



Isotopic constraints on the atmospheric sources and formation of nitrogenous species in clouds influenced by biomass burning

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Abstract. Predicting tropospheric cloud formation and subsequent nutrient deposition relies on understanding the sources and processes affecting aerosol constituents of the atmosphere that are preserved in cloud water. However, this challenge is difficult to address quantitatively based on the sole use of bulk chemical properties. Nitrogenous aerosols, mainly ammonium (NH_4^+) and nitrate (NO_3^-), play a particularly important role in tropospheric cloud formation. While dry and wet (mainly rainfall) deposition of NH_4^+ and NO_3^- are regularly assessed, cloud water deposition is often underappreciated. Here we collected cloud water samples at the summit of Mt. Tai (1545 m above sea level) in eastern China during a long-lasting biomass burning (BB) event and simultaneously measured for the first time the isotopic compositions (mean $\pm 1\sigma$) of cloud water nitrogen species ($\delta^{15}\text{N-NH}_4^+ = -6.53\text{‰} \pm 4.96\text{‰}$, $\delta^{15}\text{N-NO}_3^- = -2.35\text{‰} \pm 2.00\text{‰}$, $\delta^{18}\text{O-NO}_3^- = 57.80\text{‰} \pm 4.23\text{‰}$), allowing insights into their sources and potential transformation mechanism within the clouds. Large contributions of BB to the cloud water NH_4^+ ($32.9\% \pm 4.6\%$) and NO_3^- ($28.2\% \pm 2.7\%$) inventories were confirmed through a Bayesian isotopic mixing model, coupled with our newly developed computational

quantum chemistry module. Despite an overall reduction in total anthropogenic NO_x emission due to effective emission control actions and stricter emission standards for vehicles, the observed cloud $\delta^{15}\text{N-NO}_3^-$ values suggest that NO_x emissions from transportation may have exceeded emissions from coal combustion. $\delta^{18}\text{O-NO}_3^-$ values imply that the reaction of OH with NO_2 is the dominant pathway of NO_3^- formation ($57\% \pm 11\%$), yet the contribution of heterogeneous hydrolysis of dinitrogen pentoxide was almost as important ($43\% \pm 11\%$). Although the limited sample set used here results in a relatively large uncertainty with regards to the origin of cloud-associated nitrogen deposition, the high concentrations of inorganic nitrogen imply that clouds represent an important source of nitrogen, especially for nitrogen-limited ecosystems in remote areas. Further simultaneous and long-term sampling of aerosol, rainfall, and cloud water is vital for understanding the anthropogenic influence on nitrogen deposition in the study region.

1 Introduction

Nitrogenous aerosols, mainly nitrate (NO_3^-) and ammonium (NH_4^+), formed from the emissions of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and ammonia (NH_3) and are major chemical components of aerosols, which serve as cloud condensation nuclei (CCN) and thus play an important role during cloud formation in the troposphere (Gioda et al., 2011; van Pinxteren et al., 2016). Cloud water nitrogenous compounds also represent a vital contributor to nitrogen (N) budgets of terrestrial (Li et al., 2016b; Liu et al., 2013; Weathers and Likens, 1997; Vega et al., 2019) and marine ecosystems (Kim et al., 2014; Okin et al., 2011). However, the sources and formation processes of cloud water N species are only poorly understood.

NO_x can be emitted from both anthropogenic and natural sources. Globally, over 50 % of the NO_x emissions derive from combustion of fossil fuels ($\sim 25 \text{ Tg N yr}^{-1}$; Jaegle et al., 2005; Richter et al., 2005; Duncan et al., 2016) with the remainder being primarily soil-related emissions ($\sim 9 \text{ Tg N yr}^{-1}$; Lamsal et al., 2011; Price et al., 1997; Yienger and Levy, 1995; Miyazaki et al., 2017) or deriving from biomass burning ($\sim 6 \text{ Tg N yr}^{-1}$) and lightning ($2\text{--}6 \text{ Tg N yr}^{-1}$) (Anenberg et al., 2017; Levy et al., 1996). The atmospheric sinks of NO_x include the production of $\text{HNO}_3(\text{g})$ and the formation of aerosol NO_3^- (Seinfeld and Pandis, 2012), the partitioning of which can vary with time (Morino et al., 2006). As for NH_3 , over 90 % of the NH_3 emissions in terrestrial ecosystems originate from agricultural production, such as livestock breeding and NH_3 -based fertilizer application (Paulot and Jacobs, 2014; Kang et al., 2016; Reis et al., 2009; Bouwman et al., 1997; Heald et al., 2012; Zhang et al., 2018; Balasubramanian et al., 2015; Huang et al., 2011). In the urban atmosphere, recent studies suggest that non-agricultural activities like wastewater discharge (Zhang et al., 2017), coal burning (Li et al., 2016a), solid waste (Reche et al., 2012), on-road traffic (Suarez-Bertoa et al., 2014), and green spaces (Teng et al., 2017) also contribute to NH_3 emissions. In reactions with H_2SO_4 and HNO_3 , NH_3 contributes to the formation of NH_4^+ salts, which typically make up from 20 % to 80 % of fine particles ($\text{PM}_{2.5}$) in the atmosphere (Seinfeld and Pandis, 2012).

