Nitrogen isotope variations of ammonium across rain events: Implications for different scavenging between ammonia and particulate ammonium☆

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ABSTRACT

Enhanced ammonia (NH_3) emissions and deposition caused negative effects on air quality and ecosystems. Precipitation is an efficient pathway to remove NH_3 and particulate ammonium (p-NH_4^+) from the atmosphere into ecosystems. However, precipitation scavenging of p-NH_4^+ in chemical transport models has often considered fine p-NH_4^+, with inadequate constraints on NH_3 and coarse p-NH_4^+. Based on distinct $\delta^{15}N$ values between NH_3 and NH_4^+ in PM$_{2.5}$ (particulate matters with aerodynamic diameters $\leq 2.5\,\mu m$) or TSP (total suspended particulates), this paper interpreted intra-event variations of precipitation NH_4^+ concentrations and $\delta^{15}N$ values ($\delta^{15}N$-NH_4^+ values) at Guiyang (Xiao et al., 2015). Generally decreased NH_4^+ concentrations across rain events reflected decreasing scavenging of NH_3 and p-NH_4^+. Using a Bayesian isotope mixing model, we found that differing contributions between ^{15}N-depleted NH_3 and ^{15}N-enriched p-NH_4^+ were responsible for the three-stage variations of intra-event $\delta^{15}N$-NH_4^+ values. The decreases of $\delta^{15}N$-NH_4^+ values across the first and third stages indicated more decreases in scavenging p-NH_4^+ than NH_3, while the increases of $\delta^{15}N$-NH_4^+ values across the second stage were resulted primarily from more increases in scavenging p-NH_4^+ (particularly fine p-NH_4^+) than NH_3. These results stressed influences of differing scavenging between NH_3 and p-NH_4^+ on precipitation $\delta^{15}N$-NH_4^+ values, which should be considered in modeling precipitation scavenging of atmospheric p-NH_4^+.

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1. Introduction

Ammonium (NH_4^+) is the dominant form of inorganic nitrogen (N) deposition from the atmosphere to most terrestrial ecosystems of the world (Galloway et al., 2008; Liu et al., 2013), mainly originating from combustion sources (e.g. fossil fuel consumption and biomass burning) and volatilized sources (e.g. fertilizer application and wastes) (Sutton et al., 2000; Huang et al., 2012; Kang et al., 2016). For example, increased NH_3 emissions in China were primarily derived from livestock wastes and synthetic fertilizer applications, which accounted for about 49% and 37% of annual NH_3 emissions on average from 1980 to 2012 (Kang et al., 2016). These emissions enhanced the NH_3 and NH_4^+ deposition over China (Liu et al., 2013), which has caused negative effects on air quality and ecosystems.

Precipitation is an efficient way to remove NH_3 and p-NH_4^+ from the atmosphere (Seinfeld and Pandis, 2006; Andronache, 2003; Kajino and Aikawa, 2015), generally accounting for over 72% of NH_4^+ deposition at different types of land use across China (Xu et al., 2015). Precipitation scavenging mechanisms of particulates are critical for parameterizing wet scavenging coefficients (WSCs, Xu et al., 2017) in chemical transport models (Wang et al., 2014; Xu et al., 2017). Since 1990s, scavenging coefficients have become quite important parameters in chemical transport models to characterize precipitation processes (Okita et al., 1996; Zhang et al., 2013). However, there have long been substantial uncertainties (such as size-specific scavenging coefficients and vertical variations of aerosols) in theoretical parameterizations of WSCs due to the complex physical and chemical processes in the atmosphere (Zhang et al., 2013; Sun et al., 2015).

There are two main scavenging processes of precipitation: rainout (in-cloud scavenging) and washout (below-cloud

