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Isotopic Constraints on the Atmospheric Sources and Formation of Nitrogenous Species in Biomass-Burning-Influenced Clouds

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Abstract

The interpretation of tropospheric cloud formation rests on understanding the sources and processes affecting aerosol constituents of the atmosphere that are preserved in cloudwater. However, this challenge is difficult to be quantitatively addressed based on the sole use of bulk chemical properties. Nitrogenous aerosols, mainly ammonium (NH_4^+) and nitrate (NO_3^-), play an important role in tropospheric cloud formation. Here we collected cloudwater samples at the summit of Mt. Tai (1545 m above sea level) in Eastern China during a long-lasting biomass burning (BB) event, and measured for the first time the isotopic compositions (mean ± 1σ) of cloudwater nitrogen species (δ^{15}N-NH_4^+ = -6.53 ± 4.96‰, δ^{15}N-NO_3^- = -2.35 ± 2.00‰, δ^{18}O-NO_3^- = 57.80 ± 4.23‰), allowing insights into their sources and potential transformation mechanism within the clouds. Large contributions of BB to the cloudwater NH_4^+ (32.9 ±4.6%) and NO_3^- (28.2 ±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 δ^{15}N-NO_3^- values suggest that NO_x emissions from transportation may have exceeded emissions from coal combustion. δ^{18}O-NO_3^- values imply that the reaction of OH with NO_2 is the dominant pathway of NO_3^- formation (57 ± 11%), yet the contribution of heterogeneous hydrolysis of dinitrogen pentoxide was almost as important (43 ± 11%).

1 Introduction

Nitrogenous aerosols, mainly nitrate (NO_3^-) and ammonium (NH_4^+), formed from the emissions of nitrogen oxides (NO_x = NO + NO_2) and ammonia (NH_3), 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). Cloudwater containing nitrogenous compounds also represent a vital contributor to nitrogen (N) budgets of terrestrial (Li et al., 2016b; Liu et al., 2013) and marine ecosystems (Kim et al., 2014; Okin et al., 2011). However, the sources and formation processes of cloudwater 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 fuel (~ 25 Tg N yr^{-1} (Jaegle et al., 2005; Richter et al., 2005; Duncan et al., 2016;)), with the remainder being primarily soil-related emissions (~ 9 Tg N yr^{-1} (Lamsal et al., 2011; Price et al., 1997; Yienger et al., 1995; Miyazaki et al., 2017)), or deriving from biomass burning (~ 6 Tg N yr^{-1}), and lightning (2-6 Tg N yr^{-1}) (Anenberg et al., 2017; Levy et al., 1996). The atmospheric sinks of NO_x include the production of $HNO_{3(g)}$ 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 et al., 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 space (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 particle ($PM_{2.5}$) 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/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, they have also shown to exert manifold effects on the 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 the ^{15}N can be preserved between the sources and sinks of NO_x and NH_3, the N isotopic composition of NO_3^- ($\delta^{15}N$-NO_3^-) and NH_4^+ ($\delta^{15}N$-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/cloudwater NO_x and NH_3, respectively (Hastings et al., 2013; Michalski et al., 2005; Morin et al., 2008; Chang et al., 2018). Moreover, the oxygen isotope composition of NO_3^- ($\delta^{18}O$-NO_3^-) is largely determined by chemical reactions rather than the source, as it is

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primarily modulated by the atmospheric exchange reactions of the oxygen isotope. Therefore, δ^{18}O-NO_3^- has the potential to indicate the relative importance of various NO_3^- formation pathways (Alexander et al., 2009; Elliott et al., 2009). To our knowledge, there are no reports on the N and O isotopic composition of nitrogenous species in cloudwater.

End of July 2015, a large-scale BB event occurred over eastern and northern China. We took advantage of this special event to collect cloudwater samples at a high-altitude mountaintop site in the North China Plain, and to calibrate the isotopic signatures BB events leave in the N pool of clouds. Integrating cloudwater nitrogenous species isotope data (δ^{15}N-NH_4^+, δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) in 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 cloudwater were quantified.

2 Materials and Methods

2.1 Cloudwater Sample Collection

Mt. Tai (117°13′ E, 36°18′ N; 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, cloudwater sampling commenced at the summit of Mt. Tai three days after the fire began (08/01/2015 19:12 to 08/03/2015 6:12; Table 1). In total, six cloudwater samples were collected 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 μm) 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).

