We greatly thank Prof. Yingjun Chen (P25-27) and three anonymous reviewers (P1-8 for referee #1; P9-14 for referee #2; P15-24 for referee #3) for their insightful comments, which we've fully addressed (in bold) point by point in our reply letter below. The revised MS with tracked changes (P28-59) is attached after the reply letter. We are deeply sorry for the delay due to the family affairs of the first author.

## Anonymous Referee #1

General Comments:

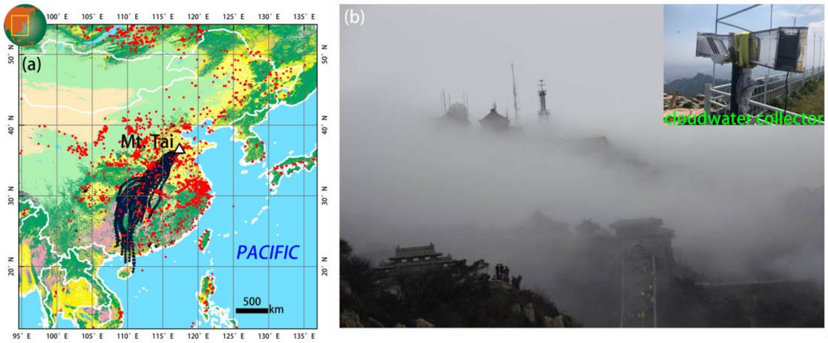
**1.** Chang et al. reported the isotopic composition of nitrogen species in cloud water at a mountain site in North China, during a biomass burning event. They analyzed the data with isotope mixing model and CQC module to investigate the sources and formation mechanisms of nitrogenous species in cloud water. The study contributes to the growing body of isotope measurements around the world, and the methods could be useful for source and chemical process analysis. The manuscript can be improved by adding more in-depth analysis/discussion on the data. Also, there are a number of places which need to be modified or clarified. The figures are not in good quality, and most of the figures are too fuzzy to see clearly.

**Many thanks for the recognition of our work. We appreciate the constructive suggestions, which have helped to greatly improved our MS. More in-depth analysis/discussion on the data have been added in the text, and where requested text sections have been clarified in the revised MS (see details below).**

**We are sorry for the difficulties with the figure quality experienced by referee #1. All three original figures have been replotted in the revised MS:**

**Figure 1**

**Original version:**



**Revised version:**

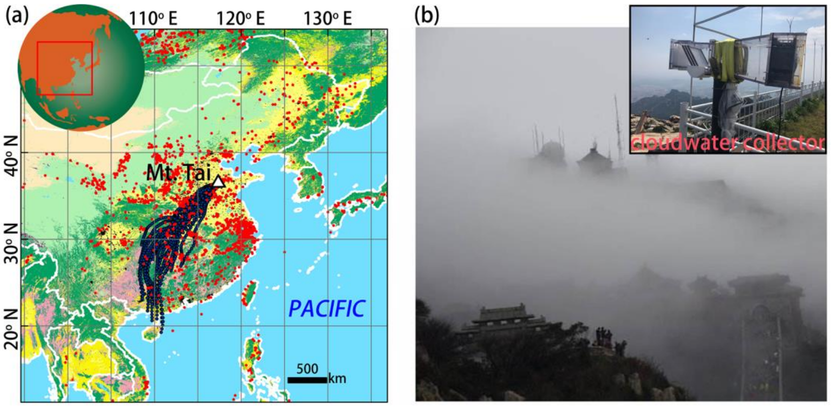
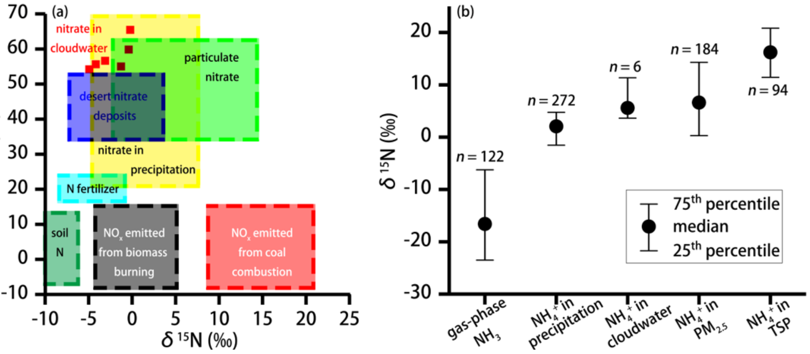
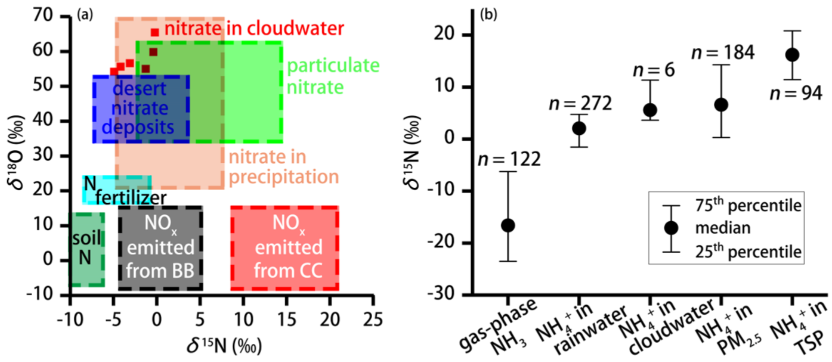


