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Bulk deposition of organic and inorganic nitrogen in southwest China from 2008 to 2013☆

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ABSTRACT

China is regarded as one of the nitrogen deposition hotspots in the world. Measurements to-date have focused mainly on the North China Plain, ignoring the fact that atmospheric chemical and physical properties vary across the country and that there may be other hotspots regions that should be investigated. For this reason we have conducted a six year study, measuring the bulk deposition of reduced (NH_4-N), oxidized (NO_3-N), and dissolved organic nitrogen (DON) at three contrasting sites in the Sichuan province, southwest China. The study sites were a high altitude forest in the Gongga Mountains (GG), an agriculture dominated region in Yanting (YT) and an urban site in the mega city Chengdu (CD). The annual average bulk deposition fluxes of total dissolved nitrogen (TDN) were 7.4, 23.1 and 36.6 kg N ha^{-1} yr^{-1} at GG, YT and CD sites, respectively, during the study period 2008 to 2013. The contributions of NH_4-N, NO_3-N and DON to the TDN were in the range of 48.4–57.8%, 28.8–43.7%, and 8.0–15.6%, respectively. DON bulk deposition was mainly dominated by agricultural activities. TDN bulk deposition fluxes showed increasing trends at the agricultural and urban sites from 2008 to 2013, but there was little change at the remote forest (GG) site. While reduced N dominated bulk N deposition at all the three sites, its contribution showed a decreasing trend, suggesting a gradual increase in the importance of oxidized N. These results reveal the value of long term monitoring in detecting changes in the atmospheric chemical composition of this rapidly changing region, and their inclusion in the policy debate regarding which sources should be controlled in order to reduce the long term impacts of N deposition, especially for southwest China, where there are few measurements of N deposition.

1. Introduction

Increased fossil fuel consumption, fertilizer application and cultivation of N-fixing legumes have resulted in an increase of reactive nitrogen (Nr) emission from approximately 34 Tg N yr^{-1} in 1860 to 109 Tg N yr^{-1} in 2010 (Fowler et al., 2013). These emissions are returned to terrestrial and marine ecosystems through wet (as precipitation with wet-only collector), dry (occurred when there is no precipitation) or bulk (as precipitation with open collector) deposition, and influence ecosystem function and services. On the one hand, nitrogen (N) as an essential nutrient, can stimulate primary production in N-limited regions, and enhance carbon storage in terrestrial ecosystems (Townsend and Howarth, 2010). On the other hand, excessive N deposition may negatively impact air quality or ecosystem health and services, such as impacting human health through PM formation, influencing the greenhouse gas balance, altering soil and water chemistry and reducing biological diversity (Stevens et al., 2015; Sutton et al., 2011; Tilman et al., 2006).

Global hotspots of N deposition fluxes include Western Europe and South- and East- Asia, with average annual deposition fluxes of 24.1, 25.3 and 29.3 kg N ha^{-1} yr^{-1}, respectively (Vet et al., 2014). Due to the implementation of stricter legislation to limit Nr emissions in Europe, N deposition fluxes have decreased or stabilized in

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Europe since the late 1980s, early 1990s (Billen et al., 2013). In China, N deposition continues on an upward trend, with annual bulk N deposition fluxes increasing from 13.2 kg N ha^{-1} yr^{-1} in the 1980s to 21.1 kg N ha^{-1} yr^{-1} in the 2000s. The available measurements in China to date are almost exclusively of wet or bulk deposition. Dry deposition although important is more difficult and many times cost-prohibitive to measure. Dry deposition has recently been included in a 43 site monitoring network across China and showed that on average bulk and dry N deposition rates were equally important (50% each) (Xu et al., 2015). This implies that trends in bulk deposition may provide a useful guide to increases in total N deposition rates. The bulk deposition rates in the industrialized and agriculturally intensive regions of China are as high as the peak bulk deposition rates in Europe in the 1980s (Liu et al., 2013). With regards to the impacts of bulk N deposition, most of the research to date has focused on the highly polluted North China Plain (Pan et al., 2012), the Yangtze river delta (Xie et al., 2008), the Pearl river delta (Fang et al., 2011), and Central China (Larssen et al., 2011). Conversely, there has been limited research on bulk N deposition over Southwest China, a large region with considerable industrial and agricultural activity. Furthermore, very few data have been reported on the relative importance of organic N deposition within the bulk N deposition budget, especially for regions outside the North China Plain.

Sichuan province has a population of 8 million and is located in Southwest China. It occupies approximately 7% of the national cropland and supplies 10% of the agricultural produce of China (Zhu et al., 2009). The steady increase in fertilizer use and livestock production made Sichuan province one of the NH_3 emission hotspots in China by 2008 and NH_3 emissions are still increasing, mainly due to a growth in livestock production (Xu et al., 2016). It was reported that NH_3 emissions from Sichuan are approximately 37 kg N ha^{-1} yr^{-1} (Deng et al., 2011). Large increases in vehicle and industrial NO_x emission have also taken place during recent decades in Sichuan (Yang et al., 2014). Bulk N deposition has been studied at only a few monitoring sites in this region, with most measurements over too short a period to quantify annual deposition fluxes (Lu and Tian, 2014). This study reports 6 years of bulk N deposition of reduced N (NH_4-N), oxidized N (NO_3-N), and dissolved organic N (DON) in a remote high altitude forest, an agricultural region, and an urban site in Sichuan province. The objectives of the study were to: (1) Quantify bulk deposition fluxes of inorganic N and DON in the Sichuan province; (2) Investigate the inter-annual variability and recent trends of bulk N deposition at sites dominated by either agricultural or urban sources of Nr; (3) Investigate the likely sources of DON in bulk deposition.

2. Materials and methods

2.1. Sampling sites

This study was conducted from January 2008 to December 2013 in the Sichuan province, a region where there is a growing concern of increasing Nr emissions leading to high air pollution. The province has a total area of approximately 4.8×10^5 km^2. Sichuan province is situated in a basin and surrounded by mountains, which is not conducive to the dispersion and mixing of pollutants. The three study sites were chosen to be representative of the three main land use types in the Sichuan province (Table 1). Sampling was conducted at Gongga Mountains (GG, 29°35′N, 101°52′E), Yanting (YT, 31°16′ N, 105°28′ E) and Chengdu (CD, 30°37′ N, 104°04′ E) (Fig. 1). The GG monitoring site is located at the Alpine Ecosystem Observation and Experiment Station of Gongga Mountains, with an annual average air temperature ranging from −2.6–14.5 °C over the past ten years and an elevation of 3000 m a.s.l. This site is in the center of the Natural Forestry Conservation Region, which has a low population density and little industrial activity (Table 1). GG is therefore regarded as a background site with limited local emission sources (Zhang et al., 2014). The annual average precipitation (rain only as there is little snowfall in the region) measured during the study period was 1836 mm, 94% of which occurred from March to October during the study period (Fig. 2). The YT monitoring site is located in the Yanting Agro-ecological Experimental Station for Purple Soils, which is a member station of the Chinese Ecosystem Research Network (CERN), Chinese Academy of Sciences. Rainfed agriculture is typical in this region and is maintained at sites with slope gradients of 3–15%. The annual average fertilizer application rate is approximately 280 kg N ha^{-1} yr^{-1} (Zhu et al., 2009). The agricultural management around the YT site is typical for the Sichuan province (Table 1). The annual mean temperature over the last ten years was 17.3 °C and the annual average precipitation was 920 mm (as rain; there is no snowfall in this region). The CD monitoring site is located in the city center of Chengdu, the capital of Sichuan Province, and is one of the leading economic centers in China. The high population density and industrial activity around CD (Table 1) has resulted in a highly polluted area. CD has a subtropical humid monsoon climate, and the annual average temperature ranged from 15.2 °C to 16.6 °C during the last ten years. The annual average precipitation during the study period was 954 mm (as rain), 85% of which occurred between May and September (Fig. 2).