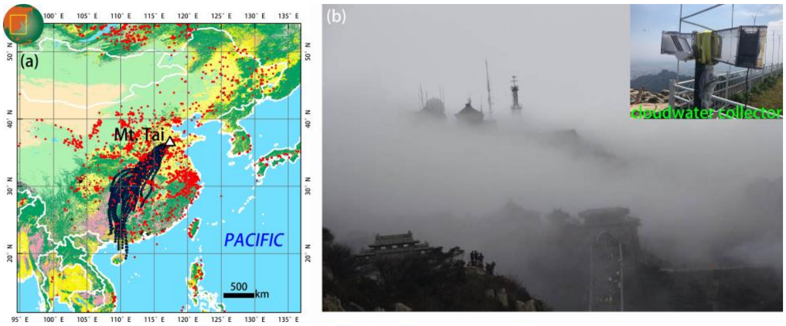

Figure 1. (**a**) Location of Mt. Tai (triangle) and twenty-four 48-h back trajectories (black lines) of air masses arriving at Mt. Tai on 1 August 2015 (4:00 UTC) at an altitude 1500-m a.s.l (http://ready.arl.noaa.gov/HYSPLIT.php). The base map of land use in China was modified from Chang et al. (2018). The red dots represent the positions of wildfires between 29 and 31 July, 2015, based on moderate-resolution imaging spectroradiometer (MODIS) (http://modis-fire.umd.edu). (**b**) Field photos of clouds-shrouded Mt. Tai and the cloudwater collector.

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 cloudwater samples were analyzed using a Dionex™ ICS-5000$^+$ system (ThermoFisher Scientific, Sunnyvale, USA). Detailed information regarding sample processing, pre-treatment, chemical analyses, analytical protocol adaption, detection limits, and method errors/reproducibility can be found elsewhere (Cao et al., 2016, 2017).

Analysis of the isotopic compositions of NH_4^+ (δ^{15}N-NH_4^+) and NO_3^-, (δ^{15}N- NO_3^- and δ^{18}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 cloudwater samples was oxidized to NO_2^- by alkaline hypobromite (BrO^-), and then reduced to N_2O by hydroxylamine hydrochloride ($NH_2OH.HCl$) (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, and sample values were corrected using conventional standard bracketing techniques. 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; Chang et al., 2018). The relative contribution of each source in Bayesian theorem is expressed as:

$$P\left(f_q \middle| data\right) = \theta\left(data \middle| f_q\right) \times P\left(f_q\right) \Big/ \sum \theta\left(data \middle| f_q\right) \times P\left(f_q\right)$$

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where $\theta(data|f_q)$ and $P(f_q)$ represent the likelihood of the given mixed isotope signature, and the pre-determined 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 sampling-importance-resampling) was used to disentangle the various potential NH_3 and NO_x sources contributing to the cloudwater NH_4^+ and NO_3^- pools, respectively, by forming the true probability distributions through generating 10000 solutions of source apportionment. Details on the model approach can be found in SI Text S1.

The measured $\delta^{15}N$-NO_3^- values of cloudwater samples depend on the $\delta^{15}N$ signatures of the original NO_x sources ($\delta^{15}N$-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^-, 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 $\delta^{15}N$-NO_3^- values of cloudwater samples.

While the N isotopic source signatures of NO_x are relatively well constrained (Table S1), this is not the case for NH_3. We recently established a pool of isotopic source signatures of NH_3 in eastern China, in which livestock breeding and fertilizer application were identified to produce NH_3 with a $\delta^{15}N$ of -29.1 ± 1.7‰ and -50.0 ± 1.8‰, respectively (Chang et al., 2016). Although fossil-fuel combustion, urban waste, and natural soils also represent potential sources of NH_3, their

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impacts are probably minor compared to that of agricultural and biomass burning emissions, at least on a regional (or greater) scale (Kang et al., 2016). For the N isotope signature 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 by 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 cloudwater samples in this study. The concentrations of NO_3^- and NH_4^+ ranged from 4.9 to 19.9 μg ml^{-1} (10.1 μg ml^{-1} on average), and from 4.9 to 18.0 μg ml^{-1} (9.1 μg ml^{-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 cloudwater samples varied between 12.1 and 35.1 μg L^{-1} (19.9 μg L^{-1} on average), and concentrations were thus one 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 of 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).