**Figure 2**

**Original version:**

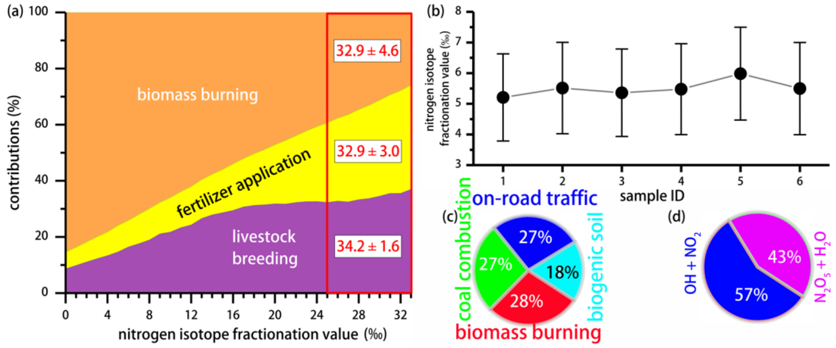


**Revised version:**

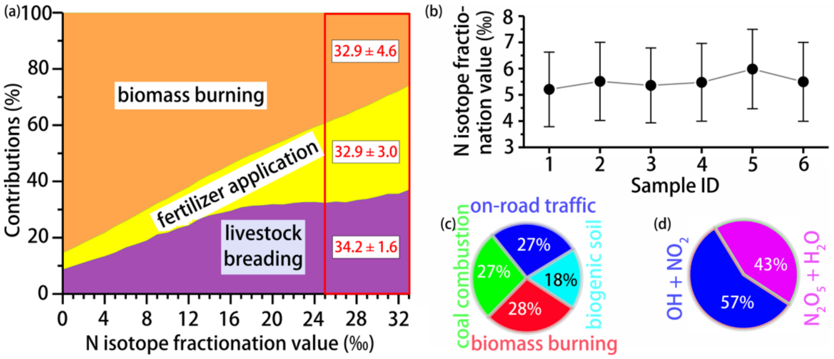


## Figure 3

**Original version:**



**Revised version:**



2. It would be interesting also to examine the isotope information in the aerosols collected at the same site during the same period. The comparison between cloud and aerosol would provide more useful and meaningful information to further understand the sources and formation mechanisms of these nitrogenous species.

**Thanks for the good advice. Unfortunately, we didn't collect aerosol samples during our study. We've added "*Further simultaneous and long-term sampling of aerosol, rainfall, and cloudwater is vital for understanding the anthropogenic influence on nitrogen deposition in the study region*" in the abstract.**

**But no doubt, we acknowledge the importance of collecting aerosol samples for isotopic analysis. This is reflected by our research project entitled "*Ammonium nitrogen isotope fractionation during atmospheric chemical and physical processes*", which has been funded by the China's National Science Foundation recently (No. 4197050309). The project aims to simultaneously collect samples of cloudwater, aerosol, and gaseous pollutants (e.g., $NH_3$) on the top of Mt. Huangshan (around 1860 m a.s.l). With the expected comprehensive isotopic data sets, we are confident to learn a lot more about the sources and formation mechanisms of nitrogenous species and will present findings in follow-up papers.**

3. I also agree with the comments of Chen, and the author should provide more information and assessment on the uncertainties of the results. The exact numbers may not be representative given the small number of samples.

**Agreed. We've expanded the discussion regarding the uncertainties of the results in the revised MS. Please refer to the discussion section in the MS with tracked changes for details (after the reply letter).**

4. In addition, I would suggest the author to further examine the influences of cloud water content

and cloud process on the change of isotopic data in the same cloud event. The changes and variations of these values may not necessarily result from the differences in source or formation mechanisms.

**Thanks for the suggestions. Given that all samples were collected during a single cloud event, the discussion on different processes of cloud evolution is beyond the scope of this study. As for the cloud water content, given that our samples were collected in ambient air (far away from the potential sources), theoretically, mass concentration or water content cannot be an important factor to influence the isotopic data. For offline isotopic analysis, during sample processing and pre-treatment, there are several steps that could change water content. We thus are certain that water content is not a factor to influence isotopic data.**

5. In section 3.3, all the equations and descriptions (page 15-17) are the same as in Chang et al., 2018. I would suggest the author condense this part and include it in the methodology section. More details may be provided in SI.

**Agreed. The equations and descriptions have been moved to the introduction section in the revised MS.**

Specific comments:

1. Line 111. Were the six cloud water samples collected during two or three isolated cloud events?

**The six cloudwater samples were collected during a long-lasting cloud event. We've clarified this in the revised MS.**

2. Line 129. The treatment and analytical protocol can be the same as previous literature, the detection limits and errors, reproducibility, recovery rates would be varied for different research. Please clarify.

**Agreed. "*Detailed information regarding sample processing, pre-treatment, 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, respectively. The analytical errors from duplicate analysis were within 5%" in the revised MS.*"**

3. Line 141. Please clarify how the sample values were corrected.

**We've added the process of data correction in the revised MS. "*Standard regressions were made based on the known isotopic values of international standards and the measured***

***standard $\delta^{15}$N values. The slope of the plot of the sample versus the standard $\delta^{15}$N (0.49) was very close to the expected slope (0.5), which can be predicted based on the fact that half N atoms were derived from the azide (McIlvin and Altabet, 2005). The $r^2$ of the regression line was 0.999.*"**

**Reference**

**McIlvin, M. R., and Altabet, M. A.: Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater, Anal. Chem., 77, 5589-5595, https://doi.org/10.1021/ac050528s, 2005.**

4. Line 189 and Table 1. Better to use consistent units.

**Agreed. The unit of "μg $ml^{-1}$" has been changed to "mg $L^{-1}$" to keep a consistent unit in the revised MS.**

5. Line 193. It is better to compare with the results at Mt Tai during non-BB seasons. The comparison with other regions cannot be used to support the author's statement.

**In the present study, we failed to collect cloudwater samples during non-BB seasons. As a compromise, we compared our results to previously published data. True, technically this does not need to support our statement. However, our measured concentrations of levoglucosan were one order of magnitude higher than observed in previous studies.**

6. Section 3.2. As mentioned above, did the variations reflect different periods of the cloud event? Will the cloud evolution process affect the results/conclusion of source analysis?

**Thanks for the good suggestion. As we stated above, our samples were collected during a single cloud event and do not account for possible changes during cloud formation.**

7. Line 209-214. This information can be included in the introduction, but it seems not useful to explain the measurement data in this study.

**We agree that this more or less general information that might distract the readers' focus on our discussion. However, we think that it serves as valuable background information that helps to understand the variability of $\delta^{15}$N and $\delta^{18}$O values of nitrate. We would prefer to leave it in the MS.**

8. Line 223-226. The statement is too speculative and does not scientifically sound. Without the

isotope analysis, you can still conclude that there is a link between different process.