Biomass burning (BB) is an important source of N in the atmosphere (Lobert et al., 1990; Souri et al., 2017). During the harvest or hot season of eastern China, agricultural BB frequently occurs and modifies the concentration and composition of aerosols in the atmosphere (Chen et al., 2017; Zhang and Cao, 2015). For example, about 50 % of the N derived from biomass combustion can be released as NH_3 and NO_x to form particulate NH_4^+ and NO_3^- , which then account for over 80 % of total nitrogenous species in BB smoke particles (Crutzen and Andreae, 1990). BB-induced aerosols have not only been associated with poor air quality and the detrimental effects on human health but have also shown to exert manifold effects on tropospheric clouds, altering regional or

even global radiation budgets (Chen et al., 2014; Norris et al., 2016; Voigt and Shaw, 2015).

The optical and chemical properties of clouds (and thus their radiative forcing) are directly related to the aerosol and precipitation chemistry (Seinfeld et al., 2016). Moreover, clouds represent reactors of multiphase chemistry, contributing to many chemical transformations that would otherwise not take place or would proceed at much slower rates (Herrmann et al., 2015; Lance et al., 2017; Ravishankara, 1997; Schurman et al., 2018; Slade et al., 2017). Understanding the sources and fate of nitrogenous species in BB-influenced clouds is particularly important to comprehensively assess the environmental impacts of BB. But this challenge is difficult to address based on the sole use of bulk chemical properties (as most often done in previous studies).

Given that ^{15}N can be preserved between the sources and sinks of NO_x and NH_3 , the N isotopic composition of NO_3^- ($\delta^{15}\text{N}\text{-NO}_3^-$) and NH_4^+ ($\delta^{15}\text{N}\text{-NH}_4^+$) can be related to different sources of NO_x and NH_3 , and thus delivers useful information regarding the partitioning of the origins of atmospheric cloud water NO_x and NH_3 , respectively (Hastings et al., 2013; Michalski et al., 2005; Morin et al., 2008; Chang et al., 2018). This is different for the O isotopes. NO_3^- production involves the oxidation of NO. The first step in the overall process is the conversion of NO into NO_2 , e.g., through the oxidation by either ozone (O_3) or peroxy radicals (Michalski et al., 2011). Significant ^{18}O enrichments and excess ^{17}O (i.e., clear evidence for mass-independent fractionation) are observed in atmospheric NO_3^- collected across the globe (e.g., Michalski et al., 2005; Hastings et al., 2003). Such diagnostic isotope signatures, as well as their variability in space and time, have been linked to the extent of O_3 oxidation (Michalski et al., 2011). Put another way, the oxygen isotope composition of NO_3^- ($\delta^{18}\text{O}\text{-NO}_3^-$) is largely determined by chemical reactions rather than the source, and it is primarily modulated by the O-atom exchange (Michalski et al., 2011) in the atmosphere. Therefore, $\delta^{18}\text{O}\text{-NO}_3^-$ has the potential to indicate the relative importance of various NO_3^- formation pathways (i.e., oxidation pathways during conversion of nitrogen oxides to NO_3^-) (Alexander et al., 2009; Elliott et al., 2009).

The O isotope fractionation during the conversion of NO_x to $\text{HNO}_3/\text{NO}_3^-$ ($\varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{HNO}_3)}/\varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{NO}_3^-)}$) involves two oxidation pathways (Hastings et al., 2003)

$$\begin{aligned} \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{NO}_3^-)} &= \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{HNO}_3)} = \gamma \times \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{NO}_3^-)_{\text{OH}}} \\ &+ (1 - \gamma) \times \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow p\text{NO}_3^-)_{\text{H}_2\text{O}}} \\ &= \gamma \times \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{HNO}_3)_{\text{OH}}} + (1 - \gamma) \times \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{HNO}_3)_{\text{H}_2\text{O}}}, \quad (1) \end{aligned}$$

where $\gamma/(1-\gamma)$ represents the contribution ratio of the isotope fractionation associated with the formation of $\text{HNO}_3/\text{NO}_3^-$ through the “OH + NO_2 ” pathway ($\varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{NO}_3^-)_{\text{OH}}}$) and the hydrolysis of dinitrogen pen-

toxicide (N_2O_5) ($\varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{NO}_3^-)_{\text{H}_2\text{O}}}$), respectively. The $\delta^{18}\text{O}$ value of HNO_3 produced by the former process reflects the O atom partitioning of two-thirds O_3 and one-third OH (Chang et al., 2018):

$$\begin{aligned} \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{NO}_3^-)_{\text{OH}}} &= \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{HNO}_3)_{\text{OH}}} = \frac{2}{3} \varepsilon_{\text{O}(\text{NO}_2 \leftrightarrow \text{HNO}_3)_{\text{OH}}} \\ &+ \frac{1}{3} \varepsilon_{\text{O}(\text{NO} \leftrightarrow \text{HNO}_3)_{\text{OH}}} \\ &= \frac{2}{3} \left[\frac{1000 ({}^{18}\alpha_{\text{NO}_2/\text{NO}} - 1) (1 - f_{\text{NO}_2})}{(1 - f_{\text{NO}_2}) + ({}^{18}\alpha_{\text{NO}_2/\text{NO}} \times f_{\text{NO}_2})} + (\delta^{18}\text{O}-\text{NO}_x) \right] \\ &+ \frac{1}{3} \left[(\delta^{18}\text{O}-\text{H}_2\text{O}) + 1000 ({}^{18}\alpha_{\text{OH}/\text{H}_2\text{O}} - 1) \right]. \end{aligned} \quad (2)$$

