Environmental Pollution 230 (2017) 486–494

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Stable isotope analyses of precipitation nitrogen sources in Guiyang, southwestern China[☆]

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ARTICLE INFO

Article history:
Received 30 November 2016
Received in revised form
5 April 2017
Accepted 3 June 2017

Keywords:
Stable isotope
Ammonium
Nitrate
Dissolved organic nitrogen
SIAR
Reactive nitrogen emission

ABSTRACT

To constrain sources of anthropogenic nitrogen (N) deposition is critical for effective reduction of reactive N emissions and better evaluation of N deposition effects. This study measured $\delta^{15}N$ signatures of nitrate (NO_3^-), ammonium (NH_4^+) and total dissolved N (TDN) in precipitation at Guiyang, southwestern China and estimated contributions of dominant N sources using a Bayesian isotope mixing model. For NO_3^-, the contribution of non-fossil N oxides (NO_x, mainly from biomass burning (24 ± 12%) and microbial N cycle (26 ± 5%)) equals that of fossil NO_x, to which vehicle exhausts (31 ± 19%) contributed more than coal combustion (19 ± 9%). For NH_4^+, ammonia (NH_3) from volatilization sources (mainly animal wastes (22 ± 12%) and fertilizers (22 ± 10%)) contributed less than NH_3 from combustion sources (mainly biomass burning (17 ± 8%), vehicle exhausts (19 ± 11%) and coal combustions (19 ± 12%)). Dissolved organic N (DON) accounted for 41% in precipitation TDN deposition during the study period. Precipitation DON had higher $\delta^{15}N$ values in cooler months (13.1‰) than in warmer months (−7.0‰), indicating the dominance of primary and secondary ON sources, respectively. These results newly underscored the importance of non-fossil NO_x, fossil NH_3 and organic N in precipitation N inputs of urban environments.

1. Introduction

High production of anthropogenic nitrogen (N) (mainly nitrogen oxides (NO_x), ammonia (NH_3), along with organic N molecules) impairs the air quality in city environments and the chemistry of atmosphere from regional to global scales (Morin et al., 2008; Hastings et al., 2013). The subsequent increases of dissolved N (mainly as nitrate (NO_3^-), ammonium (NH_4^+), dissolved organic N (DON)) in precipitation directly enhance the levels of atmospheric N deposition and influence ecosystem structure and function (Neff et al., 2002; Kendall et al., 2007; Koba et al., 2010). The compositions and deposition levels of NO_3^-, NH_4^+, DON in precipitation are key information for accurately budgeting N deposition and evaluating N pollution (Neff et al., 2002; Cape et al., 2004, 2011). Natural ^{15}N abundance (expressed as $\delta^{15}N$ values) of NO_3^-, NH_4^+ and DON in precipitation provides 'fingerprint' identification of major N sources (Cornell et al., 1995; Knapp et al., 2005; Altieri et al., 2014, 2016). Such information is important for making strategies to reduce airborne N pollution (Alexander et al., 2009; Hastings et al., 2009) and for tracing the biogeochemistry of deposited N in ecosystems (Michalski et al., 2004; Elliott et al., 2007; Altieri et al., 2016).

Precipitation N observations have mostly focused on NO_3^- and NH_4^+, whereas DON has seldom been analyzed extensively or routinely. Actually, DON is an ubiquitous and significant component in total dissolved N (TDN) of precipitation, excluding DON introduces substantial uncertainties in estimating levels and critical

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[☆] This paper has been recommended for acceptance by Dr. Hageman Kimberly Jill.