**Agreed. We've deleted "*For cloudwater, the observed δ$^{15}$N and δ$^{18}$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.*" in the revised MS.**

9. Line 232. Please provide reference or evidence to support the statement.

**The reference below was added in the revised MS to support our statement:**

**Zheng, X. D., Liu, X. Y., Song, W., Sun, X. C., and Liu, C. Q.: Nitrogen isotope variations of ammonium across rain events: Implications for different scavenging between ammonia and particulate ammonium, Environ. Pollut., 239, 392-398, doi:10.1016/j.envpol.2018.04.015, 2018.**

10. Line 233-235. Was this 'no significant difference' found in this measurement? Otherwise, how could the author deduce the conclusion here?

**We came to this conclusion because all δ$^{15}$N-$NH_4^+$ values in cloudwater samples fall with the range of δ$^{15}$N-$NH_4^+$ values for fine particles. This is not the case for other phases of $NH_x$. To avoid any misunderstanding, we've changed "*no significant difference in the δ$^{15}$N-$NH_4^+$ exists between fine particles ($PM_{2.5}$) and cloudwater*" to "*all δ$^{15}$N-$NH_4^+$ values in cloudwater samples fall within the observed range of δ$^{15}$N-$NH_4^+$ values for fine particles ($PM_{2.5}$), providing putative evidence that $NH_4^+$ in cloudwater is primarily derived from particulate $NH_4^+$ rather than $NH_3$ absorption.*" in the revised MS.**

11. Section 3.3. More information on the uncertainty of the numbers is needed. In addition, considering the uncertainty, the significance digit can be rounded.

**Agree. More information regarding the uncertainty of partitioning estimates are included in the revised MS. Please refer to the section 3.3 in the MS with track changes (after the reply letter) for details.**

12. Line 289-291. The measurement data in six samples can be affected by different factors and doesn't necessarily to be the same as the emission inventory.

**We agree. In a way the emission inventory data are used to validate the isotope approach. But the isotope-based source apportionment estimates can also be seen as a second, independent assessment verifying existing inventory data. In fact, the discrepancies, where observed, may point to the fact that current emission inventories need to be revised. We**

**mention this in the MS, writing that $NO_x$ emissions by anthropogenic activities changed since 2010.**

13. Line 291-296. These descriptions are generally correct and reasonable. However, this discussion seems not directly link to the data/result in this study.

**We think these descriptions are critically important because they can support one of the most important findings in our study: 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 $\delta^{15}N\text{-}NO_3^-$ values suggest that $NO_x$ emissions from transportation may have exceeded emissions from coal combustion. We thus decide to leave this section in our MS.**

14. Line 326-328. It is better to compare with low-altitude data in the same region. Otherwise, the comparison may not make sense.

**We agree. Given that there is a lack of similar studies in this region, we compared our field-measured results to previous modeling results.**

15. Line 345-346. It seems the author did not discuss the production pathways in clouds, which can be very interesting if the author can do further analysis in this area.

**We actually discuss the production pathways of nitrate in clouds, quite prominently in fact. For example in the abstract we write "*$\delta^{18}O\text{-}NO_3^-$ 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%)*".**

**Given that the $\delta^{15}N$ values are primarily controlled by the reactive N sources, the discussion of the production pathways of cloud ammonium is not included in our study.**

Anonymous Referee #2

General Comments:

1. This study utilizes the isotopic composition of nitrate and ammonium captured in cloudwater during a major biomass burning event to delineate the sources and chemistry that contribute to the inorganic N concentrations. Overall, the methods are sound, and the study yields interesting results. The interpretation is well constructed, but there are a number of aspects that need to be better justified and better referenced to make the study's findings stronger. Please see below.

**Thanks for the favorable comments and helpful suggestions, which we've carefully considered. Please see below.**

2. As motivation for the work, the authors invoke the difficulty of addressing tropospheric cloud formation and its importance for radiative forcing of climate. Further, they state the importance of cloud properties linked to aerosol and precipitation chemistry. In the end, however, there is not a direct connection back to how understanding and quantifying the sources of nitrate and ammonium in this case actually link to clouds, cloudwater or their properties. It would be useful if the authors could make a stronger link in the end of the work or edit the motivation to better fit the outcomes of the study.

**Indeed, we failed to better describe the rationale of this study in the original MS. Now in the revised MS we stress that cloudwater is also a form of nitrogen deposition, which has been proved to be an important source of nitrogen, particularly in nitrogen-limited regions. Although $NH_4^+$ and $NO_3^-$ in dry (aerosol and gas pollutants) and wet (mainly rainfall) deposition are regularly assessed, cloudwater deposition is often overlooked. Our current understanding of natural versus anthropogenic influence on nitrogenous species in cloudwater is extremely limited. We thus believe that the most important implication of our work is, for to isotopically explore the sources of $NH_4^+$ and $NO_3^-$ in cloudwater. Hopefully, our work will spark more studies on cloudwater deposition.**

**We've strengthened the descriptions on the motivation of our study in the abstract and the introduction. Please see the MS with track changes.**

3. There are several instances of discussing the link between nitrate formation pathways and the oxygen isotopic composition of nitrate without references. This is fairly well established in the literature already – with an emphasis on D17O in works such as Michalski et al. (2003, 2004, 2005, 2011 etc), Alexander et al. (2009), Morin et al. (2011), and an emphasis on d18O in works such as Hastings et al. (2003, 2004, 2013), Elliott et al. (2009). Many of these works are already cited by the authors, but it should be made clearer in several places in the manuscript where the framework for interpreting d18O comes from. The text reads as if this current study is establishing that the oxygen isotopic signature (d18O) comes from chemical formation of nitrate – yet this was established as early as in Hastings et al. (2003). For instance, please add references to the first line on page 5; to line 216 on page 11; discuss more how equations 1-4 are generated and the fact that they are largely based upon previous work (for instance Hastings

et al. 2003 and Michalski et al. 2011!).

**We've added citations where appropriate, and in particular acknowledge the wok by Hastings et al. (2003). Following up on the comment by referee #1, equations 1-4 have been move to the introduction section. We also expanded the discussion related to equations 1-4.**

4. Related to this, the authors should compare the quantification of the oxidation chemistry with the expectations set forth in Alexander et al., 2009. While Alexander et al. is a modeling study, with significant uncertainties, it still would be helpful to understand a greater context for the findings in this study and whether they reflect what we expect in terms of atmospheric chemistry in the extratropics or whether the observations are suggesting something new that modelers need to be thinking about. Furthermore, it needs to be justified why only the OH and N2O5 pathways for HNO3 formation are used (page 15). In biomass burning plumes (and in initial emissions measured in the laboratory), a great deal of organics is also found. This makes it likely that RO2 and/or H-abstraction pathways would be important as well. How can this not be included here?