As for the $\delta^{18}\text{O}$ value of HNO_3 formed during hydrolysis of N_2O_5 , five-sixths of the O atoms are derived from O_3 and one-sixth from OH (Hastings et al., 2003):

$$\begin{aligned} \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{NO}_3^-)_{\text{H}_2\text{O}}} &= \varepsilon_{\text{O}(\text{NO}_x \leftrightarrow \text{HNO}_3)_{\text{H}_2\text{O}}} = \frac{5}{6} (\delta^{18}\text{O}-\text{N}_2\text{O}_5) \\ &+ \frac{1}{6} (\delta^{18}\text{O}-\text{H}_2\text{O}), \end{aligned} \quad (3)$$

where f_{NO_2} refers to the fraction of NO_2 in the total NO_x pool. Values for f_{NO_2} vary between 0.2 and 0.95 (Walters and Michalski, 2015). $\delta^{18}\text{O}-X$ is the O isotopic composition of X . The range of $\delta^{18}\text{O}-\text{H}_2\text{O}$ can be approximated using an estimated tropospheric water vapor $\delta^{18}\text{O}$ range of -25‰ to 0‰ (Zong et al., 2017). The $\delta^{18}\text{O}$ of NO_2 and N_2O_5 varies between 90‰ and 122‰ (Zong et al., 2017). ${}^{18}\alpha_{\text{NO}_2/\text{NO}}$ and ${}^{18}\alpha_{\text{OH}/\text{H}_2\text{O}}$ represent the equilibrium O isotope fractionation factors between NO_2 and NO and OH and H_2O , respectively, which is temperature dependent:

$$\begin{aligned} 1000 ({}^m\alpha_{X/Y} - 1) &= \frac{A}{T^4} \times 10^{10} + \frac{B}{T^3} \times 10^8 + \frac{C}{T^2} \\ &\times 10^6 + \frac{D}{T} \times 10^4, \end{aligned} \quad (4)$$

where A, B, C, and D are experimental constants over the temperature range of 150–450 K. Based on Eqs. (1)–(4) and measured values for $\delta^{18}\text{O}-\text{NO}_3^-$ of cloud water, a Monte Carlo simulation was performed to generate 10 000 feasible solutions. The error between predicted and measured $\delta^{18}\text{O}$ was less than 0.5‰ .

At the end of July 2015, a large-scale BB event occurred over eastern and northern China. We took advantage of this special event to collect cloud water samples at a high-altitude mountaintop site in the North China Plain and to calibrate the isotopic signatures that BB events leave in the N pool of clouds. Integrating cloud water nitrogenous-species isotopic data ($\delta^{15}\text{N}-\text{NH}_4^+$, $\delta^{15}\text{N}-\text{NO}_3^-$, and $\delta^{18}\text{O}-\text{NO}_3^-$) into a Bayesian isotopic mixing model coupled with a newly developed computational quantum chemistry module (Chang

et al., 2018), and using an isotopic mass balance approach, the sources and production pathways of inorganic nitrogen in cloud water were quantified. Although numerous studies have been conducted that involved the chemical characterization of fog water or cloud water, to our knowledge there are no reports on the N (and O) isotopic composition of both NO_3^- and NH_4^+ in cloud water.

2 Materials and methods

2.1 Cloud water sample collection

Mt. Tai ($36^\circ 18' \text{N}$, $117^\circ 13' \text{E}$; 1545 m above sea level) is a world-recognized geopark of key natural, historical, and cultural significance, located in the eastern North China Plain (Fig. 1). It belongs to China's most important agricultural and industrial production areas, and the composition of the atmosphere near the mountain can be considered representative with regards to the quality and levels of atmospheric pollution in the region (Li et al., 2017; Liu et al., 2018). Given the opportunistic nature of this study, cloud water sampling commenced at the summit of Mt. Tai 3 d after the fire began (8 January 2015 19:12 LT (local time) to 8 March 2015 06:12 LT; Table 1). In total, six cloud water samples were collected during the long-lasting cloud event using a single-stage Caltech active strand cloud water collector (CASCC), as described by (Demoz et al., 1996). The cloud collector was cleaned prior to each sampling using high-purity deionized water. After sampling, cloud samples were filtered immediately using disposable syringe filters ($0.45 \mu\text{m}$) to remove any suspended particulate matter and then stored in a freezer at -80°C until further analysis. More details on the monitoring site and sampling procedures can be found elsewhere (Li et al., 2017).

2.2 Chemical and isotopic analysis

Inorganic ions (including SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , and Na^+), as well as levoglucosan (a specific tracer of biomass burning), in cloud water samples were analyzed using a Dionex™ ICS-5000+ system (Thermo Fisher Scientific, Sunnyvale, USA). The IC (ion chromatograph) system was equipped with an automated sampler (AS-DV). Cloud water samples were measured using an IonPac CG12A guard column and a CS12A separation column with an aqueous methanesulfonic acid (MSA, 30mM L^{-1}) eluent at a flow rate of 1mL min^{-1} . Detailed information regarding sample processing, pretreatment, chemical analyses, and analytical protocol adaption can be found elsewhere (Cao et al., 2016, 2017). The detection limits for Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , and levoglucosan are 0.06, 0.03, 0.12, 0.08, 0.13, 0.64, 1.11, 2.67, 1.41, and 1.29 ppb (parts per billion by weight in solution), respectively. The analytical errors from duplicate analyses were within 5 %.

