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A comparison of various approaches used in source apportionments for precipitation nitrogen in a mountain region of southwest China☆

Jian Cui [a, *], Fengwu Zhou [a], Min Gao [a], Liuyi Zhang [a], Leiming Zhang [b], Ke Du [c], Qiangmei Leng [a], Yuanzhu Zhang [d], Dongyi He [a], Fumo Yang [a, e, **], Andy Chan [f]

[a] *Centre of Atmospheric Environment Research, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing, 400714, China*
[b] *Air Quality Research Division, Science and Technology Branch, Environment and Climate Change Canada, Toronto, M3H 5T4, Canada*
[c] *Department of Mechanical and Manufacturing Engineering, University of Calgary, Calgary, T2N 1N4, Canada*
[d] *Chongqing Key Laboratory of Karst Environment, School of Geography Science, Southwest University, Chongqing, 400715, China*
[e] *Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China*
[f] *Faculty of Engineering, University of Nottingham Malaysia Campus, Jalan Broga, Semenyih, 43500, Selangor Darul Ehsan, Malaysia*

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A B S T R A C T

Six different approaches are applied in the present study to apportion the sources of precipitation nitrogen making use of precipitation data of dissolved inorganic nitrogen (DIN, including NO_3^- and NH_4^+), dissolved organic nitrogen (DON) and $\delta^{15}N$ signatures of DIN collected at six sampling sites in the mountain region of Southwest China. These approaches include one quantitative approach running a Bayesian isotope mixing model (SIAR model) and five qualitative approaches based on in-situ survey (ISS), ratio of NH_4^+/NO_3^- (R_N), principal component analysis (PCA), canonical-correlation analysis (CCA) and stable isotope approach (SIA). Biomass burning, coal combustion and mobile exhausts in the mountain region are identified as major sources for precipitation DIN while biomass burning and volatilization sources such as animal husbandries are major ones for DON. SIAR model results suggest that mobile exhausts, biomass burning and coal combustion contributed 25.1 ± 14.0%, 26.0 ± 14.1% and 27.0 ± 12.6%, respectively, to NO_3^- on the regional scale. Higher contributions of both biomass burning and coal combustion appeared at rural and urban sites with a significant difference between Houba (rural) and the wetland site ($p < 0.05$). The R_N method fails to properly identify sources of DIN, the ISS and SIA approach only respectively identifies DON and DIN sources, the PCA only tracks source types for precipitation N, while the CCA identify sources of both DIN and DON in precipitation. SIAR quantified the contributions of major sources to precipitation NO_3^- but failed for precipitation NH_4^+ and DON. It is recommended to use ISS and SIAR in combination with one or more approaches from PCA, CCA and SIA to apportion precipitation NO_3^- sources. As for apportioning precipitation NH_4^+ sources, more knowledge is needed for local ^{15}N databases of NH_3 and DON and ^{15}N fractional mechanisms among gaseous, liquid and particulate surfaces in this mountain region and similar environments.

1. Introduction

Human activities associated with industrialization, urbanization and intensive agriculture development have greatly altered the global nitrogen (N) cycle including enhanced atmospheric deposition N (Galloway et al., 2004; Liu et al., 2013; Vet et al., 2014; Goodman et al., 2016; Prieto-Parra et al., 2017). Wet deposition has been monitored widely for assessing ecological impacts of atmospheric pollutants (Cui et al., 2011; Liu et al., 2011; Amodio et al., 2014; Mohan, 2016). Nitrogen sources contributing to precipitation N need to be identified and quantified in order to assess and abate N deposition impacts on sensitive ecosystems. Sources for precipitation N are very complex, including not only primary sources from agriculture, biomass burning, fossil-fuel burning, and

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* Corresponding author.
** Corresponding author. Centre of Atmospheric Environment Research, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing, 400714, China.
E-mail addresses: cuijian@cigit.ac.cn (J. Cui), fmyang@cigit.ac.cn (F. Yang).

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water and soil surfaces, but also secondary sources from chemical transformation (Krupa, 2003; Yan et al., 2003; Felix et al., 2013; Vet et al., 2014; Bittman et al., 2017; Hansen et al., 2017).

The current source tracking methods for wet deposition N reported in the literature can be classified as qualitative and quantitative methods. Five qualitative methods were found including (1) conducting in-situ survey of local sources (ISS), (2) analyzing the ratio of NH_4^+/NO_3^- (R_N), (3) conducting principal component analysis (PCA), (4) conducting canonical-correlation analysis (CCA), and (5) using the stable isotope ($\delta^{15}N$) approach (SIA). ISS requires labour-intensive field survey of special human activities, geographic features, and meteorological conditions, which is practical at single sampling site or within a small region and may only provide special N sources such as for dissolved organic N (Cui et al., 2014a). R_N approach is a relatively simple method and can be used for reflecting the relative strength of NH_4^+ and NO_3^- and further to assess the relative contributions of agricultural and industrial sources (Xie et al., 2008; Cui et al., 2014b; Xu et al., 2015). PCA reveals relationships between precipitation ions and other pollutants known to be produced from specific agricultural and industrial sources (Coelho et al., 2011; Ciezka et al., 2016; Wang et al., 2018). CCA investigates relationships between two sets of variables e.g., N and K^+ in precipitation, the latter is known from biomass burning sources (Zuncket et al., 2003; Hardoon et al., 2004; Migliavacca et al., 2004; Khare et al., 2004; Walna et al., 2013; Rapkin et al., 2017). SIA uses specific $\delta^{15}N$ of NH_3 and NO_x or $\delta^{15}O$-NO_x from N emission sources to relatively accurately track N sources in wet deposition (Ciezka et al., 2016; Liu et al., 2017a; Leng et al., 2018), but cannot cover all the possible sources (Heaton et al., 1997; Altieri et al., 2014; Liu et al., 2017a). There is also a quantitative method that has been widely applied in water researches for N source identification (Cable et al., 2011; Fang et al., 2011; Xue et al., 2012; Proemse et al., 2013; Matiatos, 2016). Such an approach was recently applied to atmospheric environment, e.g., by running a Bayesian isotope mixing model (Liu et al., 2017a; Zong et al., 2017). One or more qualitative methods mentioned above have been applied for source appointment analysis for N wet deposition (Xie et al., 2008; Liu et al., 2017a; Leng et al., 2018). However, there was a lack of studies assessing these methods and comparing their results.