**Theoretical modeling results by Alexander et al. (2009) show that globally, nearly 76%, 18%, and 4% of annual inorganic nitrate are formed via pathways/reactions involving OH, $N_2O_5$, and DMS or HC ($NO_3$ reacts with dimethylsulfide (DMS) or hydrocarbons (HC) predominantly at night), respectively. We agree that, in certain cases, reactive uptake of $NO_3$ by organic aerosols is an important oxidation pathway for aerosol nitrate formation. The stable O isotopic composition of atmospheric nitrate is a powerful proxy for assessing, which oxidation pathways are important for converting $NO_x$ into nitrate under changing environmental conditions (e.g., polluted, volcanic events, climate change). In the same line, in this study, the average $\delta^{18}O$ value of $NO_3^-$ in cloudwater was 57.80‰, suggesting that $NO_3^-$ formation was dominated by the following pathways: the reaction of $NO_2$ with OH, and almost equally important, the hydrolysis of dinitrogen pentoxide ($N_2O_5$) with $H_2O$.**

**Reference**

**Alexander, B., M. G. Hastings, D. J. Allman, J. Dachs, J. A. Thornton, and S. A. Kunasek (2009), Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition ($\Delta^{17}O$) of atmospheric nitrate, *Atmos. Chem. Phys.*, *9*(14), 5043-5056.**

5. Also, what is assumed for the initial d18O-NOx in equation 2. It appears there are more unknowns than knowns for equation 2 as currently discussed in the manuscript. In the end, it is hard to justify the conclusion (like 330) that N2O5 is particularly important in cloudwater without further justification as to why only OH and N2O5 pathways are important to begin with. (On BB emissions and plumes: this is just a sampling of relevant literature and there may be better studies to reference that are more relevant to the field location in China in this study – Akagi et al., 2013; Alvarado et al. 2009a and 2009b and 2015; Burling et al., 2011; Yokelson et al. 2008 and references therein).

**Following Zhong et al. (2017), the $^{18}$O values for $NO_2$ were assumed to range from 90‰ to 122‰. The relevant reference has been added in the revised MS to support our statement.**

**Reference**

**Zong, Z., Wang, X., Tian, C., Chen, Y., Fang, Y., Zhang, F., Li, C., Sun, J., Li, J., and Zhang, G.: First Assessment of $NO_x$ Sources at a Regional Background Site in North China Using Isotopic Analysis Linked with Modeling, Environmental Science & Technology, 51, 5923-5931, 10.1021/acs.est.6b06316, 2017.**

6. What is the expectation for lifetime of the nitrate and ammonium in this study? Models suggest that the lifetime of NOx should be 1 – 1.5days at this latitude (Levy et al., 1999) and that the lifetime of nitrate and ammonium aerosols (globally) is on the order of 3-5 days (Xu and Penner, 2012). The other tracers (e.g. levoglucosan) and transport patterns help to establish the likely influence of the biomass burning smoke, but this should be better integrated in the manuscript with expectation for the formation and transport of nitrate and ammonium, since the different tracers would be expected to have different lifetimes.

**Please see our answer to the next comment.**

7. The methods section should include the details of the HYSPLIT back-trajectories –what meteorological dataset is used? At what heights? Etc. Also, it should be justified why 48-hours is used and tied to the question above regarding expected lifetimes for nitrate and ammonium.

**We fully understand the consideration of referee #2. We mention the HYSPLIT configuration briefly in the caption of Fig. 1 in the revised MS. In our study, we don't think that we should overload the method section with details on the HYSPLIT model configuration. We think that this is standard. Different from most studies, the HYSPLIT model in this study was simply used to examine whether there was an overlap between the back trajectories of air masses and the intensive biomass burning areas. Since our sampling site is on the top of a mountain (around 1500 m) and far away from the cropland, the modeling height and air mass transport period were set as 1500 m and 48 hours (still shorter than the lifetime of aerosol ammonium and nitrate), respectively.**

8. On page 8, line 165-167 it is stated that the raw d15N-NO3- data was corrected to the calculate the N isotope fractionation. How is this done? What values were found? How does this compare with expectations in the literature for the computed fractionations (i.e. Walters and Michalski (2015), Walters et al. (2016) and Chang et al. (2018))?

**The N isotope fractionation was calculated based on a computational quantum chemistry module, which we have briefly introduced in the MS and elaborated in detail in Chang et al. (2018). N isotope fractionation values for each sample (ranging from 5.21‰ to 5.98‰)**

**are reported in Fig. 3b in our MS, which is slightly lower than that of Chang et al. (2018) in biomass-burning source area (10.99 ± 0.74‰).**

9. There is discussion of the fractionation of conversion from NH3 gas to NH4+ aerosol on pages 11-13. The authors should also consider newer work on this subject – Walters et al. (2019) as it is highly relevant to the discussion here.

**Walters et al. (2019) focused on theoretical computations, while our conclusions were based on actual field measurements. In fact, the work of Walter et al. (2019) is highly relevant for our companion study ("Nitrogen Isotope Effects of Ammonia Gas-to-Aerosol Conversion and Implications for Determining Isotopic Source Signatures and Tracing Atmospheric Ammonium Origins"), in which the Walter et al. citation already served as a valuable reference to compare our data**

Additional specific comments:

Line 26: This phrasing is awkward – perhaps change to "However, this challenge is difficult to address quantitatively based on the sole use of bulk chemical properties."

**Revised accordingly.**

Line 94: there is one study in Hawaii that includes fog deposition at a high altitude site that might be relevant here (Carillo et al., 2002). Even if the data is not directly comparable it should be considered that the current manuscript is not the only measurements that exist.

**Thanks for pointing us to this reference. We didn't actually claim that we are the first study in terms of measuring the chemical components of fog water or cloud water. As referee #2 pointed out, Carrillo et al. had published relevant results in 2002. However, the current work represents the first study that include simultaneously measurements of the isotopic compositions of ammonium and nitrate in cloudwater. We clarified this in the revised MS.**

Line 225-230: The discussion of the 33 per mil isotope effect found by Heaton should be cited as such. It is mentioned here as if this is well established, but Heaton himself in this work considers the study preliminary. Also please see Walters et al. (2019).