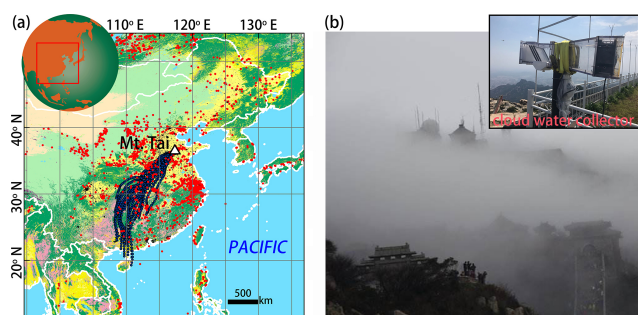


Figure 1. (a) Location of Mt. Tai (triangle) and twenty-four 48 h back trajectories (black lines) of air masses simulated by the HYSPLIT model (<http://ready.arl.noaa.gov/HYSPLIT.php>, last access: 10 August 2019) based on the Global Data Assimilation System (GDAS) meteorological data set arriving at Mt. Tai on 1 August 2015 (04:00 UTC) at an altitude 1500 m a.s.l (close to the altitude of our sampling site). The base map of land use in China was modified from Chang et al. (2018). The red dots represent the positions of wildfires between 29 and 31 July 2015, based on the Moderate Resolution Imaging Spectroradiometer (MODIS) (<http://modis-fire.umd.edu>, last access: 10 August 2019). (b) Field photos of cloud-shrouded Mt. Tai and the cloud water collector.

Analysis of the isotopic compositions of NH_4^+ ($\delta^{15}\text{N-NH}_4^+$) and NO_3^- ($\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$) was based on the isotopic analysis of nitrous oxides (N_2O) after chemical conversion of the respective target compound. More precisely, dissolved NH_4^+ in cloud water samples was oxidized to NO_2^- by alkaline hypobromite (BrO^-) and then reduced to N_2O by hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) (Liu et al., 2014). NO_3^- was initially transformed to NO_2^- by cadmium and then further reduced to N_2O by sodium azide (NaN_3) in an acetic acid buffer (McIlvin and Altabet, 2005; Tu et al., 2016). The produced N_2O was analyzed using a purge and cryogenic trap system (Gilson GX-271, Isoprime Ltd., Cheadle Hulme, UK), coupled to an isotope ratio mass spectrometer (PT-IRMS) (Isoprime 100, Isoprime Ltd., Cheadle Hulme, UK). In order to correct for any machine drift and procedural blank contribution, international NH_4^+ (IAEA N1, USGS 25, and USGS 26) and NO_3^- (IAEA N3, USGS 32, and USGS 34) standards were processed in the same way as samples. Standard regressions were made based on the known isotopic values of international standards and the measured standard $\delta^{15}\text{N}$ values. For the NO_3^- -derived NO_2^- analysis, the slope of the plot of the sample versus the standard $\delta^{15}\text{N}$ (0.49) was very close to the expected slope (0.5), which can be predicted based on the fact that half of the N atoms were derived from the azide (McIlvin and Altabet, 2005). The r^2 of the regression line was 0.999. The analytical precision for both multiple N and O isotopic analyses was better than 0.3‰ ($n = 5$).

2.3 Bayesian mixing model analysis

By taking the uncertainty associated with the N isotopic signatures of multiple sources and associated isotope fractionation during (trans-)formations into account, the Bayesian method is more appropriate than simple linear mixing modeling to yield estimates on the source partitioning of a mixture like air pollutants (Chang et al., 2016, 2018). The relative contribution of each source in the Bayesian theorem is expressed as

$$P(f_q | \text{data}) = \theta(\text{data} | f_q) \times P(f_q) / \sum \theta(\text{data} | f_q) \times P(f_q), \quad (5)$$

where $\theta(\text{data} | f_q)$ and $P(f_q)$ represent the likelihood of the given mixed isotope signature and the predetermined probability of the given state of nature, based on prior information, respectively. The denominator represents the numerical approximation of the marginal probability of the data. Here the Bayesian mixing model MixSIR (stable isotope mixing models using the sampling-importance-resampling method) was used to disentangle the various potential NH_3 and NO_x sources contributing to the cloud water NH_4^+ and NO_3^- pools, respectively, by forming the true probability distributions through generating 10 000 solutions of source apportionment. Details on the model approach can be found in Appendix A.

The measured $\delta^{15}\text{N-NO}_3^-$ values of cloud water samples depend on the $\delta^{15}\text{N}$ signatures of the original NO_x sources ($\delta^{15}\text{N-NO}_x$), the N isotope fractionation between nitrogen oxides (i.e., NO and NO_2 ; Walters et al., 2016), and the N isotope enrichment factor (ϵ_N) associated with the kinetic transformation of NO_x to HNO_3 (Walters and Michalski, 2015). ϵ_N is considered a hybrid of two dominant processes: one is the reaction of NO_2 and OH radicals to form NO_3^- and the other is the heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) with water to form NO_3^- . We recently developed a quantum chemistry computation module to quantify the N fractionation during nitrate formation, which had been validated by field measurements (Chang et al., 2018). Here this module was adopted to calculate the N isotope fractionation during NO_3^- formation, and in turn to correct the raw $\delta^{15}\text{N-NO}_3^-$ values of cloud water samples.