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http://dx.doi.org/10.1016/j.envpol.2017.06.010
0269-7491/

loads of N deposition (Cornell et al., 2003; Aneja et al., 2011; Cornell, 2011). To analyze precipitation DON concentrations and deposition levels in polluted environments is necessary for understanding the provenance and importance of DON in elevated N deposition (Carrillo et al., 2002; Cape et al., 2004). Atmospheric DON can originate from terrestrial and oceanic, natural and anthropogenic, primary and secondary sources (Cornell et al., 2001; Neff et al., 2002). Components and sources of terrestrial DON in the atmosphere are more diverse and complex than those of oceanic ones (Cornell et al., 1995; Russell et al., 1998). Natural DON can be derived from sea spray droplets and plant pollen (Prospero et al., 1996), while anthropogenic DON includes primary emissions directly from fossil-fuel and biomass combustion, fertilizers and secondary production from inorganic N species via the reaction with non-N-containing organic compounds (Chang and Novakov, 1975; Prospero et al., 1996; Cornell et al., 2001; Neff et al., 2002). For example, the transformations of NH_3 to ON have been clearly verified in experimental studies (Na et al., 2007; Nozière et al., 2009), which is a potential source of ON in atmospheric dry and wet deposition. The $\delta^{15}N$ values of DON in urban precipitation provide source information of atmospheric DON under N-polluted environments. However, a robust separation of detailed DON components for direct $\delta^{15}N$ analysis of remain difficult (Cornell et al., 1995; Feuerstein et al., 1997; Knapp et al., 2005). Using the ultraviolet photo-oxidation of DON to NO_3^- and subsequent reduction of NO_3^- to N_2 (Rendell et al., 1993), Cornell et al. (1995) first measured $\delta^{15}N$ values of DON in rain and snow samples, showing a wide distribution of −7.3‰ to +7.3‰. By comparing with $\delta^{15}N$ values of potential sources, Cornell et al. (1995) attributed the negative $\delta^{15}N$ values of rain DON at marine sites to anthropogenic NO_x and NH_3 sources or products of marine denitrification, while positive values at continental sites to primary sources from soil and vegetation. Using the same method, Russell et al. (1998) observed more positive $\delta^{15}N$ values of precipitation DON (−0.5‰ to +14.7‰) in Chesapeake Bay region, speculating common origins between DON and NO_3^- from fossil-fuel combustions. However, both studies (Cornell et al., 1995; Russell et al., 1998) emphasized that the direct processing using UV light irradiation may underestimate the contribution of DON in N deposition, especially causing worse precision in samples with high inorganic N and low DON. Alternatively, $\delta^{15}N$ values of DON can be calculated through a $\delta^{15}N$ mass balance equation between TDN and dissolved inorganic N (DIN) plus DON (TDN = DON + DIN), which has been widely performed on water and soil samples (Koba et al., 2010, 2012; Altieri et al., 2013, 2016). Using this method, a wider $\delta^{15}N$ distribution of aerosol DON (+13.2 ± 18.6‰) was recently observed on the island of Bermuda in the western North Atlantic Ocean (Altieri et al., 2016).

Precipitation $\delta^{15}N$ studies were mostly conducted on NO_3^- and NH_4^+ since 1950s (Hoering, 1957). However, precise analyses of NO_3^- and NH_4^+ sources in precipitation have been always prevented from the fact that each of these ions in the atmosphere is derived from a mixture of multiple emission sources and is a product of complicate physical and chemical processing on the emission sources. **Therefore, there are two important conditions or assumptions for that $\delta^{15}N$ values of precipitation NH_4^+ or NO_3^- can differentiate contributions of major emissions sources**.