**The most important finding in Walters et al. (2019), in our view, is that using computational quantum chemistry methods, a relatively small isotope effect was reported for the ammonia-ammonia equilibrium isotope exchange at the gas-liquid interface (4‰ at 298 K). In fact, Walters et al. (2019) computed the equilibrium N isotope effects across**

**various phases of $NH_x$ systems at 298.1 K including $NH_{3(aq)}/NH_{3(g)}$ ($\Delta^{15}\delta_{NH_{3(aq)}-NH_{3(g)}}$ = 4 ± 3‰), $NH_4^+{}_{(aq)}/NH_{3(g)}$ ($\Delta^{15}\delta_{NH^+_{4(aq)}-NH_{3(g)}}$ = 32 ± 3‰), $NH_4^+{}_{(aq)}/NH_{3(aq)}$ ($\Delta^{15}\delta_{NH^+_{4(aq)}-NH_{3(aq)}}$ = 37 ± 4‰), and $NH_4^+{}_{(s)}/NH_{3(g)}$ ($\Delta^{15}\delta_{NH^+_{4(s)}-NH_{3(g)}}$ = 31 ± 4‰). The N isotope effect for the $NH_4^+{}_{(aq)}/NH_4^+{}_{(s)}$ conversion was considered minor ($\Delta^{15}\delta_{NH^+_{4(aq)}-NH^+_{4(s)}}$ ≈ 0).**

**Walter et al. (2019) didn't falsify the work of Heaton: "*our theoretical calculated values matched experimental data reported by Urey and co-workers*".**

**In fact, we hardly observe 33 per mil isotope effect in the real atmosphere. Thus, in our study, 33 per mil was set as upper limit value of the isotope effect (see Fig. 3 in the MS). Here we would like to share results of our unpublished work: (see figure below). In this work (to be submitted soon), we describe time-resolved N isotopic discrimination factors, i.e., the offsets between $\delta^{15}$N values of ambient aerosol $NH_4^+$ and $NH_{3(g)}$, which reflect the combined N isotope effects during $NH_3$ gas-to-aerosol conversion and are most often significantly lower than 33‰.**

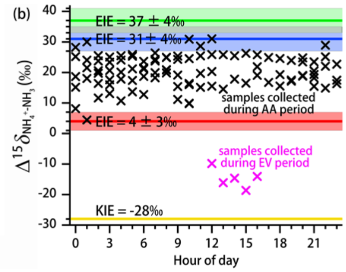


**Figure caption. Observed $\Delta^{15}\delta_{NH_4^+-NH_3}$ plotted against sampling hour in the ambient air (AA) experiment. The data points fall within the theoretically-calculated range (mean ± 1σ) of equilibrium isotope effects associated with different chemical processes involved in $NH_3$ gas-particle conversion (theoretical estimates for EIEs from Walters et al., (2019)). Green: $\Delta^{15}\delta_{NH^+_{4(aq)}-NH_{3(aq)}}$; blue: $\Delta^{15}\delta_{NH^+_{4(s)}-NH_{3(g)}}$; red: $\Delta^{15}\delta_{NH_{3(aq)}-NH_{3(g)}}$. The yellow line represents the kinetic N isotope effect (-28‰) based on the differential diffusion rates of $^{15}NH_3$ relative to $^{14}NH_3$.**

Line 256: The idea that this validates the approach seems circular in logic. The isotope ranges and fractionations incorporated into the mixing model begins with assumptions about what sources should be important; the fact that the modeling then yields the conclusion that biomass burning is an important source follows from the initial assumptions, it does not in fact justify those initial assumptions. Additional data of other kinds that suggest the same conclusion are more appropriate for making this claim.

**We stated in Line 256 that "*it is evident that biomass burning represents an important $NH_3$ source*". This statement was independently validated in section 3.1, based on the measurement of levoglucosan, a specific tracer of biomass burning. We make use of these independent data to validate the isotopic approached used, and we clarify this in the revised MS.**

Supplement: please consider more recent observations of d15N-NOx for vehicles and especially for soils (Miller et al. 2017, 2018; Yu and Elliott, 2017) and the issues related to previous collection techniques for source signatures (Fibiger et al., 2014). The references listed for the biogenic soil emissions are not really relevant.

**Thanks for recommending these papers, which we are aware of. There are reasons for the exclusion of their reported $\delta^{15}N\text{-}NO_x$ in our pool of isotopic source signatures.**

**In Miller et al. (2017), a wide range of soil $\delta^{15}N\text{-}NO_x$ ($n = 37$) was observed (from -44.2 to -14.0‰), covering almost all reported isotopic source signatures of $NO_x$. The motivation, or implication, of this work, in our view, was not to determine a robust N isotopic signature of soil-emitted $NO_x$. The large variation of $\delta^{15}N$ values was associated with different fertilizer management, which implies that "*$\delta^{15}N\text{-}NO_x$ can be a valuable observational tracer of soil emissions and varies with fertilizer management practices*".**

**In Miller et al. (2018), vehicle/transport-related $NO_x$ samples were not directly collected from road tunnel or vehicle tailpipes, and the interference from other $NO_x$ sources cannot be ruled out.**

**In Yu and Elliott (2017), only the $\delta^{15}N$ values of soil-emitted NO were determined. This work represents an important contribution. However, in the atmosphere, $NO_2$ is much more abundant than NO. $NO_3^-$ production is initiated by the oxidation of NO, and the first step is the conversion of NO to $NO_2$ (through oxidation by either $O_3$ or peroxy radicals). The conversion of NO to $NO_2$ may induce large a large N isotope fractionation (Chang et al., 2018), thus the $\delta^{15}N\text{-}NO$ values determined in Yu and Elliott (2017) are not necessarily representative of $\delta^{15}N\text{-}NO_x$ in the atmosphere.**

Anonymous Referee #3
General Comments:

The objective of the submitted manuscript "Isotopic Constraints on the Atmospheric Sources and Formation of Nitrogenous Species in Biomass-Burning-Influenced Clouds" was to apply stable isotope techniques to determine sources and pathways of inorganic nitrogen in cloudwater. Although the presented work provides a very limited data set, it is the first of its kind to measure $^{15}$N-$NH_4^+$ in cloudwater and second of its kind to measure $^{15}$N-$NO_3^-$ in cloudwater and apply these values to determine potential sources of the nitrogen species. Understanding the dynamics of nitrogen species in cloudwater is important since cloudwater has recently been reported to be a significant contributor to nitrogen deposition in various regions. If the authors adequately address the issues outlined below, I believe the work can be a valuable addition to the current atmospheric nitrogen literature and should be accepted to Atmospheric Chemistry and Physics.