While the N isotopic source signatures of NO_x are relatively well constrained (Table B1 in Appendix B), this is not the case for NH_3 . We recently established a pool of isotopic source signatures of NH_3 in eastern China, from which livestock breeding and fertilizer application were identified to produce NH_3 with a $\delta^{15}\text{N}$ of $-29.1\text{‰} \pm 1.7\text{‰}$ and $-50.0\text{‰} \pm 1.8\text{‰}$, respectively (Chang et al., 2016). Although fossil fuel combustion, urban waste, and natural soils also represent potential sources of NH_3 , their impacts are probably minor compared to those of agricultural and biomass burning emissions, at least on a regional (or greater) scale (Kang et al., 2016). For the N isotope sig-

nature of biomass-burning-derived NH_3 , we assumed 12‰ (Kawashima and Kurahashi, 2011), a value that has also been applied in other recent isotope-based source apportionment studies (e.g., Chellman et al., 2016; Wang et al., 2017a).

3 Results and discussion

3.1 Chemical characterization of biomass-burning-influenced clouds

The Moderate Resolution Imaging Spectroradiometer (MODIS) wildfire map (Fig. 1) shows that there were intensive biomass burning events occurring over mainland China, end of July 2015, just before the study period. Moreover, analysis of the back trajectories of air masses at the study site revealed the strong influence of atmospheric transport from regions that also experienced intensive biomass burning events shortly before the sampling campaign. It can thus be assumed that large amounts of BB-related pollutants were transported from the southwest to the sampling site at Mt. Tai. Table 1 compiles sample information and results from the chemical and isotopic analysis of cloud water samples in this study. The concentrations of NO_3^- and NH_4^+ ranged from 4.9 to 19.9 mg L^{-1} (10.1 mg L^{-1} on average) and from 4.9 to 18.0 mg L^{-1} (9.1 mg L^{-1} on average), respectively, much higher than during non-BB seasons (Chen et al., 2017; Desyaterik et al., 2013; Li et al., 2017, 2018; Lin et al., 2017). Similarly, levoglucosan in our cloud water samples varied between 12.1 and 35.1 $\mu\text{g L}^{-1}$ (19.9 $\mu\text{g L}^{-1}$ on average), and concentrations were thus 1 order of magnitude higher than those documented during non-BB seasons (Boone et al., 2015; Fomba et al., 2015). Although levoglucosan can be oxidized by OH radicals in the tropospheric aqueous phase (Sang et al., 2016), it is nevertheless a reliable marker compound for BB due to its high-emission factors and relatively high concentrations in the ambient aerosols (Hoffmann et al., 2010). In our study, the concentrations of NO_3^- ($r^2 = 0.55$) and NH_4^+ ($r^2 = 0.66$) are strongly correlated with that of levoglucosan, suggesting that the pronounced increase in NO_3^- and NH_4^+ levels observed here can at least be partly attributed to BB activities during the study period. Globally, BB accounts for around 10% of NH_3 and NO_x emissions (Benkovitz et al., 1996; Bouwman et al., 1997; Olivier et al., 1998; Schlesinger and Hartley, 1992).

3.2 Isotopic characterization of biomass-burning-influenced clouds

The N (and O) isotopic composition of cloud water nitrogenous species was more (NH_4^+) or less (NO_3^-) variable (Table 1), with the average $\delta^{15}\text{N}$ values of 6.53‰ and -2.35‰ for NH_4^+ and NO_3^- , respectively. The average $\delta^{18}\text{O}$ - NO_3^- value was 57.80‰. These values are generally different from gas, rainwater, and aerosol values measured worldwide

(Fig. 2). Various atmospheric processes can influence the isotopic composition of atmospheric nitrogenous species including the original emission source of NO_x , seasonality of oxidation pathways, isotope fractionation during transport, partitioning between wet and dry components, and spatial gradients in atmospheric chemistry (Elliott et al., 2007; Hastings et al., 2003). These aspects may affect the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values differentially. For example, the $\delta^{15}\text{N}$ of atmospheric NO_3^- retains spatial changes in the original NO_x signature quite well, in contrast to the $\delta^{18}\text{O}$. On the other hand, the $\delta^{18}\text{O}$ most strongly depends on the oxidation chemistry and formation pathway in the atmosphere (see Eqs. 1–4).

