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Wet deposition and sources of inorganic nitrogen in the Three Gorges Reservoir Region, China☆

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ABSTRACT

Precipitation samples were collected at five rural and one urban sites in the Three Gorges Reservoir Region (TGR), China from March 2014 to February 2016. The inorganic reactive nitrogen (Nr) contents were analysed to investigate their wet deposition flux, budget, and sources in the area. Annual Nr wet deposition varied from 7.1 to 23.4 kg N ha^{-1} yr^{-1} over the six sites during the two-year study campaign. The six-site average Nr wet deposition flux was 17.1 and 11.7 kg N ha^{-1} yr^{-1} in 2014 and 2015, respectively, with 71% from NH_4^+ and 29% from NO_3^-. Dry deposition flux was estimated using the inferential method, which combined the measured ambient concentrations and modelled dry deposition velocities. The total (dry + wet) Nr deposition fluxes were estimated to be 21.4 kg N ha^{-1} yr^{-1} in 2014 and 16.0 kg N ha^{-1} yr^{-1} in 2015 at rural sites, and 31.4 and 25.3 kg N ha^{-1} yr^{-1} at the urban site. Annual average volume weighted mean (VWM) concentrations in precipitation at all the six sites differed little for NO_3^- but up to a factor of 2.0 for NH_4^+ with the highest value at the urban site. Industrial emissions, agricultural emissions, soil dust, and biomass burning were identified as potential sources of the major inorganic ions in precipitation using factor analysis and correlation analysis. Conditional probability function (CPF) analysis indicated that the urban site was predominantly affected by industrial emissions from a power plant, cement manufactory, and salt chemical facility located ~13 km southeast of the sampling site.

1. Introduction

Since the mid-1800's, the global population growth and associated demands for food and energy have led to dramatic increases in anthropogenic emissions of sulfur and reactive nitrogen (Nr) to the atmosphere and corresponding deposition fluxes to Earth surface (Galloway et al., 2004). There is evidence that sulfur deposition has decreased or at least stabilized in the last two decades, whereas Nr deposition still showed a strong increase in many countries as a result of amplified emissions from intensive agricultural practices and fossil fuel combustion (Yang et al., 2012; Liu et al., 2013; Keene et al., 2014, 2015; Pascaud et al., 2016). Therefore, besides sulfur deposition, Nr deposition should also be quantified for assessing acidic deposition effects on sensitive terrestrial and aquatic ecosystems. Furthermore, high ambient concentrations and excessive atmospheric deposition of Nr will cause multiple detrimental impacts on human health and terrestrial and aquatic systems, such as respiratory disease caused by exposures to high concentrations of NO_2 and fine particles, nitrate contamination of drinking water, eutrophication, harmful algal blooms, and nitrogen saturation of forest soils (Vedal, 1997; Aneja et al., 2001; Liu et al., 2011; Badruzzaman et al., 2012; Lepori and Keck, 2012; Binkley and Hogberg, 2016).

To assess the long-term trends and spatial patterns of atmospheric Nr (and other pollutants) deposition, monitoring networks have been established around the world, such as the Canadian Air

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and Precipitation Monitoring Network (CAPMoN, http://www.ec.gc.ca/rs-mn), the National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu/ntn), the Clean Air Status and Trends Network (CASTNET, https://www.epa.gov/castnet), the European Monitoring and Evaluation Programme (EMEP, http://www.emep.int), the IGAC/DEBITS Africa network (IDAF, http://www.idaf.sedoo.fr), and the Acid Deposition Monitoring Network in East Asia (EANET, http://www.eanet.asia/). Extensive Nr dry and wet deposition data have been generated from these networks (Sickles and Shadwick, 2007; Zhang et al., 2009; Endo et al., 2011; Flechard et al., 2011; Adon et al., 2013; Vet et al., 2014; Akpo et al., 2015; Cheng and Zhang, 2017).

In China, the Nitrogen Deposition Monitoring Network (NNDMN) was established in 2010, including 41 monitoring sites covering urban, rural and background sites across China (Xu et al., 2015). Results obtained from the NNDMN showed that north, southeast and southwest of China were hotspots of Nr deposition, with multi-year (2010-2014) average annual deposition fluxes of 56.2, 41.7 and 37.8 kg N ha^{-1} yr^{-1}, respectively. Furthermore, wet deposition is the major process scavenging Nr compounds from the atmosphere in south of China, whereas dry deposition was more important in other regions of China. This is consistent with previous results that wet deposition of Nr accounted for 70% of the total deposition fluxes in Chengdu and Wanzhou in southwest of China (Wang et al., 2016b).