Line 30: The authors state "…measured for the first time the isotopic compositions of cloudwater nitrogen species…". This may have been the case during the measurements or manuscript submission process but there has been a recent paper published that would be considered a cloudwater study of nitrate isotopes (Vega et al., 2019). However, it is likely the first with ammonium isotopes and nitrate isotopes in this region. The instances alluding to the "first time" or novelty of the data should be changed accordingly.

**We thank referee #3 for pointing us to this latest paper that is highly relevant to our work. Clearly, in light of this the "first time" is not appropriate, and we have toned this down.**

**In the conclusion (Line 334-335 in the original MS), we removed "For the first time," completely.**

**In the abstract (Line 30 in the original MS), "*…and measured for the first time the isotopic compositions (mean ± 1σ) of cloudwater nitrogen species ($\delta^{15}$N-$NH_4^+$ = -6.53 ± 4.96‰, $\delta^{15}$N-$NO_3^-$ = -2.35 ± 2.00‰, $\delta^{18}$O-$NO_3^-$ = 57.80 ± 4.23‰)…*" has been changed to "*…and simultaneously measured for the first time the isotopic compositions (mean ± 1σ) of cloudwater nitrogen species ($\delta^{15}$N-$NH_4^+$ = -6.53 ± 4.96‰, $\delta^{15}$N-$NO_3^-$ = -2.35 ± 2.00‰, $\delta^{18}$O-$NO_3^-$ = 57.80 ± 4.23‰)…*".**

The % deviation associated with the authors' source apportionment model will significantly vary depending on the range in nitrogen emission sources. The authors use $^{15}$N-$NH_3$ signatures of -29.1 ± 1.7‰ and -50.0 ± 1.8‰ for livestock and fertilizer emission sources. According to the literature this source range and standard deviation isn't realistic and likely doesn't reflect source ranges that occur due to various chemical and physical factors associated creating this source signature. Elliott et al. 2019 has a thorough compilation of literature $^{15}$N-$NH_3$ signatures. The authors did an adequate job when compiling the $^{15}$N-$NO_x$ source signatures and the mixing model for $NH_3$ would benefit from a similar approach.

**Frankly, we do not fully agree with the suggestion. The reasons are:**

**(1) Different from $\delta^{15}$N-$NO_x$ studies and different from sporadic studies of $^{15}$N-$NH_3$, we've**

**established a comprehensive pool of $NH_3$ isotopic source signatures in our previous work (Chang et al., 2016; Chang and Ma, 2016), which have been successfully applied in China (Chang et al., 2016; Chang et al., 2019). <u>We believe that our comprehensive, and more importantly, locally robust isotopic source signatures, is one of the strengths of the approach used to infer potential sources of aerosol ammonium in China.</u>**

**Reference:**

**Chang, Y., Liu, X., Deng, C., Dore, A. J., and Zhuang, G.: Source apportionment of atmospheric ammonia before, during, and after the 2014 APEC summit in Beijing using stable nitrogen isotope signatures, Atmospheric Chemistry and Physics, 16, 11635-11647, 10.5194/acp-16-11635-2016, 2016.**

**Chang, Y., and Ma, H.: Comment on "Fossil Fuel Combustion-Related Emissions Dominate Atmospheric Ammonia Sources during Severe Haze Episodes: Evidence from $^{15}N$-Stable Isotope in Size-Resolved Aerosol Ammonium", Environmental Science & Technology, 50, 10765-10766, 10.1021/acs.est.6b03458, 2016.**

**Chang, Y., Zou, Z., Zhang, Y., Deng, C., Hu, J., Shi, Z., Dore, A. J., and Collett, J. L.: Assessing Contributions of Agricultural and Nonagricultural Emissions to Atmospheric Ammonia in a Chinese Megacity, Environmental Science & Technology, 53, 1822-1833, 10.1021/acs.est.8b05984, 2019.**

**(2) Only after submission of the original MS we had noticed the work of Elliott et al. (2019), in which existing published data (including our work) related to the "isotopic source signatures" of $NH_3$ and $NO_x$ were compiled. One challenge, however, is the large variability of the observed $\delta^{15}N\text{-}NH_3$ values. Once released into the atmosphere, $NH_3$ undergoes a number of potential physical (e.g., deposition) and chemical processes (e.g., particle nucleation and condensation) that can alter their primary isotopic "fingerprints" and the isotopic composition of their reaction products (e.g., aqueous and solid $NH_4^+$).**

**Here we would like to share results of our unpublished work to prove that not all published $\delta^{15}N\text{-}NH_3$ values can necessarily be used as fingerprints to trace $NH_3$ sources: "*In a "lab-in-the-field" approach, we describe time-resolved N isotopic discrimination factors (Figure below), i.e., the offsets between $\delta^{15}N$ values* $(\text{mean}_{\text{min}}^{\text{max}} \pm 1\sigma)$ *of ambient aerosol $NH_4^+$ and $NH_{3(g)}$* $(\Delta\delta^{15}N_{NH_4^+\text{-}NH_3} = [\delta^{15}N\text{-}NH_4^+ - \delta^{15}N\text{-}NH_3])$*, which reflect the combined N isotope effects during $NH_3$ gas-to-aerosol conversion. We found clear evidence for kinetic N isotope fractionation, with enrichment of $^{15}N$ in the $NH_3$* $(1.58_{-7.16}^{9.41} \pm 6.10‰, n = 24)$ *relative to $NH_4^+$ pool* $(-20.17_{-25.49}^{-16.1} \pm 3.77‰, n = 5)$ *near a $NH_3$ point source. Multiple lines of evidence support the dominant role of the KIE related to the neutralization of $NH_{3(g)}$ with $H_2SO_{4(g)}$ during nucleation (i.e., formation of $NH_4HSO_4$ and $(NH_4)_2SO_4$) in determining the net* $\Delta\delta^{15}N_{NH_4^+\text{-}NH_3}$ $(-14.65_{-18.62}^{-9.81} \pm 3.23‰, n = 5)$*. In contrast, in ambient air further away from the point source, when more time has passed after $NH_3$ was released, Bayesian mixing modeling revealed that equilibrium N isotope exchange between $NH_{3(aq)}/NH_{3(g)}$ (25±12%),***