At present, there are no other reports on the isotope ratios of both NO_3^- and NH_4^+ in cloud water, and a comparison is possible only with isotopic data from precipitation and aerosol N. Recently, Vega et al. (2019) reported the $\delta^{15}\text{N}$ ($-8\text{‰} \pm 2\text{‰}$) and $\delta^{18}\text{O}$ ($71\text{‰} \pm 3\text{‰}$) values of NO_3^- in fog water at a forest site in Sweden. The relatively high $\delta^{15}\text{N}$ values in our study (-2.35‰) suggest more NO_x was emitted from combustion processes. In contrast, the much higher $\delta^{18}\text{O}$ values in Vega et al. (2019) indicate a much greater contribution from O_3 in sub-Arctic environments. In Fig. 2a, N isotopic differences for NO_x sources are greater (35‰) than for $\delta^{18}\text{O}$ - NO_x . In fact, the oxygen isotope signature of NO_x is mainly driven by chemistry rather than determined by the source (see discussion below), and thus $\delta^{18}\text{O}$ measurements cannot be used to address the uncertainty in the NO_x sources that may remain when just looking at $\delta^{15}\text{N}$ values alone. As shown in Fig. 2b, the $\delta^{15}\text{N}$ values of aerosol NH_4^+ are systematically higher than that of NH_3 . Significant ϵ_N during the conversion of gas to aerosol (up to 33‰) has been proposed to alter the $\delta^{15}\text{N}$ values during the transformation of the source (NH_3) to the sink (particulate NH_4^+). Indeed, our compilation of previous results (Fig. 2b) reveals that particulate NH_4^+ (particularly in the coarse aerosol fraction) is more enriched in ^{15}N than NH_3 (by > 23‰ on average), as well as NH_4^+ in precipitation (by 18‰ on average). This can most likely be attributed to the preferential absorption of ^{14}N - NH_3 associated with washout processes during precipitation (Zheng et al., 2018). We are aware of the fact that our sample and data used here are limited, resulting in a relatively large uncertainty with regards to the N isotope-based source apportionment. However, all $\delta^{15}\text{N}$ - NH_4^+ values in cloud water samples fall within the observed range of $\delta^{15}\text{N}$ - NH_4^+ values for fine particles ($\text{PM}_{2.5}$), providing putative evidence that NH_4^+ in cloud water is primarily derived from particulate NH_4^+ rather than NH_3 absorption.

3.3 Isotope-based assessment of the sources and formation of nitrogenous species in clouds

Using the MixSIR model, the relative contribution of four NH_3 sources to NH_4^+ can be calculated, based on the isotope data of ambient $\delta^{15}\text{N}$ - NH_4^+ and considering the N fractionation and prior information on the site. As upper limit

Table 1. Sampling details and results of chemical and isotopic analysis for collected cloud water samples.

Date	Local time	NO_3^- (mg L^{-1})	NH_4^+ (mg L^{-1})	Levoglucosan ($\mu\text{g L}^{-1}$)	$\delta^{15}\text{N-NO}_3^-$ (‰)	$\delta^{18}\text{O-NO}_3^-$ (‰)	$\delta^{15}\text{N-NH}_4^+$ (‰)
1 Aug	19:12–22:58	19.86	17.99	35.06	−0.22	65.46	3.62
	23:45–08:25	4.88	4.92	12.11	−1.28	55.01	3.85
2 Aug	09:10–12:19	5.57	5.81	23.60	−0.40	59.84	0.05
	12:55–18:30	13.24	11.51	18.67	−4.18	55.66	11.34
	20:02–23:06	10.06	7.74	13.63	−3.11	56.63	12.99
	23:48–06:12	6.71	6.59	16.42	−4.92	54.19	7.33

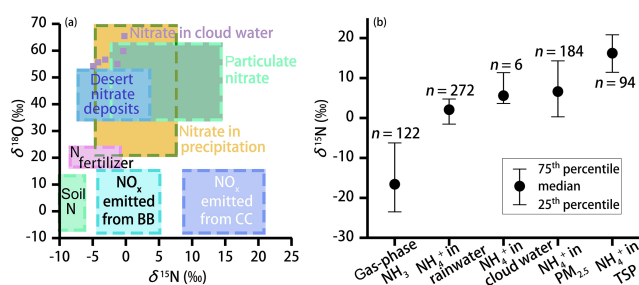


Figure 2. (a) Observed range of typical $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of NO_3^- and NO_x for different sources (adapted from Fenech et al., 2012). BB and CC represent biomass burning and coal combustion, respectively. The light purple squares represent nitrate isotope data in cloud water (this study). (b) The 25th percentiles, median, and 75th percentiles for the $\delta^{15}\text{N}$ values of the ambient NH_3 (Chang et al., 2016; Felix et al., 2013; Savard et al., 2018; Smirnoff et al., 2012) and NH_4^+ in precipitation (Fang et al., 2011; Leng et al., 2018; Yang et al., 2014; Zhang et al., 2008), cloud water (this study), $\text{PM}_{2.5}$ (particulate matter with aerodynamic diameter less than $2.5\ \mu\text{m}$; Lin et al., 2016; Park et al., 2018; Proemse et al., 2012; Smirnoff et al., 2012), and TSPs (total suspended particles with aerodynamic diameter less than $100\ \mu\text{m}$ (Kundu et al., 2010; Savard et al., 2018; Yeatman et al., 2001) are shown.

for the N isotope enrichment factor associated with the conversion of NH_3 to NH_4^+ ($\varepsilon_{\text{NH}_4^+-\text{NH}_3}$), we assumed 33‰ when using MixSIR but also considered lower values for $\varepsilon_{\text{NH}_4^+-\text{NH}_3}$ (Fig. 3a) (given the conflicting evidence with regards to $\varepsilon_{\text{NH}_4^+-\text{NH}_3}$; e.g., Deng et al., 2018; Li et al., 2012). Dependent of the choice for $\varepsilon_{\text{NH}_4^+-\text{NH}_3}$ (between 0‰ and 33‰ proposed by Heaton et al., 1997) the relative contribution of biomass burning, fertilizer application, and livestock breeding to NH_4^+ in cloud water ranges from 25.9% to 85.4%, 5.9% to 37.0%, and 8.7% to 85.4%, respectively. Irrespective of the uncertainty related to $\varepsilon_{\text{NH}_4^+-\text{NH}_3}$, the measurement of levoglucosan provides compelling evidence that biomass burning represents an important NH_3 source, independently validating our isotope approach. Our sampling site is located in the North China Plain, also known as the granary of China. Although nonagricultural NH_3 emissions like on-road traffic are important in the urban atmosphere (Chang et al., 2016), their contribution must be considered insignifi-