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scavenging) (Andronache, 2003). The rainout and washout mechanisms of particulates include the activation of cloud condensation nuclei in supersaturation conditions and the collection of aerosols by falling hydrometeors, respectively (Andronache, 2003; Aikawa and Hiraki, 2009). For rainout, individual cloud droplets initially start their lives as cloud condensation nuclei. The critical supersaturation and the particulate diameters (particularly around one hundred nanometers) are the key factors of cloud condensation nuclei concentrations (Köhler, 1936; Dusek et al., 2006). The washout dominates the removal of atmospheric particulates due to high p-NH$_4^+$ concentrations below cloud and thus is a crucial process in chemical transport models (Aikawa and Hiraki, 2009; Kajino and Aikawa, 2015; Xu et al., 2017). To reduce uncertainties of parameters in models, some field studies were conducted on the WSCs of aerosols (Okita et al., 1996; Andronache, 2004; Yamagata et al., 2009). The current below-cloud WSCs of p-NH$_4^+$ are based on the assumption that precipitation NH$_4^+$ (w-NH$_4^+$) mainly comes from fine particulates (with aerodynamic diameters $\leq$ 2.5 μm; PM$_{2.5}$) (Kajino and Aikawa, 2015; Xu et al., 2017). However, this assumption remains uncertain due to inadequate consideration on NH$_3$ and coarse p-NH$_4^+$. During the precipitation, it is difficult to measure the real-time and vertical variations of atmospheric NH$_3$ and p-NH$_4^+$ concentrations (Asman et al., 1998). Both p-NH$_4^+$, especially in coarse particulates, and NH$_3$ concentrations decreased greatly with the altitude (Georgii and Muller, 1973; Zhang et al., 2009; Li et al., 2015), approaching zero over cloud base heights (e.g., 1687 m on average; Zhang et al., 2009; Xu et al., 2017). For p-NH$_4^+$, the scavenging coefficients of coarse particulates (with diameters >2.5 μm) are higher than those of PM$_{2.5}$ because of gentler Brownian motion and smaller inertia of fine ones (Greenfield, 1957; Andronache, 2003). Therefore, low below-cloud concentrations of coarse p-NH$_4^+$ relative to fine p-NH$_4^+$ do not necessarily represent a negligible contribution to w-NH$_4^+$ due to its higher scavenging coefficients (Greenfield, 1957; Andronache, 2003; Li et al., 2014). For NH$_3$, the Henry constant for solution in pure water is about 6.0×10^{-1} mol m^{-3} Pa^{-1} (Sander, 2015). Theoretical studies indicated that in addition to NH$_3$, fine p-NH$_4^+$ and coarse p-NH$_4^+$ substantially contributed to w-NH$_4^+$ (Behera et al., 2013; Li et al., 2014). A study at Canadian rural locations estimated high NH$_3$ scavenging contributions (ca. 30%) to w-NH$_4^+$ (Cheng and Zhang, 2017). However, based on the precipitation NH$_4^+$ concentrations (expressed as [NH$_4^+$]), it is difficult to differentiate the relative importance among NH$_3$, fine p-NH$_4^+$ and coarse p-NH$_4^+$ for precipitation scavenging, which is very important to estimate below-cloud WSCs of p-NH$_4^+$ (Yamagata et al., 2009; Xu et al., 2017).

Natural N isotopes (expressed as δ^{15}N values) of w-NH$_4^+$ are important parameters in recording sources and precipitation scavenging processes of atmospheric NH$_3$ and p-NH$_4^+$ (Moore, 1977; Freyer, 1978; Heaton, 1987; Altieri et al., 2014). Since 1950s, δ^{15}N values of precipitation NH$_4^+$ (δ^{15}N-NH$_4^+$ values) have been applied for tracing major sources of atmospheric NH$_3$ (Hoering, 1956; Leng et al., 2017; Liu et al., 2017), mostly based on direct δ^{15}N comparisons between NH$_4^+$ in daily- or event-based rainwater and NH$_3$ from emission sources (e.g. Felix et al., 2013). There is a lack of knowledge on the relative importance of NH$_3$, fine p-NH$_4^+$, and coarse p-NH$_4^+$ to w-NH$_4^+$, which is important for better interpreting precipitation δ^{15}N-NH$_4^+$ values and variations. Due to the development of δ^{15}N analytical methods (Garten, 1992; Liu et al., 2014), δ^{15}N values of NH$_3$ and p-NH$_4^+$ were characterized in different field circumstances in past decades (Fig. 1). The observed δ^{15}N values showed distinct differences among NH$_3$, NH$_4^+$ in PM$_{2.5}$ and TSP (total suspended particulates) (hereafter expressed as PM$_{2.5}$-NH$_4^+$ and TSP-NH$_4^+$, respectively) (Fig. 1). Due to the large kinetic isotope fractionations during agricultural NH$_3$ volatilization, the δ^{15}N values (mean $\pm$ SD values) of NH$_3$ (-16.7 ± 11.5‰; n = 122; Smirnoff et al.,
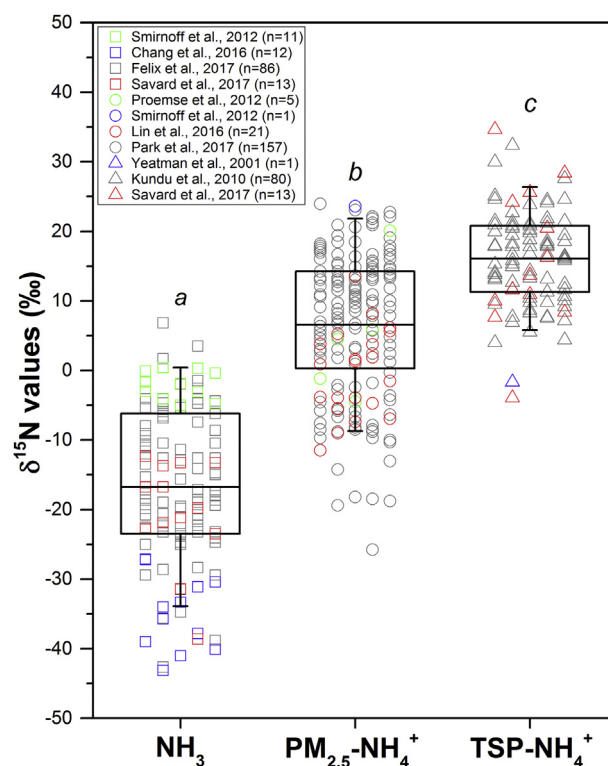
Fig. 1. δ^{15}N values of atmospheric NH$_3$, PM$_{2.5}$-NH$_4^+$, and TSP-NH$_4^+$. Different symbols showed scattered values. The boxes encompass the 25th − 75th percentiles, the line in each box marks the mean value, and whiskers are SD values. Different letters (a, b, c) above the boxes mark significant differences at the level of $P < 0.05$.