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

Date	Local time	NO_3^- (mg L^{-1})	NH_4^+ (mg L^{-1})	levoglucosan (μg L^{-1})	$\delta^{15}N$-NO_3^- (‰)	$\delta^{18}O$-NO_3^- (‰)	$\delta^{15}N$-NH_4^+ (‰)
Aug 1	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
Aug 2	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

3.2 Isotopic characterization of biomass-burring-influenced clouds

The N (and O) isotopic composition of cloudwater nitrogenous species was more (NH_4^+) or less (NO_3^-) variant (Table 1), with the average $\delta^{15}N$ values of 6.53‰ and -2.35‰ for NH_4^+ and NO_3^-, respectively. The average $\delta^{18}O$-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 $\delta^{15}N$ and $\delta^{18}O$ values differentially. For example, the $\delta^{15}N$ of atmospheric NO_3^- retains spatial changes in the original NO_x signature quite well, in contrast to the $\delta^{18}O$. On the other hand, the $\delta^{18}O$ most strongly depends on the oxidation chemistry and formation pathway in the atmosphere (see below).

At present, there are no other reports on the isotope ratios of NO_3^- and NH_4^+ in cloudwater, and a comparison is possible only with isotope data from precipitation and aerosol N. In Fig. 2a, N isotopic differences for NO_x sources are greater (35‰), than for $\delta^{18}O$-NO_x. In fact, the oxygen isotope signature of NO_x is mainly determined by chemistry rather than by the source (see discussion below), and thus, $\delta^{18}O$ measurements cannot be used to address the uncertainty of the NO_x sources that may remain when just looking at $\delta^{15}N$ values alone. For cloudwater, the observed $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- (the secondary product of NO_x) overlap with that of precipitation and particulate matter, suggesting that there is a link between different scavenging processes of atmospheric pollutants. As shown in Fig. 2b, the $\delta^{15}N$ 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 $\delta^{15}N$ 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 ^{14}N-NH_3 associated with washout during precipitation. However, no significant difference in the $\delta^{15}N$-NH_4^+ exists between fine particles ($PM_{2.5}$) and cloudwater, indicating that NH_4^+ in cloudwater is primarily derived from particulate NH_4^+ instead of NH_3 absorption.

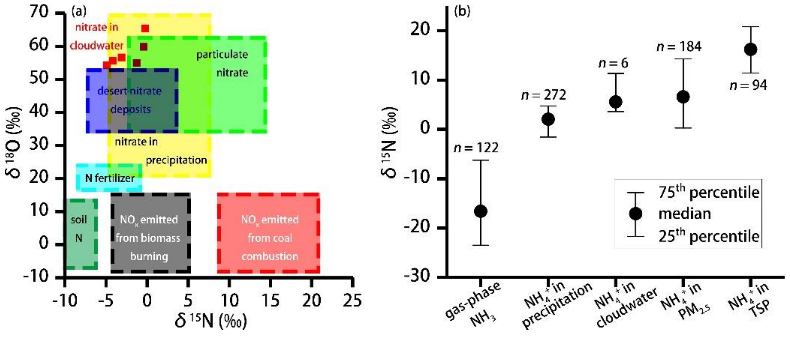

Figure 2. (**a**) Observed range of typical $\delta^{18}O$ and $\delta^{15}N$ values of NO_3^- and NO_x for different sources (adapted from Fenech et al. (2012)). The red squares represent nitrate isotope data in cloudwater (this study). (**b**) The 25th percentiles, median and 75th percentiles for the $\delta^{15}N$ 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), cloudwater (this study), $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 μm; (Lin et al., 2016; Park et al., 2018; Proemse et al., 2012; Smirnoff et al., 2012), and TSP (particulate matter with aerodynamic diameter less than 100 μm (Kundu et al., 2010; Savard et al., 2018; Yeatman et al., 2001) are shown.