***$NH_4^+{}_{(aq)}/NH_{3(aq)}$ (34±13%), and $NH_4^+{}_{(aq/s)}/NH_{3(g)}$ (32±15%) is much more important, explaining together over 90% of the observed*** $\Delta\delta^{15}N_{NH_4^+\text{-}NH_3}$ $(20.38_{4.44}^{31.01} \pm 5.20‰,\ n = 99)$**.”**

**In brief:** **<u>Our results suggest that the large variability of $NH_3$ N isotopic source signatures reported in previous work may be partly attributed to the differential N isotope alteration due to kinetic isotope fractionation.</u>**

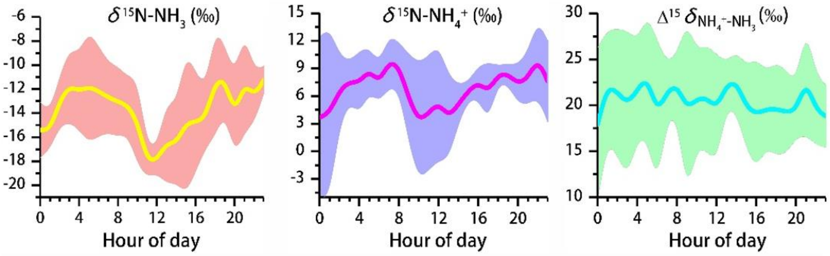


**Figure caption. Diurnal variation of $\delta^{15}$N-NH$_3$ (a), $\delta^{15}$N-NH$_4^+$ (b), and** $\Delta^{15}\delta_{NH_4^+-NH_3}$

**(3) Other recent (sorry, also still unpublished) work suggests that the pool of NH$_3$ isotopic source signatures we established can be used to explain the variations of $\delta^{15}$N values of ambient NH$_3$ in tropical Savanna environments in northern Thailand (see figures below). This greatly enhances our confidence to use our own isotopic source pool to trace NH$_3$ sources.**

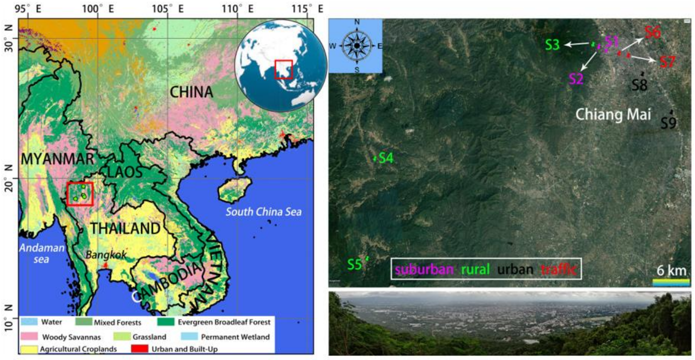


**Figure 1. Location of sampling sites.**

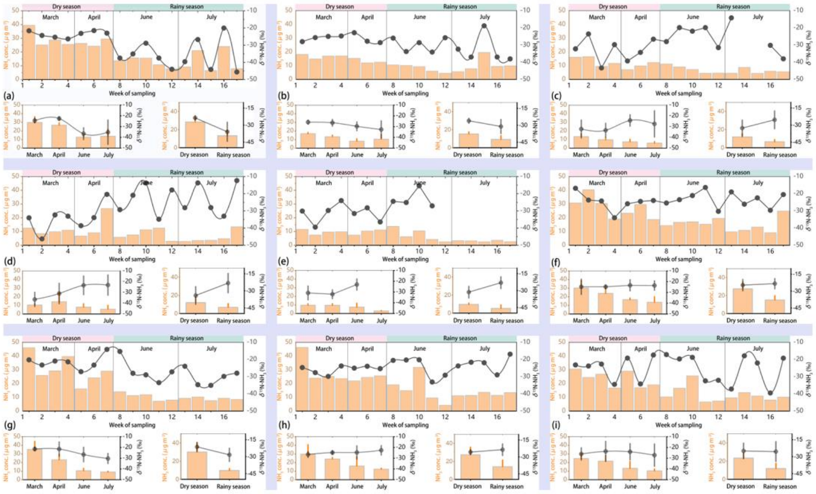


**Figure 2. Temporal variations of NH$_3$ concentrations and $\delta^{15}$N-NH$_3$ values at each site. "a" to "i" represents the results of site 1 (S1) to site 9 (S9). The error bar indicates one standard deviation.**

The authors dismiss fossil fuel combustion (vehicles and power plants) as an emission source in this study region when discussing contribution to atmospheric NH$_3$ but argue for its significance in this region when discussing NO$_x$ source apportionment. For NH$_3$: "Although fossil-fuel combustion, urban waste, and natural soils also represent potential sources of NH$_3$, their 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). 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)." For NO$_x$: "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%). "…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." The argument for and against these fossil fuel sources, as outlined above, may confuse the reader especially since high NH$_3$ concentration have been linked to traffic and the authors contribute a significant amount of NO$_x$ to vehicles. Also, the authors mention "ultra-low emissions" techniques when referring to NO$_x$ contributions and these techniques would include SCR technology in coal combustion plants that lead to $NH_3$ emissions. The authors should clear up their arguments in this section so there aren't contradictory statements or so the readers understand why the arguments seem contradictory.