2.2. Measurement techniques

Each sampling site included one “standard rain gauge” (SDM6, Tianjin Weather Equipment Inc., China) to collect precipitation samples. The standard rain gauge was designed for the European National Monitoring Network for precipitation chemistry research (Cape et al., 2012). Since these rain collectors were always open the measured deposition is composed of wet and some dry deposition. Therefore we refer to these measurements as ‘bulk deposition’. All rain gauges were situated within the grounds of CAS research stations at open areas without surrounding obstacles. The amount of precipitation was determined using a measuring cylinder (scale range: 0–10 mm; division: 0.1 mm). The rain gauges (stainless) and collection vessels (glass) were cleaned with deionized water after each sample collection, and when there was no rainfall once every two days in order to minimize contamination with dry deposited material. Sample collection procedures and analytical approaches were the same as described in the European Monitoring and Evaluation Program (Fagerli and Aas, 2008). The rain gauges were checked every morning at 8 a.m., and accumulated precipitation samples were collected then to minimize evaporation. The precipitation samples were transferred to clean polyethylene bottles and frozen (−20 °C) until chemical analysis within one month. The bottles were reused, after being cleaned by soaking overnight in HCl (2%) and then rinsed with deionized water 4 times. The climate at the three locations is mild, only a few snowfall events occurred at the mountain site (GG) accounting for 6% of the total annual precipitation. Snow that had accumulated in the collectors was melted and then transferred to bottles, as done for the rainwater samples. No snowfall occurred at YT and CD and there were no fog events at the three study sites. A small number of samples with visible contamination (e.g., bird droppings), representing <0.5% of all samples collected at GG and <2.5% at YT and CD, were excluded from the data analysis. Instead, concentrations were assumed to be the average monthly concentration, and the actual precipitation of these contaminated samples was used to calculate the monthly or annual bulk N deposition fluxes.

Table 1
Descriptions of the three sampling sites in Sichuan province, Southwest China.

	Gongga Mt. (GG)	Yanting (YT)	Chengdu (CD)
Coordinates	29°35′N, 101°52′E	31°16′N, 105°28′E	30°37′N, 104°04′E
Elevation (m a.s.l.)	3000	420	500
Annual Precipitation (mm)	1836	920	954
Temperature (Min/Max)	−14.1/24.1	−0.3/30	3/31.4
Land use	Forest	Agricultural	Urban
Population Density[a] (Persons km^{-2})	7.0	235.8	1128
Per Capita GDP[a] (10^4 Yuan)	1.3	2.3	4.6

[a] Data were derived from the Statistical Yearbook of Sichuan Province from 2009 to 2014, and can be accessed online (http://www.sc.stats.gov.cn/tjcbw/tjnj/).

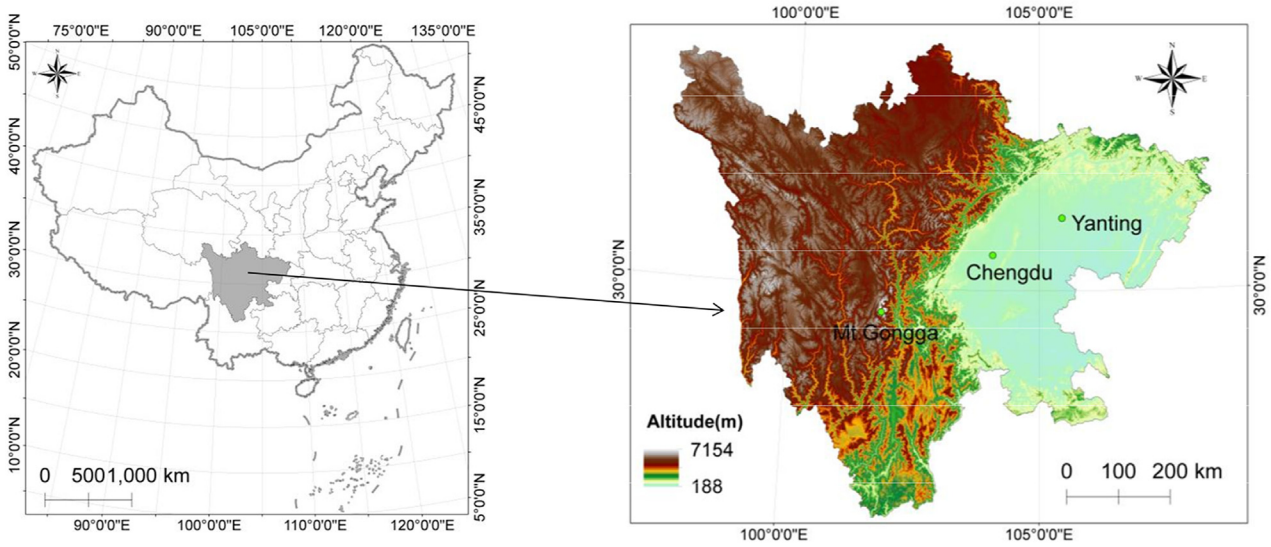

Fig. 1. Map of the three sampling sites in Sichuan province.

2.3. Analytical procedures

Once defrosted, the collected samples were filtered through 0.45-μm membrane filters to remove insoluble particulates, and then were analyzed using a flow injection auto-analyzer (Bran + Lubbe, Norderstedt, Germany) for NH_4-N and NO_3-N. The detection limits were 0.01 mg N l^{-1} for NH_4^+ and NO_3^-. It should be noted that NO_3^- was converted to NO_2^- during the chemical analysis. Therefore, the NO_3^- results are the sum of NO_3^- and NO_2^- in rainwater. The total dissolved N (TDN) concentration was measured using the alkaline potassium persulfate digestion-continuous flow analyzer (Rowland and Haygarth, 1997). DON concentrations were defined as the difference between the TDN and inorganic N (NH_4-N and NO_3-N) concentrations (Bronk et al., 2000). Rainwater samples were analyzed in duplicates and each analysis run consisted of 10 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 0–7, 0–7 and 0–20 mg l^{-1} for NH_4-N, NO_3-N and TDN, respectively.

