2012). Furthermore, NH₃ and NO_x are important precursors for the secondary inorganic aerosol formation and can thus promote the formation of haze (Pan et al., 2016a, b).

Grassland in China is the most vastly-distributed vegetation type, covering nearly 40% of the surface area (Ni, 2004). Inner Mongolia grassland, an important part of China's grassland, makes a great contribution to the global carbon cycle. As an important component of green ecological barrier in North China, the Inner Mongolia grassland is of vital significance for the maintenance and conservation of biodiversity. However, in recent years, due to influences of over-fertilization, unreasonable utilization of land resources, the grassland continues to suffer from land degradation and desertification (Wang et al., 2017). Negative impacts of N deposition on grassland biodiversity have been observed by numerous field experiments in China (Bai et al., 2010; Duprè et al., 2010) and abroad (e.g., Bobbink et al., 2010). The negative impacts include ultimate alteration of the community structure and ultimate reduction of the primary net productivity in grassland ecosystems (Ceulemans et al., 2017; Tang et al., 2017).

However, opposing voices questioned the aforementioned negative impacts of N deposition and speculated that the negative impacts may be artifacts of simulation manipulations (Ochoa-Hueso et al., 2011; Nogueira et al., 2017). In recent years, Chinese scientists have also conducted a series of studies to quantify the impacts of N deposition on grasslands (Liu et al., 2011; Song et al., 2012; Li et al., 2015). However, observations, especially long-term continuous observations, of the wet/bulk and dry depositions in the grassland ecosystems of Inner Mongolia are still scarce and most of the existing observations are from the North China Plain (Shen et al., 2009; Pan et al., 2012; Luo et al., 2013; Xu et al., 2016), the Yangtze River Delta (Yang et al., 2010), and the Pearl River Delta (Wang et al., 2013).

In order to fill the research geographic gaps of N deposition in grassland ecosystems and to provide data for national evaluation of N deposition, we conducted a 3-year study in grassland of Duolun County in the southeastern part of the Inner Mongolia grassland. The purposes of this work were: (1) to estimate the concentrations of Nr components and the deposition fluxes, and (2) to characterize the seasonal variations of dry and wet/bulk N deposition.

2 Materials and methods

2.1 Study site

The study was conducted in a semi-arid grassland in Duolun County, Inner Mongolia Autonomous Region, China. The sampling site is situated in a meteorological observation station of the Chinese Academy of Sciences (42°22'N, 116°49'E; 1324 m a.s.l.). This site features a typical semi-arid continental monsoon climate. The average annual precipitation is 380 mm and the maximum precipitation occurs in July. The growing season generally starts in May and continues until the end of September, with a length of about 150 days. Precipitation amount in the growing season accounts for 88% of the total annual precipitation. The annual average temperature is 2.2°C and the monthly average temperature ranges from -16.9°C in January to 19.4°C in July. The dominant soil type is chestnut soil. Livestock grazing and crop cultivation are the two major land-use practices in this area.

2.2 Sampling and N deposition analysis

2.2.1 Dry N deposition

Reactive nitrogen (Nr) components, including NH_3 , NO_2 , HNO_3 , particulate NH_4^+ (pNH_4^+) and particulate NO_3^- (pNO_3^-), were sampled monthly from July 2013 to December 2015. NH_3 , HNO_3 , pNH_4^+ and pNO_3^- were measured with a DELTA (DENuder for Long Term Atmospheric sampling) system. The DELTA system consisted of three parts: a circular sampling chain with diffusers and a particle collection device, a small low-volume pump (0.2–0.4 L/min) and a high-precision gas flow meter. Details about the DELTA system have been described in detail previously (Flechard et al., 2011; Xu et al., 2015). Briefly, when ambient air passes through the DELTA system, HNO_3 and other acidic gases are captured by two long diffusion tubes coated on the inner wall with a mixed solution of 10 g/L K_2CO_3 and 10 g/L glycerol in methanol; and NH_3 is captured by another two short diffusion tubes coated with citric acid (5% (m/v) in methanol). Subsequently, the acidic particulate aerosols are collected by a filter membrane with basic adsorbent in the DELTA train membrane system, and the alkaline particulate aerosols are collected by a membrane with acidic adsorbent.