2012; Chang et al., 2016; Felix et al., 2017; Savard et al., 2017) are significantly lower than those of PM$_{2.5}$-NH$_4^+$ (δ^{15}N$_{PM2.5-NH4+}$: 6.6 $\pm$ 10.2‰; n = 184; Smirnoff et al., 2012; Proemse et al., 2012; Lin et al., 2016; Park et al., 2017) and TSP-NH$_4^+$ (δ^{15}N$_{TSP-NH4+}$: 16.1 $\pm$ 6.8‰; n = 94; Yeatman et al., 2001; Kundu et al., 2010; Savard et al., 2017) (p < 0.05) (Fig. 1). For atmospheric NH$_3$, the relative contributions of different NH$_3$ emission sources directly determine its δ^{15}N signatures and ranges. Differently, ^{15}N enrichment in p-NH$_4^+$ relative to NH$_3$ is mainly caused by the large fractionations of equilibrium reaction between NH$_3$ and p-NH$_4^+$ (Heaton et al., 1997). The p-NH$_4^+$ is mostly produced by the secondary reactions of NH$_3$ with acids, with quite lower contributions from primary particulates. Accordingly, different NH$_3$ emission sources with different NO$_x$ and SO$_2$ emissions (Seinfeld and Pandis, 2006; Wang et al., 2013) potentially influence the NH$_3$ $\leftrightarrow$ NH$_4^+$ equilibrium and associated isotope effects thus the δ^{15}N values of corresponding p-NH$_4^+$. Depending on in-situ physical and chemical conditions, p-NH$_4^+$ may experience more equilibrium exchanges with NH$_3$ during the long-range transportation (Skinner et al., 2004, 2006; Felix et al., 2014). As fine particulates have already included in and mixed with the coarse particulates during the collection of TSP, δ^{15}N$_{TSP-NH4+}$ values were virtually the bulk δ^{15}N values of fine and coarse p-NH$_4^+$. If the equilibrium isotope effects with NH$_3$ do not differ between TSP-NH$_4^+$ and PM$_{2.5}$-NH$_4^+$, one possible reason for higher δ^{15}N values in TSP-NH$_4^+$ than PM$_{2.5}$-NH$_4^+$ is that TSP includes more primary NH$_4^+$ sources (e.g., δ^{15}N = about 20 − 34‰ for primary p-NH$_4^+$ from livestock wastes; Savard et al., 2017) than PM$_{2.5}$ (Wang et al., 2011, 2013; Guo et al., 2014). Differently, PM$_{2.5}$-NH$_4^+$ is chiefly produced by the secondary reactions between ^{15}N-depleted NH$_3$ (Fig. 1) and acids (Seinfeld and Pandis, 2006; Wang et al., 2013).