The detection limit for DON concentrations was assumed to be the sum of detections limits of the three measured concentrations (TDN, NH_4-N and NO_3-N), 0.03 mg N l^{-1}. As in previous research, it is inevitable that some samples with very small DON concentrations will be below the detection limit or even lead to negative values for DON (Benítez et al., 2009). The DON concentrations of samples below this detection limit were not included in the data analysis.

2.4. Deposition calculation

Bulk N deposition fluxes were calculated as the product of the precipitation amount and the concentration of Nr species in rainwater (Liu et al., 2013). The monthly or annual bulk deposition flux (BDF) of Nr species was expressed using the following equation:

$$\text{Monthly or annual BDF}\left(\text{kg ha}^{-1}\ \text{yr}^{-1}\right) = 0.01 \sum_{i=1}^{n} C_i P_i$$

Where C is the measured concentration of N in rainwater (mg N l^{-1}); P is the rainwater amount of an individual precipitation event (mm); n is the number of precipitation events at the corresponding monthly or annual scale; and i is the number of precipitation events. The monthly or yearly N volume-weighted concentrations (VWC) of N species were calculated by the following equation:

$$\text{Monthly or annual VWC}\left(\text{mg N l}^{-1}\right) = 100 \times \text{BDF} / \sum_{i=1}^{n} P_i$$

The statistical analysis of the data, including Pearson correlation and linear regression analyses were performed using the SPSS software package, version 14.0 (SPSS Inc., Chicago, IL). When conducting the Pearson correlation and linear regression analyses, significance was evaluated using a significance level (p) of 0.05.

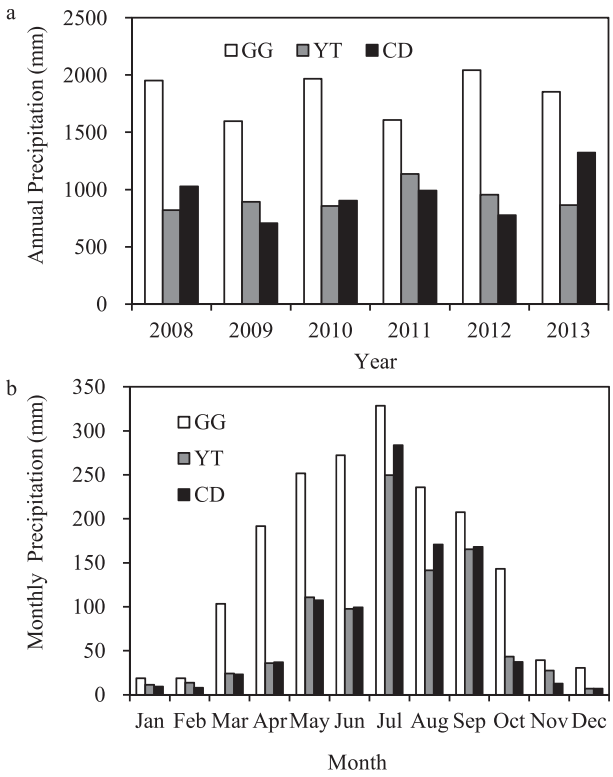

Fig. 2. Distribution patterns of the total annual precipitation (a) and the average monthly precipitation (b) at the Gongga Mt. (GG), Yanting (YT) and Chengdu (CD) sites for the study period 2008 to 2013.

3. Results

3.1. Total average bulk N deposition fluxes at the three study sites

Over the 6 year study period (2008–2013) a total of 766 deposition events at GG, 214 at YT and 265 at CD were collected and analyzed for inorganic and organic N compounds (Table 2). The difference in sample number reflects the average annual precipitation amount, which was 2 times larger at the forest site GG, when compared to the agricultural YT and urban CD site (Table 1). Also monthly precipitation amounts at GG were larger than at YT and CD, with the largest differences in the period March to June and in October (Fig. 2). For the individual rain events, GG had the smallest NH_4-N, NO_3-N, DON concentrations and deposition fluxes (Table 2); they were 5, 6 and 7 times smaller than at YT, respectively (Table 2). These differences were statistically significant ($p < 0.01$). Differences in average NH_4-N, NO_3-N concentrations and deposition fluxes between YT and CD sites were small and not significant. At CD average NH_4-N and NO_3-N, concentrations and deposition fluxes were larger than at YT, but YT had the largest DON concentrations and deposition fluxes ($p < 0.01$) (Table 2).

Table 2
Average, median, minimum, maximum and standard deviation (sd) of N concentration and deposition fluxes for Nr species at the Gongga Mt. (GG), Yanting (YT) and Chengdu (CD) sites from January 2008 to December 2013. Values are based on individual samples collected over the six year period. "n" indicates the total number of valid samples collected during the study period.

		Concentration (mg N l^{-1})			Deposition (kg N ha^{-1})		
		NH_4-N	NO_3-N	DON	NH_4-N	NO_3-N	DON
GG	Average	0.33	0.23	0.13	0.05	0.03	0.03
	Median	0.15	0.11	0.05	0.02	0.02	0.02
	Min	0.01	0.01	0.03	0.01	0.01	0.01
	Max	1.94	1.93	1.71	2.05	3.31	0.26
	sd	0.31	0.27	0.04	0.08	0.04	0.03
	n	766	766	366	766	766	366
YT	Average	1.66	1.32	0.90	0.27	0.18	0.22
	Median	1.34	0.90	0.55	0.13	0.11	0.07
	Min	0.03	0.01	0.03	0.01	0.01	0.01
	Max	7.16	7.46	4.71	2.31	1.63	2.16
	sd	1.35	1.23	0.96	0.35	0.24	0.47
	n	214	214	180	214	214	180
CD	Average	1.92	2.48	0.81	0.32	0.31	0.14
	Median	1.70	1.62	0.36	0.20	0.19	0.05
	Min	0.03	0.07	0.03	0.01	0.02	0.01
	Max	8.78	13.64	10.36	1.81	1.86	1.07
	sd	1.17	2.52	0.28	0.37	0.34	0.05
	n	265	265	195	265	265	195

Average TDN concentrations and deposition fluxes (in brackets) for individual events over the 6 year study period were 0.69 (0.11), 3.88 (0.67), and 5.21 (0.77) mg N l^{-1} (kg N ha^{-1}) at GG, YT and CD, respectively. At GG and YT NH_4-N was the dominant compound of TDN, whereas at CD average NO_3-N concentrations were larger than NH_4-N ($p < 0.01$) concentrations, but deposition fluxes were similar (Table 2).

3.2. Inter-annual variability of annual average NH_4-N, NO_3-N and DON concentrations and deposition fluxes

At the forest site GG, TDN concentrations ranged from 0.36 to 0.47 mg N l^{-1} and did not change significantly between the years. However there was a shift from NH_4-N being the main source of TDN in the years 2008–2012 to NO_3-N in 2012 and 2013. NH_4-N deposition fluxes decreased by 34% from 4.8 kg N ha^{-1} yr^{-1} (2008–2011) to 3.17 kg N ha^{-1} yr^{-1} (2012 and 2013) and NO_3-N increased by 81% from 1.66 kg N ha^{-1} yr^{-1} (2008–2011) to 3.00 kg N ha^{-1} yr^{-1} (2012 and 2013). These differences were significant at $p < 0.01$ for NH_4-N, and not significant for NO_3-N ($p = 0.186$). DON concentrations and deposition fluxes only changed by 20% and 12%, respectively, throughout the six year period (Fig. 3).