NO_2 was monitored with Gradko passive tubes (Gradko International Limited, Winchester, UK), which are composed of an acrylic acid tube (71.0 mm in length and 11.0 mm in internal diameter), two polyethylene caps (gray and white, located at both ends of the diffuser) and two layers of stainless steel wire. The NO_2 was absorbed into 20% triethanolamine solution coated onto two stainless steel wire meshes in the gray cap. The sampling heights of the DELTA system and NO_2 diffusion tubes were kept at 2 m above ground. Three NO_2 sampler replicates were deployed for monthly sampling. Exposed DELTA sample trains and NO_2 diffusion tubes were replaced with new ones at the end of a month and were preserved in a refrigerator at 4°C, and then analyzed immediately after collection. The gaseous HNO_3 collected in glass denuders of the DELTA sampling train system and the pNO_3^- on the filter membrane were extracted using 10 mL 0.05% H_2O_2 solution, and the NH_3 and pNH_4^+ denuders and membranes were extracted using 6 and 10 mL high purity water, respectively. An AA3 continuous flow analyzer (Bran+Luebbe GmbH, Norderstedt, Germany) was utilized to measure NH_4^+ and NO_3^- concentrations in the extracted solutions. NO_2 in the Gradko passive sampler was extracted with a mixed solution of sulfonamide, H_3PO_4 , and N-1-naphthylethylene-diamine, and NO_2 concentration was determined by absorbance at a wavelength of 542 nm. For quality assurance purposes, we set up monthly blank samples both in the laboratory and in the field and analyzed them using the same procedures outlined above.

2.2.2 Wet/bulk N deposition

Wet/bulk N deposition was collected by a precipitation gauge (SDM6, Tianjin Weather Equipment Inc., China) at the sampling site from May 2013 to November 2015. The precipitation gauge was a passive sampler without power input, consisting mainly of a stainless steel funnel and a glass container. Precipitation was automatically collected by the precipitation gauge and the amount was measured with a graduated cylinder of the gauge. Before being taken to the laboratory of

China Agricultural University for chemical analysis, the collected precipitation was recorded, mixed, and put into a clean polyethylene bottle (50 mL) inside a refrigerator (-18°C). It should be noted that we rinsed the precipitation gauge with high purity water after each collection to avoid sample contamination. The precipitation samples were filtered by $0.45\ \mu\text{m}$ filter membranes, then 15 mL filtered fluid was taken out, frozen and kept in a polyethylene bottle. $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ were determined by a continuous flow analyzer (Bran+Luebbe GmbH, Norderstedt, Germany), as mentioned above, within a month.

2.3 Calculations of N deposition flux

We calculated the wet/bulk N deposition flux based on $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ concentrations and precipitation amount in each precipitation event. The volume-weighted mean concentration of Nr components (C_w ; mg N/L) was obtained with Equation 1:

$$C_w = \frac{\sum_{i=1}^n (C_i \times P_i)}{\sum_{i=1}^n P_i}, \quad (1)$$

where C_i is the inorganic Nr concentration in the i^{th} precipitation event (mg N/L); P_i is the precipitation amount in the i^{th} precipitation event (mm); n is the number of precipitation events. The wet/bulk deposition flux of Nr components (D_w ; kg N/hm²) was calculated using Equation 2:

$$D_w = 0.01 \times C_w \times \sum_{i=1}^n P_i. \quad (2)$$

Dry N deposition is affected by various chemical and environmental factors like meteorological conditions, physicochemical properties of Nr components, roughness of underlying surface, and the ability of the underlying surface to capture and absorb Nr components (Flechard et al., 2011). Extra issues arise concerning characteristics of the bidirectional flow of N, making the quantification of dry deposition a challenge. Nr emission is the predominant process when the concentration in the surface is higher than that in the atmosphere, while deposition is expected when the gradient reverses. Inferential models have previously been extensively used as operational tools to determine dry N deposition in many monitoring networks all over the world, such as NADP (National Atmospheric Deposition Program) and EMEP (European Monitoring and Evaluation Program). Using the inferential method, we obtained the monthly dry deposition flux of Nr components by multiplying the concentrations of Nr components measured in our field samples with deposition velocities obtained from simulation results of a global atmospheric chemical transport model. The dry deposition flux of Nr components was expressed by Equation 3:

$$F_d = C_z \times V_d, \quad (3)$$

where F_d is the dry deposition flux of an Nr component (kg N/hm²); C_z is the measured atmospheric concentration of the Nr component ($\mu\text{g N/m}^3$); and V_d is the dry deposition velocity (cm/s). It should be noted that V_d was obtained from a nested-grid version of the Goddard Earth Observing System (GEOS)-Chem chemical transport model (Chem CTM) for Asia. The model has a spatial horizontal resolution of 0.50° latitude \times 0.67° longitude and a temporal resolution of 6 h. The V_d estimation of dry N deposition follows a standard big-leaf resistance-in-series model, which is determined by meteorological conditions and land-use types (grassland in the present study). We averaged the hourly V_d data to obtain monthly values of dry deposition velocities of all Nr components. Details about the model description and the simulation of dry N deposition fluxes can be found in Zhang et al. (2012). It should be mentioned that a part of the wet/bulk and dry N deposition results (e.g., data from July 2013 to September 2014) in present work was published previously by Xu et al. (2015).

3 Results

3.1 Concentrations of Nr components in atmosphere

Monthly concentrations of NH_3 , NO_2 , HNO_3 , pNH_4^+ and pNO_3^- in atmosphere were in the ranges

of 0.34–6.79, 0.24–6.92, 0.01–0.53, 0.84–5.63 and 0.33–1.48 $\mu\text{g N/m}^3$, respectively, from July 2013 to December 2015 (Fig. 1). The seasonal variation of NH_3 was remarkable with an annual mean concentration of 2.33 $\mu\text{g N/m}^3$. The highest concentration of NH_3 occurred in summer (June–August) while the lowest in winter (December–February). The annual mean concentration of NO_2 was 1.90 $\mu\text{g N/m}^3$ with the highest concentration in April and the lowest in January. The annual mean concentration of HNO_3 was 0.18 $\mu\text{g N/m}^3$. Compared with NH_3 and NO_2 , the monthly concentrations of HNO_3 were lower and also less variable, except that the concentration in September was notably higher than those in other months. The lowest concentration of HNO_3 occurred in May. The annual mean concentration of pNH_4^+ was 1.42 $\mu\text{g N/m}^3$ with the maximum monthly concentration in July and the minimum in January. Similar to pNH_4^+ , the monthly concentrations of pNO_3^- also showed the highest value in July. The annual mean concentration of pNH_4^+ was 0.62 $\mu\text{g N/m}^3$.

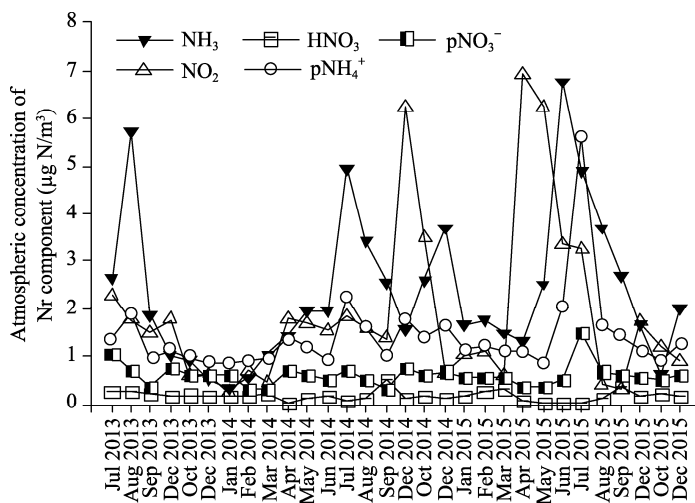


Fig. 1 Monthly concentrations of Nr (reactive nitrogen) components (including NH_3 , NO_2 , HNO_3 , pNH_4^+ and pNO_3^-) in the atmosphere from July 2013 to December 2015

3.2 Concentrations of Nr components in precipitation

During the monitoring period (i.e., from May 2013 to December 2015), the monthly volume-weighted concentrations of NH_4^+ and NO_3^- in precipitation varied from 0.27 to 12.19 and 0.10 to 11.68 mg N/L, respectively (Fig. 2). The average annual concentrations of NH_4^+ -N and NO_3^- -N in precipitation were 2.71 and 1.99 mg N/L, respectively. Compared with NO_3^- -N, the NH_4^+ -N concentration in precipitation was generally higher except for values in September and October, 2013. Higher concentrations of NO_3^- -N and NH_4^+ -N were observed in the months (February–May) when the precipitation was lower, while lower concentrations were always accompanied by higher monthly precipitation (June–September). The precipitation amount, to a large extent, affected the concentrations of NO_3^- -N and NH_4^+ -N.

