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Wet-only deposition of atmospheric inorganic nitrogen and associated isotopic characteristics in a typical mountain area, southwestern China

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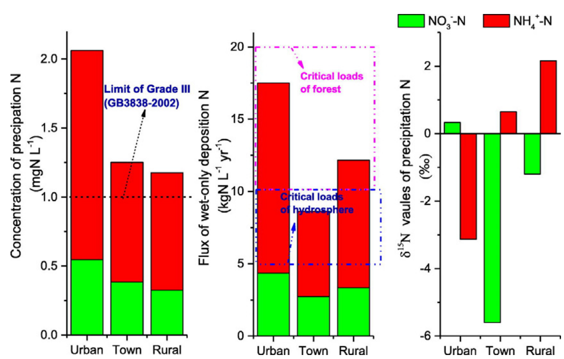
HIGHLIGHTS

- Wet-only N deposition fills the gap in mountain regions, Southwestern China.
- Precipitation $\delta^{15}N$ at urban, town and rural sites were presented for the first time.
- The urban site was N hotspot and had a different N source from rural and town sites.
- Precipitation N had a potentially negative risk on aquatic and forest ecosystems.

GRAPHICAL ABSTRACT



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ABSTRACT

To quantify and compare atmospheric nitrogen (N) deposition and its N isotopic ratio are critical for constraining N sources and effective reduction of reactive N emissions. In this study, a total of 223 rainwater samples were collected by wet-only auto-samplers, and wet-only deposition and isotopic composition ($\delta^{15}N$) of reduced (NH_4^+-N) and oxidized (NO_3^--N) N were measured at three typical mountain sites, including an urban (Wanzhou, WZ), a town (Gaoyang, GY) and a rural (Dade, DD) site in Chongqing, southwestern China in 2016. The wet-only inorganic N deposition (DIN, sum of NO_3^--N and NH_4^+-N) were 17.50, 8.63 and 12.16 kg N ha^{-1} yr^{-1} at WZ, GY and DD site, respectively. Annual $\delta^{15}N$-NH_4^+ values of rainwaters were negative at the urban site (-3.12 ± 3.21‰, WZ) and positive at both town and rural site (0.65 ± 12.51‰, GY; 2.16 ± 6.11‰, DD). Annual $\delta^{15}N$-NO_3^- values, on the contrary, were positive at the urban site (0.33 ± 7.87‰, WZ) and negative at both town and rural site (-5.59 ± 2.20‰, GY; -0.39 ± 8.89‰, DD). These results reveal the urban site was wet-only DIN hotspot and had a different N source compared with the town-rural site in the mountain area. Moreover, precipitation DIN had a potentially negative risk on both aquatic and forest ecosystems.

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1. Introduction

Human activities associated with industrialization, urbanization and intensive agriculture development have greatly altered global nitrogen (N) cycle including atmospheric N deposition (Galloway et al., 2004; Vet et al., 2014). Excessive N inputs can negatively impact air quality, human health through particulate matters and cause adverse ecological effects including soil acidification and water eutrophication especially in ecological-fragile regions (Cui et al., 2014; Vet et al., 2014; Zhao et al., 2017). Global hotspots of N deposition have reduced to Western Europe and South-and East-Asia, with average annual fluxes of 24.1, 25.3 and 29.3 kg N ha^{-1} yr^{-1}, respectively (Vet et al., 2014; Waldner et al., 2014). In China, N deposition increased from 13.2 kg N ha^{-1} yr^{-1} in the 1980s to 21.1 kg N ha^{-1} yr^{-1} in the 2000s (Liu et al., 2013). Given the various underlying surfaces and the transfer of industry bases from eastern to western China, there is a long-term work on quantifications of atmospheric N deposition and identifications of its N sources in China.

Quantifying atmospheric N (both dry and wet) deposition at local and regional scales is needed for assessing potential negative ecological impacts (Zhang et al., 2009; Flechard et al., 2011; Cui et al., 2012; Liu et al., 2013; Wang et al., 2013), and identifying contributing sources of N deposition is necessary to reduce and prevent future increases in N deposition (Fang et al., 2011; Xiao et al., 2012a; Vet et al., 2014).Usually, stable isotopic composition of precipitation $\delta^{15}N$ values have been used for identifying sources of N deposition (Zhang et al., 2008; Fang et al., 2011; Proemse et al., 2013; Walters et al., 2015; Felix et al., 2017). Also, reported studies have showed that emission sources had wide $\delta^{15}N$ ranges for characters of inner source and external conditions such as temperature, precipitation and lightening (Xie et al., 2008a, 2008b; Xiao et al., 2012a; Felix and Elliott, 2014). Thus, a comprehensive characterization of isotopic compositions is required for various N emission sources.

Knowledge on atmospheric N deposition in China has been gradually progressing in recent years (Fang et al., 2011; Liu et al., 2013; Wang et al., 2013; Xu et al., 2015; Pan et al., 2016). However, most of the research to date has focused on the highly polluted plain areas of central-eastern China (Zhang et al., 2008; Fang et al., 2011; Cui et al., 2014; Pan et al., 2016). Conversely, there has been limited research on N deposition over southwest China especially in mountain regions with a total areas of 1374,400 km^2, accounting for 14.4% of China. Moreover, the famous Three Gorges Reservoir (TGR) and its catchment (~ 56,700 km^2), one of typical ecological-fragile regions, are located there. By means of numerical simulation methods, environmental issues, including reactive N pollution (oxidized and reduced N), are critical to both the catchment and regions surrounding the Yangtze River regarding their ecological safety, and their sustainable development is influenced (Yu et al., 2014; Wang et al., 2016; Zhao et al., 2017). Thus, it is urgent to accurately quantify N flux and its sources by spot observations in this area.