China has been suffering from serious atmospheric N pollution since the late 1970s with the rapid economic development (Hu et al., 2010; Liu et al., 2011) and has been a global hotspot for atmospheric nitrogen deposition (Vet et al., 2014). The mountain region of the Southwest China, in particularly the Sichuan province and the Chongqing municipality, was among the top polluted regions in China, partly due to the movement and transfer of the industry bases from the east to the west in China (Cheng and Zhao, 2015; Qi et al., 2015; Peng et al., 2017; Tao et al., 2017; Zhao et al., 2017). This region has mountainous terrain, which is conducive to pollutants accumulation (Guo et al., 2014; Peng et al., 2017; Wang et al., 2018), and has many ecosystems that are sensitive to acid or excessive N deposition (Zhao et al., 2017; Leng et al., 2018; Xu et al., 2018). In the present study, six sampling sites were selected in the Chongqing municipality covering different land types such as urban, town, rural and wetland. Monthly precipitation samples were analyzed and were used for apportion N sources using the five qualitative (ISS, R_N, PCA, CCA, and SIA) and one quantitative (Bayesian isotope mixing model for Stable Isotope Analysis in R, SIAR) model mentioned above. Advantages and disadvantages of these methods are revealed through a comparison of analysis results from using these methods and collected precipitation N data.

2. Methodology

2.1. Sampling sites

Precipitation samples were collected at six monitoring sites in Chongqing municipality including one urban site in Wanzhou district (WZ), one town site in Gaoyang town of Yunyang county, three rural sites in Dade town (DD) and Houba town (HB) of Kaizhou district and Renhe town (RH) of Yunyang county, and one wetland site of Qukou town (QK) of Kaizhou district (Table 1; Fig. 1). The Wan-Kai-Yun region is in the upper regions of the Yangtze River with the sub-tropical climate, often swept by moist monsoons with four distinct seasons (a warm winter, early spring, hot summer and cool autumn). In 2016, annual rainfall ranged from 928.4 mm at RH site to 1243.3 mm at DD site (Table 1), with the six-site average of 1109.4 mm, which was similar to the long-term record (1022.9 mm) in Chongqing during 2006–2015 (Peng et al., 2017). The prevailing wind direction was from the northeast and wind speed was very low with seasonal ranges of 13.3–16.1 mm s^{-1} in the region (Fig. S1). Residents in this region usually preserve pork by smoke-curing with fresh pine branches in winter. In the rural areas, crop stalks and plant wastes are burnt in the open area or as rural fuels during the plant harvest seasons. The average usage of chemical fertilizers in above counties is 300 kg ha^{-1} yr^{-1} N during 2009–2014 (Peng et al., 2017).

2.2. Sample collection and chemical analysis

Precipitation samples were collected for each rain episode using auto-samplers (APS-3A, Changsha Xianglan Science Apparatus Ltd., China) and each sampler consists of a sensor for recording rainfall and two collectors for collecting rainwater and dust, respectively (Leng et al., 2018). Samples were immediately stored in 1 L plastics bottles in the refrigerator (4 °C) after collection, and 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.

All precipitation samples were analyzed for dissolved inorganic N (DIN, including NH_4^+-N and NO_3^--N) and other ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, and F^-) using an ion-chromatography (IC) (Dionex 600, Dionex Corp., USA) and for dissolved total N (DTN) using a TOC analyser (vario TOC, Elementar Analysensysteme GmbH, Germany). Dissolved organic N (DON) in precipitation was then estimated from the concentration difference between DTN and DIN.

Before determining $\delta^{15}N$, precipitation samples stored in the freezer (−20 °C) during any month were thawed and then consolidated into one monthly sample in every three months. Both NH_4^+ and NO_3^- in precipitation were finally converted into nitrous oxide (N_2O) (Liu et al., 2014a; Wang et al., 2015) and then were measured by an isotope ratio mass spectrometer (PT-IRMS, IsoPrime 100, IsoPrime Ltd., Germany), as detailed in Leng et al. (2018).

2.3. Source appointment approaches

Five qualitative (ISS, R_N, PCA, CCA and SIA) and one quantitative (SIAR) approaches were used for determining the sources of precipitation N in the mountain region of Southwest China. ISS is the essential approach for generating the basic knowledge of source distributions, which are needed for further in-depth source-apportionment analysis. R_N is simply an approach roughly indicating the relative contributions between industrial and agricultural sources.

PCA is a pattern recognition technique that attempts to interpret