3.3 N deposition flux

Monthly dry deposition velocities of each Nr component are listed in Table 1. Based on these values, we calculated the annual dry deposition fluxes of NH_3 , NO_2 , HNO_3 , pNH_4^+ and pNO_3^- (Fig. 3). Specifically, annual dry deposition fluxes were 3.17, 1.13, 0.63, 0.91 and 0.36 kg N/($\text{hm}^2\cdot\text{a}$) for NH_3 , NO_2 , HNO_3 , pNH_4^+ and pNO_3^- , respectively, during the monitoring period. It should be noted that the monitoring data in 2013 were not included in the calculation of annual dry deposition flux since the data were not complete for 2013. During the monitoring period (excluding the data of 2013), the summed annual dry deposition flux of the five atmospheric Nr components (i.e., NH_3 , NO_2 , HNO_3 , pNH_4^+ and pNO_3^-) averaged 6.21 kg N/($\text{hm}^2\cdot\text{a}$). Due to the high concentration of NH_3 , the dry deposition flux of NH_3 was also the largest one among the five

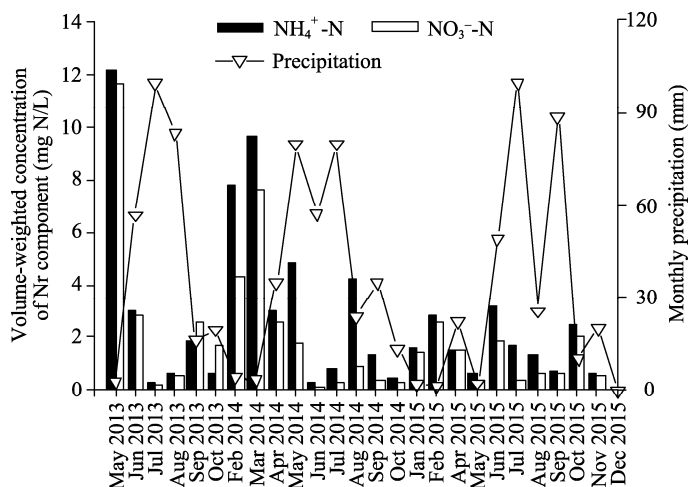


Fig. 2 Monthly volume-weighted concentrations of Nr components (including NO_3^- -N and NH_4^+ -N) in precipitation from May 2013 to December 2015

atmospheric Nr components, followed by NO_2 , HNO_3 , pNH_4^+ and pNO_3^- . Generally, NH_3 contributed 51% to the total dry N deposition, being higher than the combined contribution of the other four Nr components (49%).

From 2013 to 2015, the annual wet/bulk deposition fluxes fluctuated in the ranges of 3.22–7.90 $\text{kg N}/(\text{hm}^2\cdot\text{a})$ for NH_4^+ -N and 2.72–3.38 $\text{kg N}/(\text{hm}^2\cdot\text{a})$ for NO_3^- -N. The average annual wet/bulk deposition flux of NH_4^+ -N (5.37 $\text{kg N}/(\text{hm}^2\cdot\text{a})$) was 1.7 times that of NO_3^- -N (3.16 $\text{kg N}/(\text{hm}^2\cdot\text{a})$). The annual wet/bulk deposition flux was averagely 8.53 $\text{kg N}/(\text{hm}^2\cdot\text{a})$ and the annual N deposition (dry deposition plus wet/bulk deposition) flux was averagely 14.73 $\text{kg N}/(\text{hm}^2\cdot\text{a})$.

Table 1 Monthly dry deposition velocities of different atmospheric Nr components

Month	NH_3	NO_2	HNO_3	pNH_4^+	pNO_3^-
	(cm/s)				
January	0.26	0.01	0.15	0.13	0.13
February	0.30	0.01	0.17	0.15	0.15
March	0.30	0.03	0.37	0.18	0.18
April	0.30	0.07	0.87	0.22	0.22
May	0.40	0.24	2.06	0.26	0.26
June	0.55	0.38	2.44	0.27	0.27
July	0.55	0.38	2.36	0.23	0.23
August	0.53	0.34	2.26	0.24	0.24
September	0.46	0.26	2.19	0.22	0.22
October	0.34	0.13	1.59	0.16	0.16
November	0.27	0.03	0.67	0.13	0.13
December	0.27	0.01	0.14	0.13	0.13