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 $\delta^{15}N$-NH_4^+, and considering the N fractionation and prior information on the site. As upper limit for the N isotope enrichment factor associated with the conversion of NH_3 to NH_4^+ ($\varepsilon_{NH_4^+-NH_3}$), we assumed 33‰ when using MixSIR, but also considered lower values for $\varepsilon_{NH_4^+-NH_3}$ (Fig. 3a) (given the conflicting evidence with regards to $\varepsilon_{NH_4^+-NH_3}$; e.g., Deng et al., 2018; Li et al., 2012). Dependent of the choice for $\varepsilon_{NH_4^+-NH_3}$ (between 0‰ to 33‰ proposed by Heaton et al. (1997)) the relative contribution of biomass burning, fertilizer application, and livestock breeding to NH_4^+ in cloudwater 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 $\varepsilon_{NH_4^+-NH_3}$, it is evident that biomass burning represents an important NH_3 source, validating our isotope approach. Our sampling site was located in the North China Plain, also known as the granary of China. Although non-agricultural NH_3 emissions like on-road traffic are important in the urban atmosphere (Chang et al., 2016), their contribution must be considered insignificant 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 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 $\varepsilon_{NH_4^+-NH_3} \geq 25‰$. For a $\varepsilon_{NH_4^+-NH_3}$ range that we consider most plausible (i.e. between 25‰ and 33‰), the relative cloudwater NH_4^+ source partitioning between biomass burning, fertilizer application, and livestock is 32.9 ± 4.6%, 32.9 ± 3.0%, and 34.2 ± 1.6%, respectively (indicated as red square in Fig. 3a).

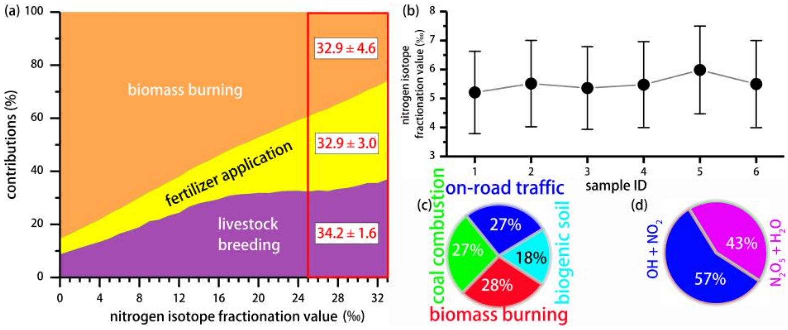

Figure 3. (**a**) Source partitioning estimates for NH_4^+ in cloudwater as a function of $\varepsilon_{NH_3 \rightarrow NH_4^+}$. The red square highlights the best-guess estimates based on $\varepsilon_{NH_4^+ - NH_3} \geq 25‰$). (**b**) Whisker plot of the N fractionation for the conversation of NO_x to NO_3^- ($\varepsilon_{NO_3^- - NO_x}$) 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 cloudwater as estimated by the MixSIR model. (**d**) Overall contribution of the two dominant pathways to NO_3^- formation in cloudwater, as estimated by the MixSIR model.

The CQC module in MixSIR has been proven a robust tool to quantify the N isotope enrichment factor during NO_x-NO_3^- conversion ($\varepsilon_{NO_3^- - NO_x}$) (e.g., Zong et al., 2017, Chang et al., 2018). Cloudwater sample-based data from this study reveal that $\varepsilon_{NO_3^- - NO_x}$ values fall into a small range (5.21‰ to 5.98‰) (Fig. 3b), suggesting robust isotope effects during the N isotopic exchange reactions. Knowing $\varepsilon_{NO_3^- - NO_x}$, the overall contribution of various NO_x sources to NO_3^- in cloudwater can be estimated (Fig. 3c). As was expected, biomass burning was the largest contributor (28.2 ± 2.7%), followed by on-road traffic (27.1 ± 2.2%), coal combustion (26.8 ± 3.4%), and biogenic soil (17.9 ± 3.9%). The fundamental importance of biomass burning-emitted

NO_x to NO_3^- in cloudwater 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 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, given that traffic-emitted NO_x likely increased as a consequence of the continuous expansion of 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 emissions changes of NO_x in a fast developing country like China.

The O isotope fractionation during the conversion of NO_x to HNO_3/NO_3^- ($\varepsilon_{O(NO_x \leftrightarrow HNO_3)} / \varepsilon_{O(NO_x \leftrightarrow NO_3^-)}$) involves two oxidation pathways

$$\begin{aligned}\varepsilon_{O(NO_x \leftrightarrow NO_3^-)} &= \varepsilon_{O(NO_x \leftrightarrow HNO_3)} = \gamma \times \varepsilon_{O(NO_x \leftrightarrow NO_3^-)_{OH}} + (1-\gamma) \times \varepsilon_{O(NO_x \leftrightarrow pNO_3^-)_{H_2O}} \\ &= \gamma \times \varepsilon_{O(NO_x \leftrightarrow HNO_3)_{OH}} + (1-\gamma) \times \varepsilon_{O(NO_x \leftrightarrow HNO_3)_{H_2O}} \qquad (1)\end{aligned}$$