At the agricultural site YT, the overall trend for TDN showed a steady increase from 17.79 kg N ha^{-1} yr^{-1} in 2008 to 28.22 kg N ha^{-1} yr^{-1} in 2012. NH_4-N was the main contributor to TDN concentrations and deposition fluxes in all years, but NO_3-N and DON also contributed to the rise in TDN. In 2012 NH_4-N, NO_3-N and DON deposition fluxes were 34%, 88%, 134% larger than the 2009 values (Fig. 3). In 2013 there was a small but not significant decline in NH_4-N and NO_3-N, relative to 2012.

Inter-annual differences in N concentrations and deposition fluxes at the urban CD site did not follow a clear pattern with time. Concentrations of TDN were larger in the years 2009, 2010, 2012 (average concentrations = 3.94 mg N l^{-1}) than in 2008, 2011, 2013 (average concentrations = 3.31 mg N l^{-1}), and the difference of the average concentrations of these two groups was significant at $p < 0.01$. However, TDN deposition fluxes were significantly ($p < 0.01$) larger in 2011 and 2013, due to significant increases ($p < 0.05$) in NO_3-N deposition fluxes, but no change in NH_4-N fluxes ($p = 0.185$). DON concentrations and deposition fluxes were significantly ($p < 0.01$) larger in 2008, 2009 and 2012 than in other years at CD. Higher rainfall in the years with high bulk deposition may be the cause of much of the inter-annual variability in bulk deposition.

3.3. Monthly variability of NH_4-N, NO_3-N and DON concentrations and deposition fluxes

Average monthly concentrations of NH_4-N, NO_3-N and DON for the whole study period, 2008 to 2013, were used to characterize the

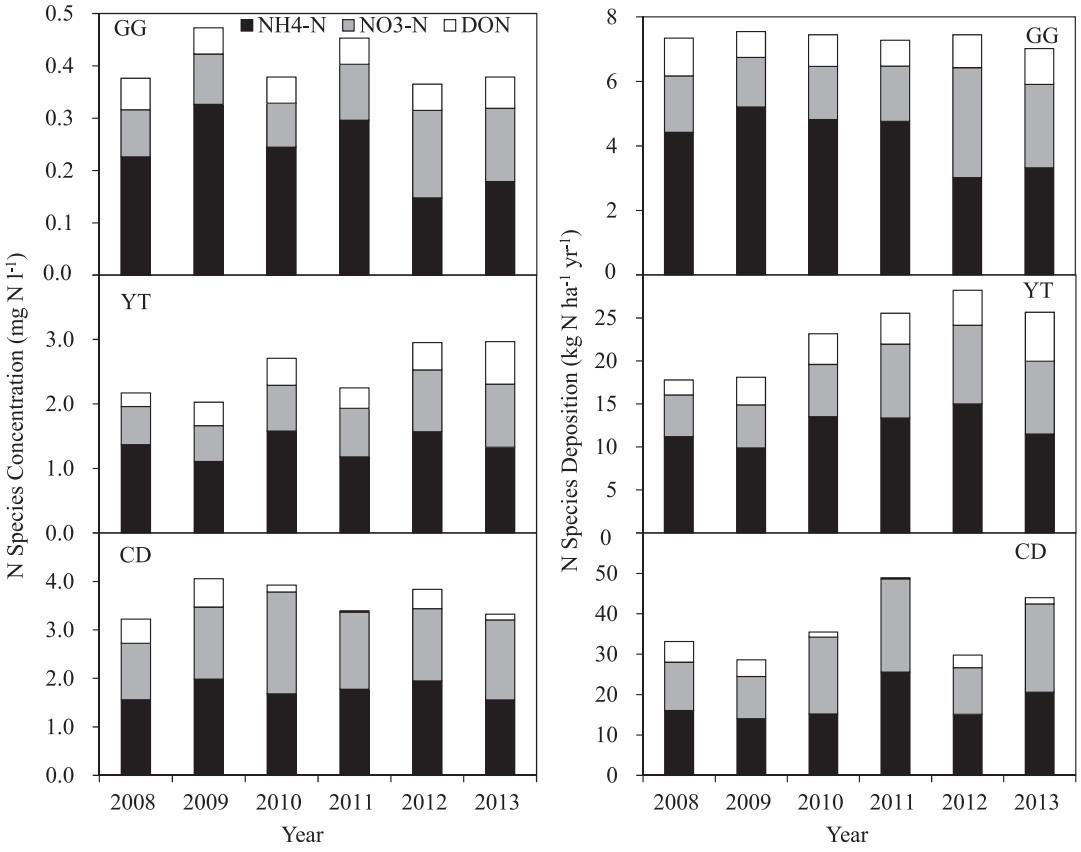

Fig. 3. Inter-annual changes of concentrations (left) and deposition fluxes (right) of NH_4-N, NO_3-N and DON at the Gongga Mt. (GG), Yanting (YT) and Chengdu (CD) sites from 2008 to 2013.

seasonal variability (Table 3). Broadly, monthly variations of NH_4-N, NO_3-N and DON concentrations and deposition fluxes showed a similar pattern, with NH_4-N providing the largest contribution to most of the monthly concentrations and deposition fluxes. Variability in the monthly concentrations over the 6 year study period was much greater at the polluted agricultural (YT) and urban (CD) locations, than at GG, with 0.21–0.37 (GG), 0.61–3.02 (YT) and 1.41–5.16 (CD) mg N l^{-1} for NH_4-N; 0.09–0.16 (GG), 0.33–2.94 (YT) and 0.82–4.52 (CD) mg N l^{-1} for NO_3-N; and 0.05–0.08 (GG), 0.17–0.86 (YT) and 0.20–0.84 mg N l^{-1} (CD) for DON.

Monthly deposition ranges are shown in Fig. 4. The seasonal dynamics of NH_4-N, NO_3-N and DON deposition fluxes were highly influenced by the rainfall distribution pattern ($p < 0.01$) at all the study sites. Dry periods lead to high concentrations, and high rainfall produced low concentrations but high deposition fluxes. The seasonal pattern of low rainfall in the winter period November

Table 3
Mean monthly concentrations of NH_4-N (a), NO_3-N (b) and DON (c) at the Gongga Mt. (GG), Yanting (YT) and Chengdu (CD) sites from 2008 to 2013. Unit: mg N l^{-1}. Data are the average values ± standard deviation of each month during the study period. "n" is the total number of valid observations of each month in the 6 year study period.