4 Discussion

4.1 Concentrations of Nr components in atmosphere and precipitation

In China, fossil fuel is intensively consumed to support the growth of population and economy, leading to large amounts of Nr emissions to the atmosphere and subsequent N deposition to the ecological ecosystems. At the same time, lack of effective measures to control atmospheric Nr emissions aggravates the increasing trend of N deposition to the ecological ecosystems (Liu et al.,

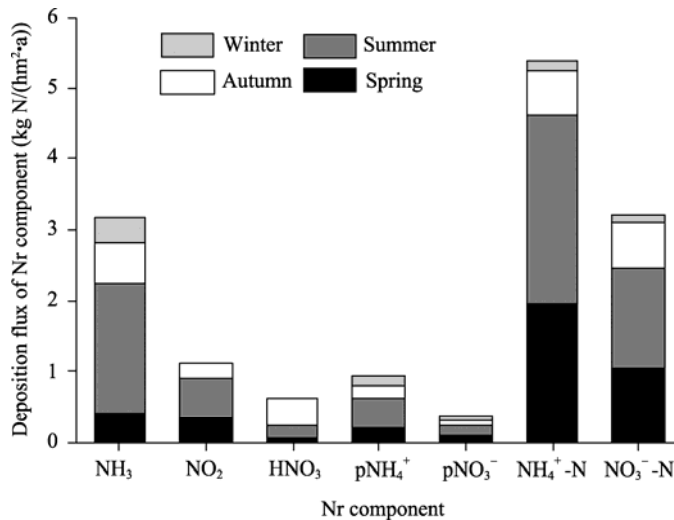


Fig. 3 Seasonal variations of dry and wet/bulk deposition fluxes of Nr components (NH₃, NO₂, HNO₃, pNH₄⁺, pNO₃⁻, NH₄⁺-N and NO₃⁻-N)

2013). Consequently, China has become one of the world's hotspots in N deposition (Vet et al., 2014) and suffered from the threat of continued and serious Nr pollution.

The current study found that monthly average concentrations of Nr components in atmosphere and in precipitation in grassland of Inner Mongolia were considerably lower than those measured in two well-developed regions: North China Plain (Luo et al., 2013; Xu et al., 2016) and Southwest China (Kuang et al., 2016). Due to the burning of fossil fuels and the intensified agricultural activities and livestock production, the North China Plain has been a hotspot of NH₃ in China (Liu et al., 2016; Pan et al., 2016a) with the largest annual mean NH₃ concentration of 16.9±5.9 µg N/m³ in Quzhou (Xu et al., 2016). This value is far higher than the annual mean NH₃ concentration observed from this study (2.33 µg N/m³). The results of atmospheric NH₃ concentrations observed in our study were higher than those observed in some European countries (Flecharth et al., 2011). Although the annual NH₃ concentration at the sampling site was within the range of regional background NH₃ concentration in China (Meng et al., 2010), it exceeded or was very close to the critical level of 3 (±1) µg N/m³ that was set for protecting the most fragile regions (Cape et al., 2009). Therefore, the observed atmospheric NH₃ concentrations posed a potential environmental threat to the grassland in Inner Mongolia. During the monitoring period, the monthly NH₃ concentrations exhibited the highest value in summer and the lowest value in winter. The seasonal variations were caused by season-related human activities and meteorological factors. In summer, high temperature was conducive to enhancing microbial activities and strengthening microbial ammonification. Moreover, high temperature favored ammonia volatilization and also favored NH₃ emission from fertilizer application during potato cultivation near the grassland. During the growing season, herdsman applied N fertilizer to the grasses to promote the growth of pastures, further elevating the NH₃ concentration in summer. In winter, however, the low temperature severely restricted biological activities and the fertilizer application was minimal. Consequently, less ammonia volatilized. High wind speeds in winter also favored the dispersion of pollutants, further lowering the NH₃ concentration.