cant with respect to fertilizer application and livestock breeding in this region (Kang et al., 2016). Besides, coal-based heating in China is suspended during summertime, and coal combustion has been demonstrated to be a minor contributor of total NH_3 emissions (Li et al., 2016a). Hence the partitioning between the three main NH_3 sources appears plausible. Moreover, existing emission inventory data confirm that the ratio of NH_3 emissions in the North China Plain from livestock breeding (1658 kt) and fertilizer application (1413 kt) was 1.17 (Zhang et al., 2010), which is very close to our estimate (between 0.98 and 1.14) when $\varepsilon_{\text{NH}_4^+-\text{NH}_3} \geq 25\%$. For a $\varepsilon_{\text{NH}_4^+-\text{NH}_3}$ range that we consider most plausible (i.e., between 25‰ and 33‰), the relative cloud water NH_4^+ source partitioning between biomass burning, fertilizer application, and livestock is $32.9\% \pm 4.6\%$, $32.9\% \pm 3.0\%$, and $34.2\% \pm 1.6\%$, respectively (indicated as red square in Fig. 3a). It is important to note that a large uncertainty existed with regards to the assessment of biomass burning, which can partly be attributed to the lack of localized isotopic source signatures in China. In addition, the isotopic fractionation from the conversion of NH_3 to NH_4^+ was approximated in this study, and it was not possible to incorporate all of the possible equilibrium and kinetic fractionation scenarios.

The computational quantum chemistry (CQC) module in MixSIR has proven to be a robust tool to quantify the N isotope enrichment factor during $\text{NO}_x-\text{NO}_3^-$ conversion ($\varepsilon_{\text{NO}_3^--\text{NO}_x}$) (e.g., Zong et al., 2017; Chang et al., 2018). Cloud water sample-based data from this study reveal that $\varepsilon_{\text{NO}_3^--\text{NO}_x}$ values fall into a small range (5.21‰ to 5.98‰) (Fig. 3b), suggesting robust isotope effects during the N isotopic exchange reactions. Knowing $\varepsilon_{\text{NO}_3^--\text{NO}_x}$, the overall contribution of various NO_x sources to NO_3^- in cloud water can be estimated (Fig. 3c). As was expected, biomass burning was the largest contributor ($28.2\% \pm 2.7\%$), followed by on-road traffic ($27.1\% \pm 2.2\%$), coal combustion ($26.8\% \pm 3.4\%$), and biogenic soil ($17.9\% \pm 3.9\%$). The fundamental importance of biomass-burning-emitted NO_x to NO_3^- in cloud water is supported by the observed correlation between the concentrations of levoglucosan and biomass-burning-derived NO_3^- ($r^2 = 0.66$). The average contribution ratio of coal combustion and on-road transportation to NO_x emissions in our study (0.99) is slightly lower

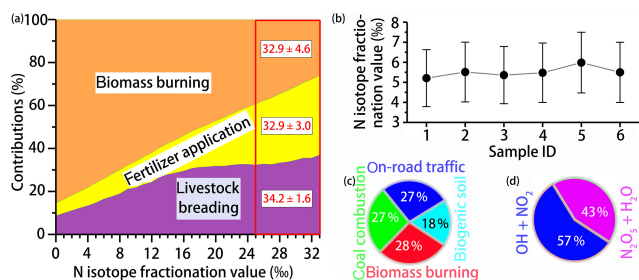


Figure 3. (a) Source partitioning estimates for NH_4^+ in cloud water as a function of $\epsilon_{\text{NH}_4^+ - \text{NH}_3}$. The red square highlights the best-guess estimates based on $\epsilon_{\text{NH}_4^+ - \text{NH}_3} \geq 25\%$. (b) Whisker plot of the N fractionation for the conversion of NO_x to NO_3^- ($\epsilon_{\text{NH}_4^+ - \text{NH}_3}$) calculated by the computational quantum chemistry (CQC) module. The upper line, dot, and bottom line indicate the 25th percentile, median, and 75th percentile, respectively. Refer to Table 1 for sample ID. (c) Overall contribution of various NO_x sources to NO_3^- in cloud water as estimated by the MixSIR model. (d) Overall contribution of the two dominant pathways to NO_3^- formation in cloud water, as estimated by the MixSIR model.

than that calculated from regional emission inventories (9.0 Tg/7.4 Tg = 1.22) (Zhao et al., 2013). The apparent difference is likely real and reflects the fact that NO_x emissions by anthropogenic activities changed significantly since 2010: a 17% total emission decrease between 2010 and 2017 can primarily be attributed to upgraded emission standards and new “ultra-low emission” techniques in the coal-fired power plant sector, and given that NO_x emitted from traffic likely increased as a consequence of the continuous expansion of the auto trade market during the last decade (Chang et al., 2018). In turn, our source partitioning estimate probably reflects the most updated status of NO_x emissions in China, where transportation-related NO_x emissions have reached levels that are comparable to NO_x emissions by coal combustion. In this regard, our study demonstrates that Bayesian-based isotopic mixing modeling can be an effective and timely approach to track rapid emission changes in NO_x in a fast-developing country like China.