The goals of the present study are to: 1) characterize annual, seasonal and spatial variations of wet N deposition in the mountain area, southwestern China; and 2) quantify the $\delta^{15}N$ values for precipitation NH_4^+-N and NO_3^--N in the catchment for determining information on the sources of the N burden. The above findings would strengthen the understanding of regional N deposition and provide insight into the control measures of water eutrophication and forest protection in the development of mountain area, southwestern China.

2. Methodology

2.1. Sampling sites

Rainwater samples were collected at three sampling sites in the northeastern Chonqing (Fig. 1). Chongqing is located in the transitional area between the Qinghai-Tibet Plateau and the plain on the middle and lower reaches of the Yangtze River in the sub-tropical climate zone with four distinct seasons. The TGR is one of the world's largest hydropower projects and the TGR catchment is west to Jiangjin district, Chongqing municipality and east to Yichang city, Hubei province (the Chongqing part is shown in Figs. 1A–B), including 26 districts and counties with a total area of 56,700 km^2 and 14.6 million populations. Also, the catchment is one of the most densely populated agricultural regions and has the largest distribution of drainage ditches, ponds and streams. Generally, the catchment has a subtropical humid monsoon climate, with annual average temperatures of 15–18 °C, precipitation amounts of 1000–1450 mm, and wind speeds of 0.9–2.1 m s^{-1} with the prevailing wind from north and northeastern directions.

The first sampling site is a mountain city site, located inside the Chongqing Three Gorges University (WZ, 108°38′E, 30°79′N), about 3 km to the south of the center of Wanzhou district, the second biggest city of Chongqing municipality. It is surrounded by residential areas, a major road with many restaurants on both sides 100 m away on the east, and the Yangtze River 600 m away on the east. A cement plant and a chemical plant are located 8 and 5.5 km, respectively, southeastern of the site. One farm with 500 chickens, another farm with 400 pigs and a wood factory on the hill are located inner 3.5 km away on the southwestern. A sampler was mounted on the rooftop of a building, about 27 m above the ground. In 2016, a total of 91 valid rain samples were collected.

The second sampling site is a mountain town site in Gaoyang (GY, 108°68′E, 31°09′N), about 24 km to the north of Yunyang County, surrounded by Pengxi river to the north and west. Usually, about 20 oil burning vessels transport goods and passengers in the river. Domestic sewage flows into the river from the town, and firewood and tree branches are used for cooking fuel. A stone-sand extractive plant is located 0.2 km in the southwest and products are often transported by trucks. A pig farm with 150 pigs is sitting 3 km in the northwestern. A sampler was on the rooftop of a residential house, about 6 m above the ground. In 2016, a total of 76 valid rain samples were collected.

The third sampling site is a flat farmland site in Dade (DD, 108°34′E, 31°21′N), the countryside of Kaizhou district, surrounded by farm lands. Usually, farmers sow coin and rice during Mar. to May and sow rape during Oct. to Nov., respectively. The average usage of chemical fertilizers in this district is 300 kg ha^{-1} yr^{-1} during 2009–2014, and three pig farms (about 1200 pigs) sprawl out in this area. A sampler was mounted on the rooftop of a farmer's house, about 10 m above the ground. In 2016, a total of 56 valid rain samples were collected.

2.2. Sample collection and chemical analysis

At each sampling site, the wet-only auto-samplers (APS-3A, Changsha Xianglan Science Apparatus Ltd., China) were installed to collect rainwater samples for one year period in 2016 for concentration analysis of NH_4^+-N, NO_3^--N, and N isotopes ($\delta^{15}N$ for NH_4^+-N and NO_3^--N). The sampler is controlled by sensors and consists of three parts: the first one is the rain sensor for recording rainfall, the second one is the rainwater collector with a diameter of 30 cm, and the third one is the dust collector with a diameter of 15 cm (Fig. 1C). As for the rainwater collector, a top cover is attached and opens to collect rainwater sample right at the beginning of each rain event and then closes right after each rain event. For each rain event, rainwater samples were immediately stored in 1 L plastics bottles and stored in the refrigerator (4 °C). All samples were then filtered through 0.45 μm membrane filters (Tianjin Jinteng Equipment Co., Ltd., China) and stored at −20 °C in the freezer for further analysis in laboratory.

NH_4^+-N and NO_3^--N concentrations were determined with an ion chromatography using a cation column (CS12A) and anionic column (AS11-HC) (Dionex 600, Dionex Corp., USA). The procedure detection limits for both NH_4^+-N and NO_3^--N were lower than 0.08 mg N L^{-1} with a relative error of 1%. Before the $\delta^{15}N$ determination, precipitation NH_4^+ is initially oxidized to nitrite (NO_2^-) by hypobromite and then NO_2^-