It is commonly accepted that NO_x is mainly produced in various combustion processes, including those associated with transportation, industry, coal use and power plants (Holland et al., 2005; Paulot et al., 2013). Due to a low level development of industrialization in the sampling site, NO₂ concentrations were remarkably lower than those reported in most urban sites in China (Xu et al., 2016). However, the annual mean NO₂ concentration during the monitoring period was more than two times higher than previous value measured by Shen et al. (2009). The recent increase in the numbers of vehicles can partially explain the increased NO₂ concentrations. The number of private cars in Inner Mongolia grew from 1.88×10⁶ in 2011 to 3.35×10⁶ in 2015

(National Bureau of Statistics of China, 2011–2015). The higher NO_2 concentrations were observed in spring and autumn, being inconsistent with typical seasonal variations (Xu et al., 2015). Higher NO_2 concentrations in spring might be attributable to coal combustion for domestic heating. HNO_3 exhibited high concentrations in autumn and low concentrations in summer, being consistent with the seasonal variations of NO_2 .

The annual mean pNH_4^+ concentration measured in the present study was much lower than many other observations in China (Xu et al., 2015) and in west Europe (Holland et al., 2005), but it was comparable to that measured at rural sites in USA (Li et al., 2016) and was higher than that reported in UK (Marnier and Harrison, 2004). The concentration of pNH_4^+ in summer was higher than those measured in spring, autumn or winter. The high NH_3 concentration and high relative humidity in summer were likely important causes of this phenomenon. High concentration of NH_3 and high relative humidity both favored the transition from gaseous NH_3 to particulate NH_4^+ , although increased temperatures did not favor particulate ammonium nitrate formation. Because of the low HNO_3 concentrations, the pNO_3^- concentrations were lower than most results measured in China (Pan et al., 2012; Xu et al., 2015). The seasonal pattern of pNO_3^- concentrations was the same as that of pNH_4^+ concentrations with the higher values in summer and lower values in other seasons.

N in precipitation mainly derived from water-soluble atmospheric Nr components. These pollutants were scavenged from the air by rainfall or snowfall. The annual concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in wet/bulk deposition in the sampling site were also lower than those reported in many previous studies conducted in urban and rural sites in China (Pan et al., 2012; Huang et al., 2013), but they were higher than those observed in a semi-arid region in Urumqi (Li et al., 2012). In our study, the highest monthly average concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ occurred in summer and the lowest in winter, showing a significant negative correlation between N concentration and precipitation. This pattern suggests a dilution effect of precipitation on N concentrations (Jia and Chen, 2010; Kuang et al., 2016). Compared with previously published data (Xu et al., 2015), annual concentration of $\text{NH}_4^+\text{-N}$ in precipitation increased by 19% while annual concentration of $\text{NO}_3^-\text{-N}$ reduced by 6% in grassland of Duolun County.

4.2 Seasonal variations of wet/bulk and dry N deposition

A different seasonal pattern of N deposition was observed at the sampling site (Fig. 4). The highest deposition fluxes of Nr components occurred in summer and the lowest values always appeared in winter with an exception of HNO_3 that had the highest deposition flux in autumn. In summer, NH_3 deposition fluxes were markedly higher than those in spring, autumn and winter, accounting for 57% of the annual NH_3 deposition flux. This is consistent with the seasonal variation of NH_3 concentration. Deposition fluxes of NO_2 and pNH_4^+ in summer dominated the annual deposition. Deposition of pNH_4^+ in spring, autumn and winter contributed equally to the annual deposition, and the seasonal variations of pNO_3^- deposition were similar to those of pNH_4^+ deposition. Compared with other Nr components, the flux of HNO_3 dry deposition showed different seasonal variations with the highest value in autumn, contributing 56% of estimated annual HNO_3 deposition. This pattern can be partially explained by the higher concentrations and higher deposition velocities of HNO_3 in autumn. Due to different emission sources and different meteorological conditions, the percentage contribution of individual Nr component to the total dry N deposition varied with geographical locations. In the current study, NH_3 contributed the most to the total dry N deposition (51%). This value was significantly higher than the contributions of NO_2 (18%), HNO_3 (10%), pNH_4^+ (15%), and pNO_3^- (6%) to the total dry N deposition. The gaseous Nr components accounted for 79% of the total dry N deposition in our study, being highly consistent with the finding in North China Plain (Xu et al., 2016).