	GG				YT				CD			
	NH4-N	NO3-N	DON	n	NH4-N	NO3-N	DON	n	NH4-N	NO3-N	DON	n
Jan	0.35 ± 0.13	0.15 ± 0.08	0.08 ± 0.05	3	2.30 ± 0.58	1.25 ± 0.39	0.66 ± 0.17	2	2.22 ± 0.01	2.51 ± 0.26	0.41 ± 0.12	1
Feb	0.37 ± 0.15	0.16 ± 0.10	0.08 ± 0.02	3	3.02 ± 0.59	1.64 ± 0.49	0.86 ± 0.28	2	3.25 ± 0.47	3.60 ± 0.60	0.60 ± 0.14	1
Mar	0.25 ± 0.06	0.11 ± 0.06	0.06 ± 0.01	4	1.98 ± 0.19	1.07 ± 0.33	0.56 ± 0.17	3	3.51 ± 0.44	3.08 ± 1.10	0.57 ± 0.36	2
Apr	0.24 ± 0.05	0.10 ± 0.04	0.05 ± 0.01	8	2.00 ± 0.25	1.09 ± 0.29	0.57 ± 0.05	4	2.79 ± 0.25	2.44 ± 1.44	0.45 ± 0.11	4
May	0.23 ± 0.06	0.10 ± 0.04	0.05 ± 0.02	18	1.87 ± 0.2	0.75 ± 0.15	0.48 ± 0.06	4	2.36 ± 0.21	2.07 ± 0.69	0.39 ± 0.16	5
Jun	0.22 ± 0.03	0.10 ± 0.03	0.05 ± 0.02	21	1.74 ± 0.36	0.65 ± 0.26	0.44 ± 0.26	3	1.78 ± 0.12	1.56 ± 0.13	0.29 ± 0.07	5
Jul	0.21 ± 0.01	0.09 ± 0.02	0.05 ± 0.04	17	1.47 ± 0.21	0.54 ± 0.11	0.37 ± 0.11	6	1.49 ± 0.13	0.82 ± 0.09	0.20 ± 0.10	9
Aug	0.24 ± 0.04	0.10 ± 0.07	0.05 ± 0.03	16	0.61 ± 0.29	0.33 ± 0.13	0.17 ± 0.19	4	1.41 ± 0.12	1.24 ± 0.18	0.23 ± 0.05	7
Sep	0.25 ± 0.02	0.11 ± 0.05	0.05 ± 0.02	15	1.14 ± 0.18	0.62 ± 0.19	0.33 ± 0.09	4	1.50 ± 0.17	1.32 ± 0.32	0.24 ± 0.18	7
Oct	0.26 ± 0.04	0.11 ± 0.04	0.06 ± 0.01	13	1.37 ± 0.20	0.74 ± 0.12	0.39 ± 0.15	2	2.23 ± 0.28	2.52 ± 0.84	0.41 ± 0.08	3
Nov	0.34 ± 0.06	0.15 ± 0.05	0.07 ± 003	4	1.11 ± 0.31	0.60 ± 0.17	0.32 ± 0.27	2	5.16 ± 0.96	4.52 ± 1.07	0.84 ± 0.09	1
Dec	0.36 ± 0.13	0.16 ± 0.11	0.08 ± 0.02	4	1.64 ± 0.03	2.94 ± 0.38	0.85 ± 0.48	1	4.45 ± 0.2	3.90 ± 1.04	0.73 ± 0.29	1
Min[a]	0.21	0.09	0.05		0.61	0.33	0.17		1.41	0.82	0.20	
Max[b]	0.37	0.16	0.08		3.02	2.94	0.86		5.16	4.52	0.84	

[a] Is the minimum.
[b] Is the maximum monthly average concentration over the 6 years.

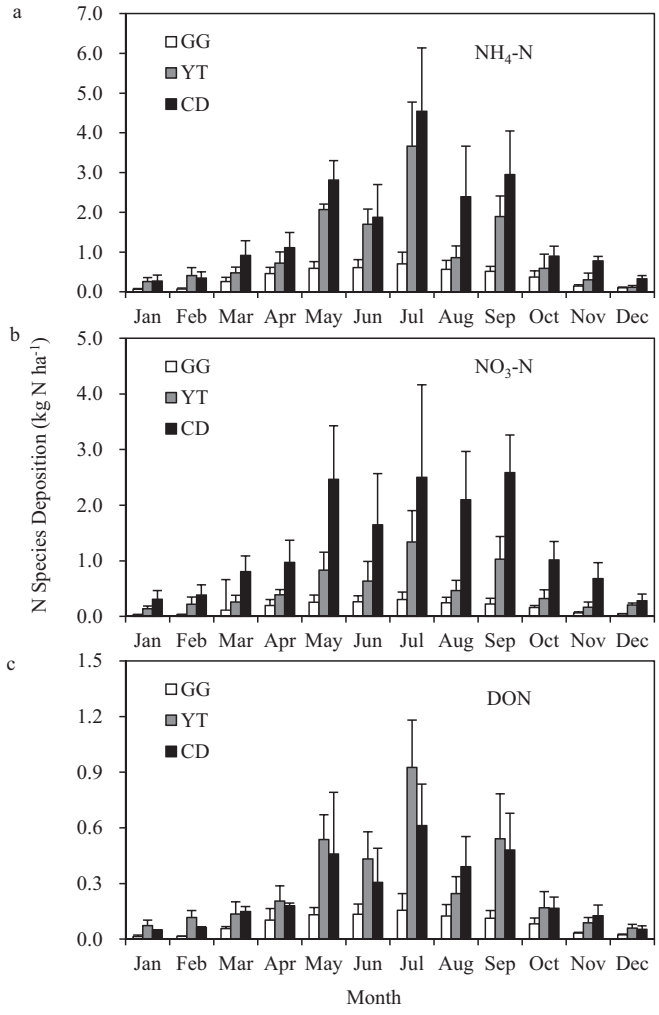

Fig. 4. Average monthly N deposition fluxes of NH_4-N (a), NO_3-N (b) and DON (c) at the Gongga Mt. (GG), Yanting (YT) and Chengdu (CD) sites from 2008 to 2013. Error bar in each column denotes standard deviation of monthly means of all single measurements during the study period.

to February was particularly pronounced at the GG mountain site. At GG, frequent rainfall (March–October) events were positively correlated with deposition fluxes, but were inversely correlated with concentrations. Deposition of NH_4-N, NO_3-N and DON increased by 4.10, 4.50 and 4.50 times, respectively, during the March to October period. Similarly, in the dry season higher concentrations but lower deposition fluxes were observed at YT. The largest concentrations were measured in the December to April period and average monthly concentrations for NH_4-N, NO_3-N and DON were 2.19, 1.60 and 0.70 mg N l^{-1}, respectively. In this same period also the smallest N deposition fluxes were measured, with average monthly deposition fluxes for NH_4-N, NO_3-N and DON of 0.40, 0.24 and 0.12 kg N ha^{-1}, respectively. At CD, there was a step change in concentrations and deposition fluxes, with significantly ($p < 0.01$) lower concentrations in the June to September period for all N compounds and significantly ($p < 0.01$) larger deposition fluxes for May to September (Table 3). Average monthly deposition fluxes for NH_4-N, NO_3-N and DON during the period of May–September were 2.91, 2.26, and 0.45 kg N ha^{-1}, respectively, while they were 0.66, 0.64 and 0.11 kg N ha^{-1}, respectively, during the period of October–April.