Using the measured $\delta^{18}\text{O}$ and Eqs. (1)–(4) (and the assumptions above), we can calculate γ and the relative importance of the two oxidation pathways of NO_3^- formation (Fig. 3d). On average, 57% NO_3^- formation can be attributed to the “ $\text{NO}_2 + \text{OH}$ ” pathway and 43% to the “ $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ ” pathway. In the low-latitude regions, where atmospheric OH concentrations are highest, particulate NO_3^- production via the $\text{NO}_2 + \text{OH}$ pathway predominates (up to 87%) (Alexander et al., 2009). Sampling during summertime, oxidation of NO_2 through OH was expected to be the dominant pathway of nitrate formation, in accordance with observations from the subtropics (Hastings et al., 2003). However, our results highlight that N_2O_5 hydrolysis can be an almost equally important process as the oxidization of NO_2 with OH

with regards to the NO_3^- formation in cloud water (Wang et al., 2017b).

4 Conclusions

In this study, we measured the isotopic composition of nitrogenous species in cloud water at the summit of Mt. Tai during a long-lasting biomass burning event in order to investigate the sources and processes involved in cloud water $\text{NO}_3^-/\text{NH}_4^+$ formation, and in turn to test our isotope-balance approach to constrain N source partitioning in cloud water. Using a Bayesian isotope mixing model, the $\delta^{15}\text{N}$ -based estimates confirm that at least transiently biomass-burning-related NH_3 and NO_x emissions are a major source of cloud water N. Moreover, our data are in accordance with regional emission inventories for both NH_3 and NO_x , validating the Bayesian isotope mixing model approach. Based on cloud water nitrate $\delta^{18}\text{O}$ measurements, the reaction of NO_2 with OH turned out to be the dominant pathway to form cloud nitrate, yet the contribution from the heterogeneous hydrolysis of N_2O_5 to NO_3^- is almost equally important. Our study underscores the value of cloud-water-dissolved inorganic nitrogen isotopes as carriers of quantitative information on regional NO_x emissions. It sheds light on the origin and production pathways of nitrogenous species in clouds and emphasizes the importance of BB-derived nitrogenous species as cloud condensation nuclei in China’s troposphere. Moreover, it highlights the rapid evolution of NO_x emissions in China. Despite an overall reduction in total anthropogenic NO_x emissions due to effective emission control actions and stricter emission standards for vehicles, the relative contribution of transportation to total NO_x emissions has increased over the last decade and may already have exceeded emissions from the power sector.

Appendix A: Bayesian isotopic mixing model

The Bayesian mixing model makes use of stable isotope data to determine the probability distribution of source contributions to a mixture, explicitly accounting for uncertainties associated with multiple sources, their isotopic signatures, and isotope fractionation during transformations. The model has been widely used in ecological studies, such as food-web analyses. In the Bayesian theorem, the contribution of each source is calculated based on mixed data and prior information, such that

$$P(f_q|\text{data}) = \theta(\text{data}|f_q) \times p(f_q) / \sum \theta(\text{data}|f_q) \times p(f_q),$$

where $\theta(\text{data}|f_q)$ and $p(f_q)$ refer to the likelihood of the given mixed isotope signature and the predetermined probability of the given state of nature, based on prior information, respectively. The denominator represents the numerical approximation of the marginal probability of the data. In a Bayesian model (stable isotope in R, SIAR), isotope signatures from the mixed data pool are assumed to be normally distributed. Uncertainty in the distribution of isotope sources and associated isotope fractionation during transformations are factored into the model by defining respective mean (μ) and standard deviation (σ) parameters. Prior knowledge about proportional source contributions (f_q) is parameterized using the Dirichlet distribution, with an interval of [0, 1]. To assess the likelihood of the given f_q , the proposed proportional contribution is combined with a user-specified isotope distribution of sources and their associated isotope effects to develop a proposed isotope distribution for the mixture. The probability of fractional source contributions (f_q) is calculated by the Hilborn sampling-importance-resampling method.

Appendix B: Isotopic signatures of NO_x emitted from various sources**Table B1.** Typical $\delta^{15}\text{N-NO}_x$ values for coal combustion, transportation, biomass burning, and soils based on literature values.

Source types	Mean (‰)	Standard (‰)	Number	Reference
Coal combustion	13.72	4.57	47	Felix et al. (2012, 2015)
Transportation	-7.25	7.80	151	Walter et al. (2015a, b), Heaton et al. (1997)
Biomass burning	1.04	4.13	24	Fibiger and Hastings (2016), Felix and Elliott (2013)
Biogenic soil	-33.77	12.16	6	Hastings et al. (2009), Felix et al. (2012)

Data availability. All data used to support the conclusion are presented in this paper. Additional data are available upon request; please contact the corresponding authors (Yanlin Zhang (dryanlinzhang@outlook.com) and Jianmin Chen (jmchen@fudan.edu.cn)).

Author contributions. YZ and JC designed the study. YC and YL conceived the study. YC, JL, LS, XZ, WZ, TH and CZ carried out the field experiments and laboratory analysis. YC wrote the paper with ML and YZ. All the authors contributed to the interpretation of the results obtained with the new approach here described and revised the paper content, giving final approval of the version to be submitted. YC and ML addressed the reviewers' comments.

Competing interests. The authors declare that they have no conflict of interest.

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