Similar to dry N deposition, wet/bulk deposition fluxes of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ and total N deposition were higher in summer than in other seasons, being in a good agreement with the seasonal distributions of precipitation at the sampling site. In summer, precipitation accounted for 62% of the annual total, while in winter, precipitation was relatively small. Positive relationships between precipitation amounts and wet N deposition fluxes have been reported in many previous

observations (e.g., Pan et al., 2012; Huang et al., 2013). Deposition fluxes of NH_4^+ -N and NO_3^- -N in summer (average values of 2.64 and 1.41 kg N/($\text{hm}^2\cdot\text{a}$), respectively) contributed 49% and 44% to the annual wet/bulk deposition, respectively. Both higher precipitation amounts and high atmospheric concentrations of Nr components contributed to the high N deposition fluxes in summer. The deposition flux of NH_4^+ -N was 1.87 times that of NO_3^- -N in summer, 1.85 times in spring, 1.07 times in autumn and 1.07 times in winter. The ratio of NH_4^+ -N concentration to NO_3^- -N concentration is widely perceived as an indicator of the sources of atmospheric Nr components (Huang et al., 2013). Specifically, when the ratio is larger than 1, it is commonly accepted that Nr mainly originated from agricultural activities; whereas it is commonly accepted that Nr mainly originated from industrial activities when the ratio is lower than 1 (Xu et al., 2015). In this study, the ratios of NH_4^+ -N concentration to NO_3^- -N concentration in summer and spring indicated that N in wet/bulk deposition mainly originated from agricultural activities. In autumn and winter, the contributions of agricultural and industrial activities to wet/bulk N deposition were equal.

4.3 Comparison of oxidized and reduced N in dry and wet/bulk deposition

During the monitoring period, the annual mean fluxes of oxidized (e.g., HNO_3 and pNO_3^-) and reduced (e.g., NH_3 and pNH_4^+) dry N deposition were 2.12 and 4.09 kg N/($\text{hm}^2\cdot\text{a}$), respectively. Dry N deposition estimated in the current study was obviously lower than those observed in northern China (Shen et al., 2009; Pan et al., 2012; Luo et al., 2013) but higher than those monitored at rural sites in Canada (Zhang et al., 2009). The reduced N accounted for 66% of dry N deposition, being consistent with previous studies conducted in China (Xu et al., 2015). NH_3 deposition accounted for 78% of dry reduced N deposition. It's universally acknowledged that the major sources of atmospheric NH_3 are livestock wastes and agricultural N fertilizers (Duan et al., 2016). According to Kuang et al. (2016), the amounts of NH_3 emitted from chemical fertilizer use and animal husbandry in China increased from 4.9 Tg N in 1980 to 8.0 Tg N in 2012. The amount of agricultural fertilizer application increased by 13% from 2011 to 2015 in Inner Mongolia (National Bureau of Statistics of China, 2011–2015). NO_2 was the largest contributor to oxidized N in dry deposition, followed by HNO_3 and pNO_3^- . The mean deposition fluxes of NO_2 , HNO_3 and pNO_3^- were 1.13, 0.63 and 0.36 kg N/($\text{hm}^2\cdot\text{a}$), respectively, corresponding to 53%, 30% and 17% of oxidized N in dry deposition. NH_3 and NO_2 were the two major contributors of dry N deposition at the sampling site, together contributing to 69% of dry N deposition. NO_2 is a precursor to HNO_3 . NH_3 can react with acid gases such as H_2SO_4 and HNO_3 in the air, promoting the formation of $\text{PM}_{2.5}$. $\text{PM}_{2.5}$ reduces atmospheric visibility and long-term exposure to elevated $\text{PM}_{2.5}$ concentrations can result in respiratory and cardiovascular diseases (Zheng et al., 2015). Due to strict standards of implementation and technical improvements to limit atmospheric pollution, NO_x emissions almost dropped by 41% from 1990 to 2010 in USA (Li et al., 2016). Butler et al. (2005) quantified the effect of reduced emission of NO_x on N deposition and the results showed that when NO_x emissions were reduced by 50%, the total NO_3^- deposition would be decreased by 37% and the total N deposition would be dropped by 25%. This work well manifested the importance of controlling NO_x emissions, especially in regions upwind of sensitive ecosystems. China also has made efforts to control NO_x emissions. For example, in the 12th Five-Year-Plan (2011–2015), NO_x emission was proposed to reduce by 10%. And, in late 2012, a stricter NO_x emission standard was released by Ministry of Environmental Protection of the People's Republic of China (<http://www.zhb.gov.cn/>). However, we still have a long way to go to controlling N deposition.