4. Discussion

4.1. Spatial variability of bulk N deposition

China is facing serious atmospheric N pollution problems due to increased anthropogenic Nr emissions (Liu et al., 2013). The new data presented here support this statement. The TDN bulk deposition fluxes measured at the three contrasting locations in the Sichuan province ranged from approximately 7.1 to 48.9 kg N ha^{-1} yr^{-1}, increasing from the remote forest site to the agricultural area and even further to the large city. The inorganic bulk N deposition flux at the GG forest site (6.4 kg N ha^{-1} yr^{-1}) was comparable with the highest N deposition level in European forests (Schmitt et al., 2005). The fluxes at the agricultural site YT (19.4 kg N ha^{-1} yr^{-1}) and urban site CD (34.1 kg N ha^{-1} yr^{-1}) were substantially larger than the bulk deposition fluxes reported in North America or Europe (http://nadp.sws.uiuc.edu/; http://www.emep.int/). The inorganic N bulk deposition fluxes at the forest GG and the agricultural site YT in Southwest China were smaller than the regional estimates for North China, 12 kg N ha^{-1} yr^{-1} for the forests and 24.8 kg N ha^{-1} yr^{-1} for agricultural region; but were higher than the urban regions (27.9 kg N ha^{-1} yr^{-1}) in North China (Pan et al., 2012). Average inorganic bulk N deposition fluxes (20.0 kg N ha^{-1} yr^{-1}) for GG, YT and CD were slightly smaller than those reported from regions with higher population densities and more mobile and stationary combustion sources, such as the North China Plain (24.6 kg N ha^{-1} yr^{-1}) and Southeast China (24.4 kg N ha^{-1} yr^{-1}). However, our bulk deposition fluxes were substantially larger than the less developed regions of Northeast China (13.6 kg N ha^{-1} yr^{-1}) and Northwest China (7.4 kg N ha^{-1} yr^{-1}) (Xu et al., 2015) and 5 and 3 times larger than bulk deposition rates reported from North America and Europe, respectively (Holland et al., 2005).

Bulk deposition measurements overestimate the actual wet deposition, since these types of rain collectors are open outside the periods of precipitation and thereby allow dry deposited material to collect onto the collection funnel, and to be washed into the collection vessel during rainfall. The contribution of dry deposition to open collectors depends on the sample collection procedures. In our case, the relative contribution of dry deposition to the open collector was fairly small for the following reasons: (1) the bulk collectors were cleaned every two days, regardless of precipitation occurring or not, and (2) precipitation was always collected within 24 h as the rain collectors were checked every morning at 8 a.m. Comparison with a wet-only collector at the agricultural site (YT) during the same study period showed that the open collector collected 2.5% more N than the adjacent wet-only collector (Kuang et al., 2016). Wet deposition measurements were not available at the urban and forest sites. As the same sampling protocol was followed, we assume that the contribution of dry deposition to the open collectors was similar at all three sites. Of course this assumption is highly uncertain. The 2.5% overestimate of wet deposition in our study is lower than measurements reported by Cape and Leith (2002) who only collected the precipitation and cleaned the collectors on a weekly basis. In their case 15%–50% of the measured dry deposition of NH_3 had accumulated in the collection vessel within the one week exposure. These findings suggest that dry N deposition values can be rather large, and should be routinely measured in future studies.

4.2. Temporal variability of bulk N deposition

In this study, N deposition fluxes showed a distinct seasonal pattern (Fig. 4) and increased with time over the 6 year period of monitoring at both the agricultural and urban sites (YT and CD), but showed little change in the remote region (GG) (Fig. 3). At YT and

CD, the ratios of NH_4-N/NO_3-N were usually higher in spring and summer (March–August; 2.2 and 1.3, respectively, at YT and CD) than in autumn and winter (September–February; 1.6 and 1.0 respectively, at YT and CD) (Table 3). This variation coincides with the time for fertilizer application which is an important source of NH_3 emissions. Additionally, high summer temperatures can increase NH_3 emissions from fertilized soil and animal husbandry (Sutton et al., 2013).

Seasonal changes of bulk N deposition are usually coupled to changes in meteorology. Due to the monsoon climate in Sichuan, precipitation is mainly concentrated in the period March–October for GG site and May–September for YT and CD. During the 6-year period, the average precipitation during the rainy season accounted for 94.1%, 82.5% and 85.5% of the total annual precipitation at GG, YT and CD, respectively. Consequently, the bulk N deposition flux in the rainy season accounted for 93.5%, 76.0% and 74.0%, of the annual bulk N deposition flux at GG, YT and CD, respectively. The seasonality of bulk N deposition in Sichuan showed a unimodal curve peaking during the summer months (Fig. 4). In contrast, the seasonality of NH_4-N and NO_3-N concentrations in precipitation over large areas of Northern Europe fit a sine curve with maximum concentrations in spring between February and May and a trough during late autumn, and only weak annual seasonality (Cape et al., 2012). In North-Western Spain, however, winter dominated precipitation led to the majority of N deposition fluxes occurring between October–April. This is the opposite of what was observed in this study in Sichuan (Calvo-Fernández et al., 2017). In Southeast China the wet N deposition in the monsoon season (April–June) accounts for 17.6–51.9% of the annual inorganic N deposition and therefore can play an important role for crop growth in the agricultural areas (Cui et al., 2014a). However N deposition rates are only rarely accounted for when calculating N fertilizer application rates. The much larger N deposition rates of reactive N on semi-natural vegetation during the growing season in the Sichuan province, relative to Europe is likely to drive rapid changes in species composition and plant community diversity (Stevens et al., 2004).

4.3. Sources of bulk N deposition

The general trend in China between 1980 and 2000 has been a doubling in reduced N deposition, most likely as a consequence of increased emissions from N fertilizer application and livestock rearing. At the same time a 3–20 fold increase in coal consumption and motor vehicles led to an increase in oxidized N deposition rates (Liu et al., 2013). The pollution gradient between the lowlands and the uplands in Sichuan province is consistent with the source distribution, which drives the majority of the spatial structure in nitrogen deposition, with relatively small contributions from more distant sources in India and from the North China plain, which are meteorologically rather distant and separated from Sichuan. Regional sources contribute to the air pollution in Sichuan province, but few source-receptor studies are available to quantify this component. In addition the pollution gradient relates to the GDP income and population density (Table 1).

Liu et al. (2016) used the Positive Matrix Factorization method to identify the main N deposition sources, based on bulk N deposition measurements across China during the period 2003–2014. This research identified fossil fuel combustion as the dominant source of NO_3-N (86.0%) and biomass burning contributed with 5.4%, whereas NH_4-N was mainly emitted from agricultural activities (85.9%) with a small contribution from fossil fuel combustion (6.0%). Analysis of the isotopic composition of $^{14/15}N$ of NH_4 and NO_3 in precipitation in the North China Plain also implied that agriculture is the dominant source of inorganic N in precipitation in rural areas, whereas a variety of sources were thought to be are responsible in urban areas (Zhang et al., 2008). Furthermore Huang et al. (2013) suggested that the bulk deposition ratio of NH_4-N to NO_3-N may be used as a proxy of the relative importance of the two major N deposition sources, agriculture for reduced N and transport/industry for oxidized N. When the ratio is greater than 1, agricultural activities, such as N fertilizer application and livestock production, are likely the main sources of Nr. Conversely, when the ratio is lower than 1, combustion activities are likely to be the major source of Nr (Huang et al., 2013). Based on these findings we proposed likely sources of reduced and oxidized N deposition at the three measurements sites as follows.