First, $\delta^{15}N$ values of dominant NH_3 or NO_x emissions are distinct and well characterized. In the urban environments, dominant emission sources for precipitation NO_3^- include ^{15}N-enriched NO_x from coal combustion and biomass burning, ^{15}N-depleted NO_x from vehicle exhausts, microbial N cycle of soil and animal/urban wastes (Table S1). For precipitation NH_4^+ sources, both volatilization NH_3 (mainly from animal wastes and fertilizers) and fossil NH_3 sources (mainly from coal combustion and vehicle exhausts) showed negative $\delta^{15}N$ values (Table S1). A potential origin of ^{15}N-enriched NH_3 is biomass burning, whose $\delta^{15}N$ value was estimated by that of aerosol NH_4^+ (12.1‰) in winter at Yurihonjo, Japan (Kawashima and Kurahashi, 2011) though direct measurements are still unavailable. Obviously, $\delta^{15}N$ values of NH_3 and NO_x emissions are still very limited and have substantial variabilities. Extant studies showed that NH_3 volatilization from animal wastes and fertilizers are temperature-dependent and can cause ^{15}N enrichments in both remaining NH_4^+ thus later NH_3 emissions over time (Mariappan et al., 2009). In the laboratory study of Li and Wang (2008), the $\delta^{15}N$ values of NO from microbial N cycle increased gradually over the time of soil incubation. $\delta^{15}N$ values of NO_x from coal combustion were influenced by the use of NO_x scrubbing technology, with significantly higher $\delta^{15}N$ values in NO_x undergone catalytic NO_x reduction (Felix et al., 2012). The $\delta^{15}N$ variations of NO_x from vehicle exhausts showed a Rayleigh pattern with the NO_x emissions, which is linked to engine warming-up and by extension local commute characteristics (Walters et al., 2015). Recently, $\delta^{15}N$ of NO_x from biomass burning was found to be a function of biomass $\delta^{15}N$ values (Fibiger and Hastings, 2016). Walters et al. (2016) observed diurnal and seasonal variations in $\delta^{15}N$ of NO_x, which might be influenced by internal isotope exchange between NO and NO_2, in turn is dependent on meteorological factors such as temperature, solar radiation, and other oxidant constituents (e.g., OH, O_3, VOC). Accordingly, it remains a challenge to well characterize and localize source $\delta^{15}N$ values, and to assign source $\delta^{15}N$ values for precipitation $\delta^{15}N$ analysis more specifically.

Second, precipitation scavenges both gaseous and particulate N species efficiently because researchers have revealed isotopic fractionations associated with the formations of NO_3^- and NH_4^+ in atmospheric particulates, then differing rainout efficiency between gaseous and particulate N species would change the initial $\delta^{15}N$ values of emission sources in precipitation (Heaton, 1987; Heaton et al., 1997; Altieri et al., 2014). In controlled experiments, large ^{15}N enrichment of particulate NH_4^+ due to the NH_3 $(g) \leftrightarrow NH_4^+$ (p) equilibrium was found (+33‰; Heaton et al., 1997), resulting in $\delta^{15}N$ values of particulate NH_4^+ higher than the remaining NH_3. For NO_3^-, NO is the major form of most initial NO_x emissions. However, the measurable NO in the atmosphere is a mixture of NO emissions and NO_2 photolysis-derived NO. Upon entering the atmosphere, most of NO emissions would be rapidly oxidized (thus NO has much shorter life time) to NO_2 then finally to NO_3^-. Isotope exchange equilibrium would occur during the NO-NO_2 cycle. In simulated experiments with very 'beneficial' conditions (e.g., closed systems, no adequate oxidants, long mixing time to achieve an equilibrium exchange) (Monse et al., 1969; Freyer et al., 1993; Heaton et al., 1997; Walters et al., 2016), N isotope equilibrium exchange fractionations were observed (>34‰; depending on the experimental conditions), making ^{15}N enrichment in more oxidized forms. Moreover, the kinetic fractionation of gaseous NO_2 oxidation to gaseous HNO_3 was simulated as −3‰ (Freyer, 1991). The equilibrium fractionation for gaseous HNO_3 and NH_4NO_3 particles was determined as +21‰ in the laboratory (Heaton et al., 1997). Differently, in the study of Geng et al. (2014), the $\delta^{15}N$ differences (−8.5 ± 2.5‰) between snow NO_3^- and gaseous HNO_3 during photolysis (Erbland et al., 2012) were assumed as the equilibrium fractionations between gaseous HNO_3 and particulate/aqueous NO_3^-. In general, these processes would result in higher $\delta^{15}N$ in particulate NO_3^- than the initial NO_x sources.

In the 'real' atmosphere systems, however, isotopic fractionations associated with NO_3^- and NH_4^+ formations have been poorly known. Researchers often assumed efficient scavenging of both gaseous and particulate N species into precipitation thus no substantial $\delta^{15}N$ difference between initial N emissions and precipitation N. For examples, NO_x from coal combustion and vehicle