Deposition fluxes of NH_4^+ -N and NO_3^- -N in precipitation at the sampling site were lower than those in regions with serious N pollution in northern China (Pan et al., 2012). However, compared with the values estimated in Europe, the wet/bulk deposition fluxes in the current study were higher (Cape et al., 2012). Wet/bulk N deposition fluxes in the current study were also higher than those in Urumqi of Xinjiang (Li et al., 2012). Zhu et al. (2015) found that wet N deposition, precipitation, N fertilizer application, and energy consumption were closely related and, therefore, wet N deposition could be reduced to acceptable levels by cutting down energy consumption and

also by lessening N fertilizer application. Reduced N dominated wet/bulk deposition with a contribution of 63%, being similar to the results reported in USA (Li et al., 2016). Li et al. (2016) pointed out that wet N deposition in USA changed in recent decades from being nitrate-dominated to ammonium-dominated and that the changes were due to decreases in nitrate wet deposition fluxes in most regions (consistent with NO_x emission reductions) and increases in ammonium wet deposition. In China, the reduced N also dominates the total N deposition, but the percentage of oxidized N in total deposition is increasing rapidly (Liu et al., 2016), demonstrating the importance of implementing continuous NO_x emission control measures.

Total inorganic N deposition (dry and wet/bulk) was $14.7 \text{ kg N}/(\text{hm}^2\cdot\text{a})$ in the present study, being close to the upper limit of the N critical load ($10\text{--}15 \text{ kg N}/(\text{hm}^2\cdot\text{a})$) (Bobbink et al., 2010). In this study, about 58% of the total N deposition was from wet/bulk deposition and 42% from dry deposition. The annual mean N deposition measured from this study was slightly higher than that estimated at Ireland grasslands (Henry and Aherne, 2014), but was lower than the values in most studies carried out in different sites in China (Pan et al., 2012; Xu et al., 2015). The fractional contribution of dry N deposition in the current study (42%) was lower than those in most studies in China (Pan et al., 2012; Wang et al., 2013; Xu et al., 2015; Kuang et al., 2016).

Reduced N constituted 64% of the total N deposition in the current study, 1.5 times higher than the contribution from oxidized N. Experimental studies have shown that reduced N is more effective than oxidized N in driving the decline of biodiversity in acidic and mesotrophic grasslands (Stevens et al., 2011). The currently recognized N saturation critical load in terrestrial ecosystems is $10\text{--}15 \text{ kg N}/(\text{hm}^2\cdot\text{a})$, a value derived from field experiments (Bai et al., 2010). Total N deposition obtained from the current study exceeded the lowest critical load value and may potentially pose threats to ecosystems. Field N addition experiments conducted on temperate grassland in Inner Mongolia indicated that increased N deposition led to a decrease of plant species richness (Zeng et al., 2016) and an alteration of species composition of plant communities (Duprè et al., 2010), posing a threat to ecosystem stability. In addition, when N deposition increases, a sizable species richness loss is expected in regions with low N deposition (Stevens et al., 2011).

5 Conclusions

Average N deposition from atmosphere and precipitation was estimated to be $14.7 \text{ kg N}/(\text{hm}^2\cdot\text{a})$ during the period from 2013 to 2015 in a semi-arid grassland in Duolun County of Inner Mongolia, being close to the upper limit of the N critical load ($10\text{--}15 \text{ kg N}/(\text{hm}^2\cdot\text{a})$) in most grassland ecosystems. Specifically, 58% of total N deposition came from wet/bulk deposition and 42% from dry deposition. Gaseous N deposition pathways dominated dry deposition with a contribution of 79%. Among gaseous Nr components, NH_3 and NO_2 were the most important parts, accounting for 69% of dry deposition. Affected by emission sources and meteorological conditions, dry depositions of most Nr components (with an exception of HNO_3) exhibited relatively similar seasonal patterns: the highest deposition flux occurred in summer and the lowest in winter. The highest concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in precipitation were observed in summer. In addition, a widely-reported negative correlation between inorganic N concentrations and precipitation amounts was also observed in the present study. Since N deposition fluxes in summer contributed the most to the annual N deposition value and high fluxes were partially attributable to agricultural and industrial activities, attentions should be paid to restraining the agricultural and industrial activities in summer in order to reduce N deposition.

Our work provides useful information on the background N deposition flux of Inner Mongolia Grassland and the results can serve as a reference when conducting manipulative field experiments in this semi-arid region. Although total N deposition measured from our study indicated that Duolun County was not as heavily polluted as many other developed regions in China, it is worth noting that the observed N deposition exceeded the lowest established critical value and could pose threats to grassland ecosystems.

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