The annual NH_4-N to NO_3-N deposition ratios at GG, YT and CD were in the range of 0.88–3.38, 1.36–2.30 and 0.80–1.34, respectively, with averages of 2.3, 1.8 and 1.1, and exhibited a decreasing trend at all three monitoring sites during the study period (Fig. 5). N deposition was relatively low in the GG region due to the lack of agricultural and industrial emission sources. The GG region is however developing into a popular tourist resort and vehicle traffic is becoming an increasingly important contributor to future local NO_x emissions. Other than transport related sources in this remote region, the main contributor to deposition is long range transport of pollutants from the industrial and agricultural regions within Sichuan. The long range transport of sulphur has declined which may reduce the atmospheric chemical transformation rate of ammonia to ammonium (Wang et al., 2013). This is consistent with the decrease in the ratio of NH_4-N to NO_3-N in the second half of the monitoring period, especially in 2012 and 2013 (Figs. 3 and 5). YT is dominated by agricultural sources but with the development of local economies, an increasing fraction of the population now has automobiles for transport. This has resulted in an increase in deposition fluxes from 17.8 kg N ha^{-1} yr^{-1} in 2008 to 23.2 kg N ha^{-1} yr^{-1} in 2010 and from 2011 onwards due to an increased proportion of NO_3-N and decreased proportion of NH_4-N (Figs. 3 and 5). In the mega city CD, elevated bulk N deposition is strongly influenced by N emissions within the urban area, including NH_3 emissions from livestock, wastewater treatments, landfills, and building construction dust; and NO_x from vehicles and fuel consumption. Energy consumption in the Sichuan province has increased at the rate of 8.4% annually from 2000 to 2008, causing NO_x emissions to increase at the rate of 6.6% (Liu et al., 2014). City traffic can also be an important source of NH_3, and NH_3 emissions from city livestock must not be ignored (Xu et al., 2017). These two sources in the mega city CD resulted in much higher NH_4-N deposition fluxes than from the agriculture dominated region YT. Furthermore, our measurements suggests that NO_3-N from fossil fuel combustion by industry and transport is increasing more rapidly than the agricultural sources of NH_3 and is now the main contributor to bulk N deposition at all three sites, as shown by the declining ratios of NH_4-N and NO_3-N in Fig. 5. These findings are in line with Wang et al., (2013) model predictions that NO_x emissions have increased at a rate of 16% over China from 2006 to 2015, while NH_3 emissions remain uncertain due to the lack of sufficient information on the past and present level (Wang et al., 2013).

The overall average DON deposition rate in this study was 2.4 kg N ha^{-1} yr^{-1}, and DON contributed with 11% to the TDN deposition fluxes. This value is smaller than reported in some previous studies. For example, Cornell, (2011) calculated that global DON deposition rates contributed with 25–35% to TDN deposition. Contrary, Zhu et al. (2015) performed a systematic evaluation of the bulk N deposition at 41 sites in China and reported an average DON bulk deposition flux of 0.5 kg N ha^{-1} yr^{-1}, representing only 3% of TDN deposition. The significant spatial variation in DON deposition flux is most likely related to the emission sources, but only a few studies to data have investigated the sources of DON. Isotope

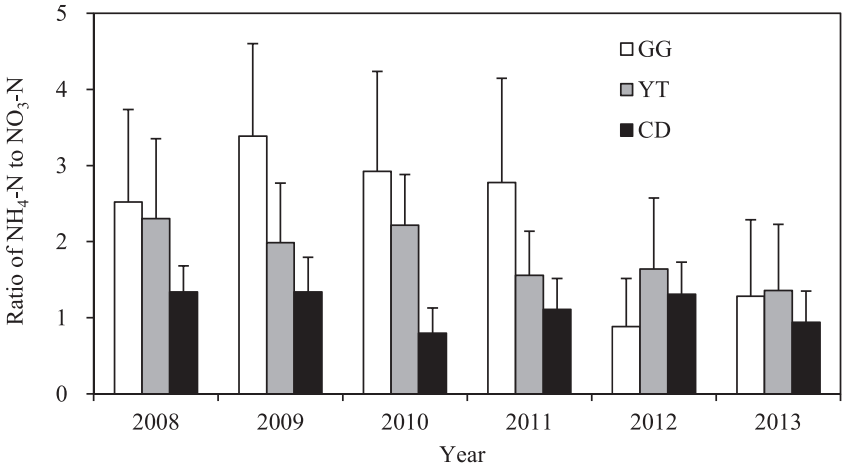

Fig. 5. Inter-annual variability of the ratios of NH_4-N to NO_3-N at the Gongga Mt. (GG), Yanting (YT) and Chengdu (CD) sites from 2008 to 2013. Error bars in each column denote standard deviation of means of all rainfall events in each year.

approaches and two-dimensional gas chromatography coupled to a nitrogen chemoluminescence detector have identified a wide range of different compounds, such as urea, amines, and amino-acids, as well as large macromolecules and humic-like substances (Kieber et al., 2005; McKenzie et al., 2016). Such analysis could not be performed in this study. However, due to the distinctly different anthropogenic sources for NH_4-N and NO_3-N, comparisons of the relationship between DON and NH_4-N or NO_3-N may reveal the origins of DON (Cornell, 2011). In the present study, DON concentrations correlated significantly with NH_4-N and also with NO_3-N concentrations (Fig. 6). Both DON concentrations and deposition fluxes at YT were substantially higher than at CD and GG. By using the same approach, studies in the agricultural North China Plain and Southeast China also found that DON concentrations were significantly correlated with agricultural activities (Cui et al., 2014b; Zhang et al., 2012). The results presented here suggest that DON deposition was primarily regulated by anthropogenic activity and that at YT the agricultural activities are a more important source of DON than industrial or transport related emissions.

4.4. Ecological effects of bulk N deposition

Atmospheric N deposition rates in the US have switched from oxidized N-dominated bulk deposition in the early 1990s to reduced N-dominated bulk deposition in the early 2010s as a result of increasing agricultural ammonia emissions and the success of regulatory policies in decreasing NO_x emissions (Li et al., 2016). At the same time a steady decline in NO_x emissions but only minor changes in reduced N emissions occurred over much of Europe (Maas and Grennfelt, 2016). The data presented here show an increasing trend in the relative importance of NO_x in bulk deposition in Southwest China, reflecting the different environmental priorities in Europe and China. In Europe oxidized N emissions peaked in the 1990s, and subsequently declined substantially, while for China it remains unclear whether peak emissions have yet occurred.