The Three Gorges Reservoir Region (TGR), known as the largest hydropower project in the world, is located in the mainstream of Yangtze River, starting from Chongqing municipality to the dam site at Yichang city, Hubei province. Since the construction of the TGR, eutrophication and harmful algal blooms have occurred occasionally in some tributaries, and appeared more frequently in recent years (Wang, 2006; Holbach et al., 2015). Non-point source pollution from agricultural activities and dramatic changes in the hydrology and ecology were likely to be the main causes of the excessive Nr loading in the TGR (Xiong et al., 2013; Wang et al., 2016a). Atmospheric deposition was another major pathway delivering anthropogenic Nr into aquatic systems, e.g., contributing 20-30% to the total Nr input in the upper Yangtze River basin in 1990–2012 (Wang et al., 2016a), and up to 48% in the Lake Taihu in Yangtze Delta River Region of China (Luo et al., 2007). To date, atmospheric Nr deposition input to the TGR is yet to be quantified (Feng et al., 2010).

The present study aims to: (1) investigate seasonal and spatial variations of NO_3^- and NH_4^+ concentrations in precipitation; (2) identify major sources of inorganic ions in precipitation and further explore the impact of local emission on the variations of Nr in precipitation; and (3) quantify annual wet and total deposition budget over the TGR. Knowledge from this study has implications for better evaluating potential ecological impacts from high Nr deposition and for synthetically making environmental and regulatory policies in the TGR.

2. Methodology

2.1. Study locations and description

The TGR is located in the upstream of the Yangtze River in southwest China, with about 80% of its area at the boundary of Chongqing municipality and the rest at that of Hubei province. Approximately 74% of its terrain is mountainous. The region is characterized by a subtropical monsoon climate with high relative humidity and low wind speeds. Thus, the air pollutants can not be easily expelled. The four seasons were defined as follows: March-May (spring), June-August (summer), September-November (autumn), and December-February next year (winter). Six sampling sites were deployed within a typical watershed in the interior of the TGR (Fig. 1). Jinglinxi (JLX), Yetangxi (YTX), Baijiaxi (BJX), Gaoyang (GY) and Shaijingcun (SJC) are situated within the Xiaojiang watershed (5172 km^2), and Wanzhou (WZ) is an urban site located in the central region of the TGR. With different eutrophication characteristics from other rivers in the same region, Xiaojiang River is one of the most typical tributaries in the TGR. The five rural sites have a dominant land use category (LUC) of agricultural lands (JLX, YTX) or forests (BJX, GY, SJC), and with no industry within 10 km. WZ has an urban LUC and is inside the campus of Chongqing Three Gorges University with a main road (Shalong) about 300 m east of the site and three industrial plants southeast of the site.

2.2. Sample collection and chemical analysis

Precipitation samples were collected using an automatic atmospheric deposition sampler equipped with a rain gauge sensor (APS-3A, Xianglan Scientific Instruments Co., Ltd., China), which collected only rainwater during raining periods without interference of dust and other unwanted materials in dry periods. The precipitation amount was recorded by the rain gauge installed inside the deposition sampler. Details on the sampling collector are available in Pan et al. (2012). The precipitation sampling campaign was conducted on a daily basis from March 2014 to February 2016 at the WZ site. However, daily precipitation samples were only collected for a one month period in each season at the five rural sampling sites (Table S1). Comparison of the monthly and seasonal volume weighted mean (VWM) concentration of NO_3^- and NH_4^+ in precipitation was conducted at the WZ site where daily data were available for one whole year. Results showed that the VWM concentrations of Nr species were comparable between using one month and three months data in any season during 2014–2015, except for NH_4^+ in winter for which a 30% bias was found in using monthly data to represent seasonal data (Fig. S1).

After collection, precipitation samples were filtered through a 0.45 μm filter and refrigerated at 4 °C. The major anions (SO_4^{2-}, NO_3^- and Cl^-) and cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) in precipitation were determined using ion chromatography (Dionex Corp., Dionex 600, USA). Anions were separated using an AS11-HC column with 30 mM KOH as an eluent at a flow rate of 1.0 ml min^{-1}. Cations were determined using a CS12A column with 20 mM MSA (methanesulfonic acid) at a flow rate of 1.0 ml min^{-1}. Individual standard solutions of SO_4^{2-}, NO_3^-, Cl^-, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} (1000 mg L^{-1}, o2si, USA) were diluted to construct the calibration curves. The correlation coefficients of the linear regression of the standard curves were all above 0.999. The detection limits were below 0.01 mg L^{-1} for NO_3^- and NH_4^+. The relative standard deviation of each ion was better than 8% for the reproducibility test. Measurements of nitrogen species in gases and $PM_{2.5}$ at the WZ site followed Wang et al. (2016b).

2.3. Data analysis

VWM Nr concentration in precipitation was calculated using

$$C_w = \sum_{i=1}^{N} C_i P_i \Big/ \sum_{i=1}^{N} P_i \quad (1)$$

Where C_w is the monthly or annual VWM concentrations of Nr (mg N L^{-1}), C_i and P_i represent the concentrations of N_r and precipitation amount (mm) in the *ith* sample, respectively. N is the total number of samples.

Wet Nr deposition flux (kg N ha^{-1}) was estimated as the product