where $\gamma/(1-\gamma)$ represents the contribution ratio of the isotope fractionation associated with the formation of HNO_3/NO_3^- through the "OH+NO_2" pathway ($\varepsilon_{O(NO_x \leftrightarrow NO_3^-)_{OH}}$) and the hydrolysis of dinitrogen pentoxide (N_2O_5) ($\varepsilon_{O(NO_x\leftrightarrow NO_3^-)_{H_2O}}$), respectively. The $\delta^{18}O$ value of HNO_3 produced by the former process reflects the O atom partitioning of 2/3 O_3 and 1/3 OH:

$$\begin{aligned}\varepsilon_{O(NO_x\leftrightarrow NO_3^-)_{OH}} &= \varepsilon_{O(NO_x\leftrightarrow HNO_3)_{OH}} = \frac{2}{3}\varepsilon_{O(NO_2\leftrightarrow HNO_3)_{OH}} + \frac{1}{3}\varepsilon_{O(NO\leftrightarrow HNO_3)_{OH}}\\ &= \frac{2}{3}\left[\frac{1000\left({}^{18}\alpha_{NO_2/NO}-1\right)\left(1-f_{NO_2}\right)}{\left(1-f_{NO_2}\right)+\left({}^{18}\alpha_{NO_2/NO}\times f_{NO_2}\right)}+\left(\delta^{18}\text{O-NO}_x\right)\right]+\\ &\quad \frac{1}{3}\left[\left(\delta^{18}\text{O-H}_2\text{O}\right)+1000\left({}^{18}\alpha_{OH/H_2O}-1\right)\right]\end{aligned} \tag{2}$$

As for the $\delta^{18}O$ value of HNO_3 formed during hydrolysis of N_2O_5, 5/6 of the O atoms is derived from O_3 and 1/6 from OH (Hastings et al., 2003):

$$\varepsilon_{O(NO_x\leftrightarrow NO_3^-)_{H_2O}} = \varepsilon_{O(NO_x\leftrightarrow HNO_3)_{H_2O}} = \frac{5}{6}\left(\delta^{18}\text{O-N}_2\text{O}_5\right)+\frac{1}{6}\left(\delta^{18}\text{O-H}_2\text{O}\right) \tag{3}$$

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). δ^{18}O-X is the O isotopic composition of X. The range of $\delta^{18}O\text{-}H_2O$ can be approximated using an estimated tropospheric water vapor $\delta^{18}O$ range of -25‰-0‰ (Zong et al., 2017). The $\delta^{18}O$ of NO_2 and N_2O_5 varies between 90‰ and 122‰ (Zong et al., 2017). ${}^{18}\alpha_{NO_2/NO}$ and ${}^{18}\alpha_{OH/H_2O}$ represent the equilibrium O isotope fractionation factor between NO_2 and NO, and OH and H_2O, respectively, which is temperature-dependent

$$1000\left({}^{m}\alpha_{X/Y}-1\right)=\frac{A}{T^4}\times 10^{10}+\frac{B}{T^3}\times 10^{8}+\frac{C}{T^2}\times 10^{6}+\frac{D}{T}\times 10^{4} \tag{4}$$

where A, B, C, and D are experimental constants over the temperature range of 150-450 K. Based on Equations 1-4 and measured values for $\delta^{18}O\text{-}NO_3^-$ of cloudwater, a Monte Carlo simulation was performed to generate 10000 feasible solutions. The error between predicted and measured $\delta^{18}O$ was less than 0.5‰.

Using the measured $\delta^{18}O$ and equations 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 "NO_2 + OH" pathway, and 43% to the "N_2O_5 + H_2O" pathway. In the low-latitude regions, where atmospheric OH concentrations are highest, particulate NO_3^- production via the "NO_2 + 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 cloudwater (Wang et al., 2017b).

4 Conclusions

For the first time, we measured the isotopic composition of nitrogenous species in cloudwater at the summit of Mt. Tai during a long-lasting biomass burning event, in order to investigate the sources and process involved in cloudwater NO_3^-/NH_4^+ formation, and in turn to test our isotope-balance approach to constrain N source partitioning in cloudwater. Using a Bayesian isotope mixing model, the $\delta^{15}N$-based estimates confirm that at least transiently biomass burning related NH_3 and NO_x emissions is a major source of cloudwater 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 $\delta^{18}O$ 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 carrier 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 emission 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.

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)).

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