The exceedances of N deposition over critical loads have led to widespread losses of sensitive plant species in both terrestrial and aquatic ecosystems (Bobbink et al., 2010; Duce et al., 2008). The critical load for temperate deciduous forests is only 10–30 kg N ha^{-1} yr^{-1}, while the N deposition level in many forests in central and east China widely exceed 20 kg N ha^{-1} yr^{-1} (Liu et al., 2011). Persistent N inputs may lead to N saturation, which is characterized by nutrient imbalances, soil acidification, nitrate leaching, and ultimately, forest decline (Venterea et al., 2004). The forest site GG in the present study is located in a remote high-elevation region, and may be more sensitive to high N deposition rates and therefore experience greater ecosystem effects compared to agricultural or urban environments. In agricultural ecosystems N deposition should be regarded as an important N input and included when calculating optimum N fertilizer application rates for China, as well as in other countries (He et al., 2010). At the agricultural site YT, bulk deposition provided 23 kg N ha^{-1} yr^{-1}, which is about 8% of the annual N fertilizer application in this region. For aquatic ecosystems, atmospheric bulk deposition can cause serious problems, such as eutrophication, algal blooms or reduced drinking water quality. The Yangtze River Basin is the largest river basin in Asia, and the N input from bulk N deposition has increased continuously from 0.24 Tg N in 1980 to 0.89 Tg N in 2010, contributing to 3% in 1980 and 5% in 2010 of the total N input to this basin (Wang et al., 2014). Sichuan province is situated in the upper reaches of the Yangtze River, and the large amounts of bulk N deposition to this catchment have the potential to cause substantial eutrophication of the aquatic ecosystem. Assessments of the fate and effects of the N deposition appears to be a priority for the region and only by reducing emissions from agricultural sources and fossil fuel combustion will the N deposition rate in this region and all over China begin to decrease.

5. Conclusions

Bulk N deposition monitoring sites were established at a remote forest site (GG), an agricultural site (YT) and a mega city (CD) in Sichuan province, Southwest China, where the air pollution is serious but only few N deposition data were available. Annual concentration and deposition fluxes of inorganic N species ranked in the order of urban (CD) > agricultural (YT) > forest (GG), while the highest DON concentration and deposition fluxes were found at the agricultural site (YT), providing evidence that agricultural sources dominated bulk deposition of DON at this site. Deposition of NH_4-N contributed the most to bulk N deposition followed by NO_3-N. The contribution of NO_3-N showed an increasing trend relative to NH_4-N during the six year study period at all three sites. DON contributed with 8.0–15.6% to TDN. The monsoon climate of the study region was responsible for a strong seasonal bulk N deposition pattern, with typically 70% of the annual bulk deposition

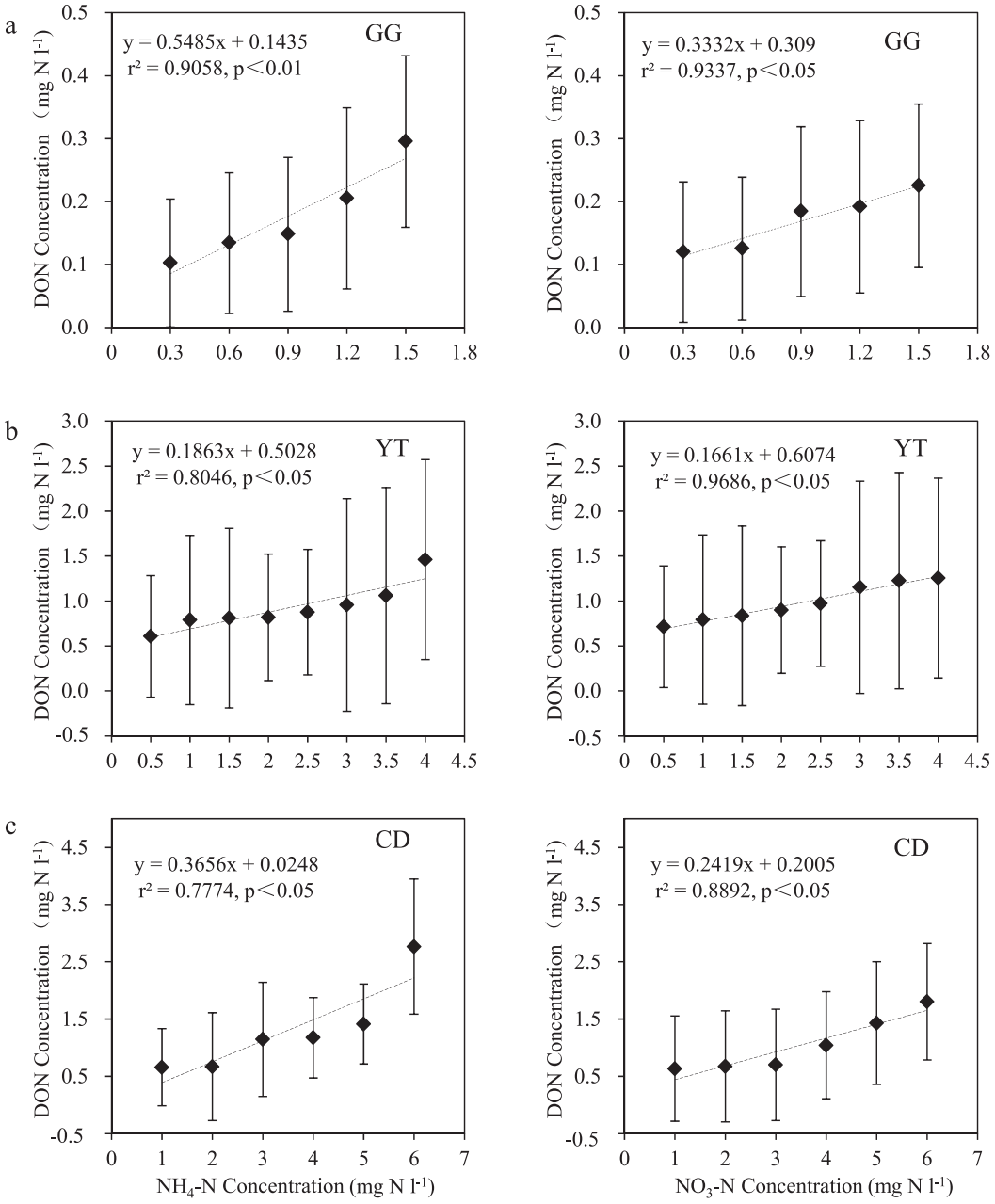

Fig. 6. Correlations between concentrations of DON with NH_4-N (left panel) and NO_3-N (right panel) concentrations at GG (a), YT (b) and CD (c) from 2008 to 2013. Values for DON concentration were the block averages (with standard deviation) of the concentration ranges to reveal trend more clearly with the large dataset.

measured in the summer months. Bulk N deposition fluxes increased by 33% and 44%, respectively, in the urban (CD) and agricultural area (YT) between 2008 and 2013, whereas only a slight change was observed in the high altitude, remote forest (GG). The results show that Sichuan province is a N deposition hotspot in China. Further research to establish source receptor matrices for the provinces of China would help quantify the inter-province exchange and the optimal control strategy for China.

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