**The statements referee #3 refers to are not contradictory. Please refer to our long answer below. The short answer is that, based on our studies and numerous previous studies by others, the $NH_3$ emission factors of vehicle (see table below), coal combustion (e.g., *Li et al., Gaseous Ammonia Emissions from Coal and Biomass Combustion in Household Stoves with Different Combustion Efficiencies, ES&TL, 3, 98-103, doi:10.1021/acs.estlett.6b00013, 2016*) and coal-fired power plants (e.g., Chang and Ma, ES&T, 2016) are at least two orders of magnitude lower than that of $NO_x$.**

**In the papers below we found that in Shanghai, vehicular $NH_3$ emissions account for around 20% of the $NH_3$ budget. Apparently, vehicular $NH_3$ emissions cannot be overlooked in urban areas like Shanghai. However, the land of China is mostly occupied by rural areas. In fact, taking all non-agricultural $NH_3$ sources (including on-road traffic) together, they only take up 5% of China's total $NH_3$ emissions (Chang, Non-agricultural ammonia emissions in urban China, Atmos. Chem. Phys. Discuss., 14, 8495-8531, 2014, doi:10.5194/acpd-14-8495-2014).**

**Se also:**

**Chang, Y., Zou, Z., Deng, C., Huang, K., Collett, J. L., Lin, J., and Zhuang, G.: The importance of vehicle emissions as a source of atmospheric ammonia in the megacity of Shanghai, Atmospheric Chemistry and Physics, 16, 3577-3594, 10.5194/acp-16-3577-2016, 2016.**

**Chang, Y., Zou, Z., Zhang, Y., Deng, C., Hu, J., Shi, Z., Dore, A. J., and Collett, J. L.: Assessing Contributions of Agricultural and Nonagricultural Emissions to Atmospheric Ammonia in a Chinese Megacity, Environmental Science & Technology, 53, 1822-1833, 10.1021/acs.est.8b05984, 2019.**

**The emission factor of vehicular-emitted $NH_3$ we determined in Chang et al. (2016) is similar to most previous studies (see table below; *Huang et al., Ammonia Emission Measurements for Light-Duty Gasoline Vehicles in China and Implications for Emission Modeling, ES&T,, 52, 11223-11231, 10.1021/acs.est.8b03984, 2018*).**

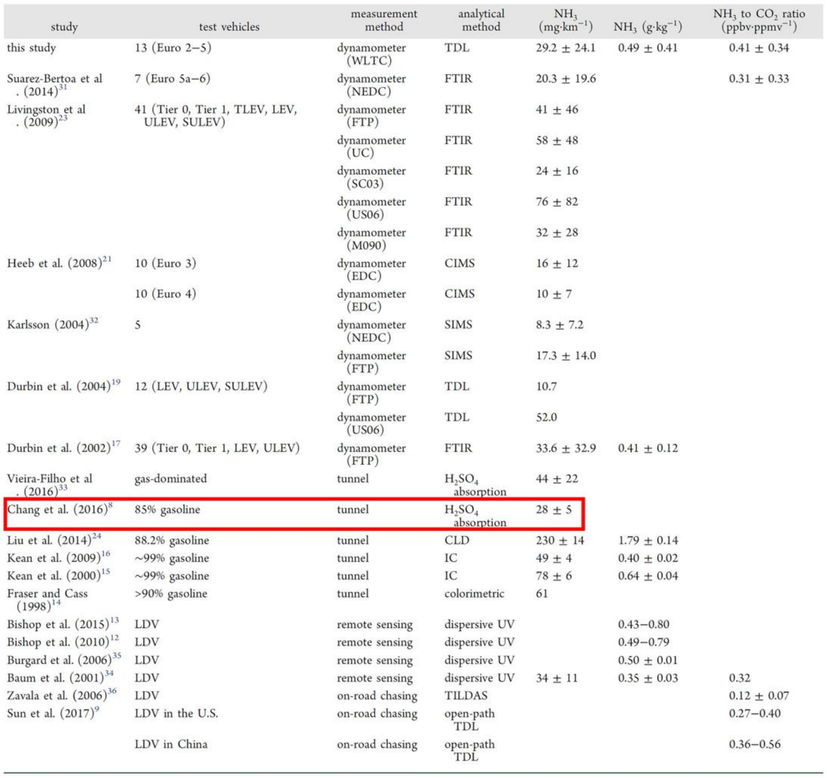
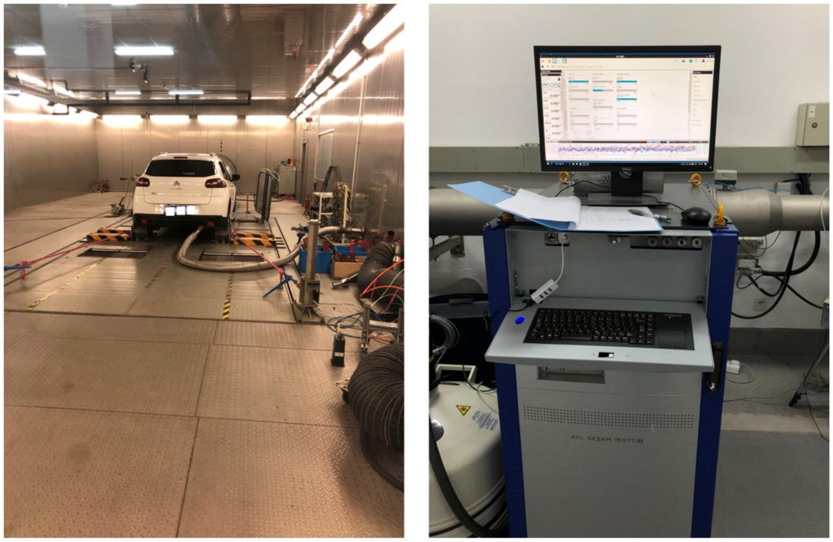


**Table 1. $NH_3$-to-$CO_2$ Ratios and Distance- and Fuel-based $NH_3$ EFs from Dynamometer, Tunnel, Remote Sensing, and On-Road Measurements**

| study | test vehicles | measurement method | analytical method | $NH_3$ ($mg \cdot km^{-1}$) | $NH_3$ ($g \cdot kg^{-1}$) | $NH_3$ to $CO_2$ ratio ($ppbv \cdot ppmv^{-1}$) |
|---|---|---|---|---|---|---|
| this study | 13 (Euro 2–5) | dynamometer (WLTC) | TDL | 29.2 ± 24.1 | 0.49 ± 0.41 | 0.41 ± 0.34 |
| Suarez-Bertoa et al. (2014)[31] | 7 (Euro 5a–6) | dynamometer (NEDC) | FTIR | 20.3 ± 19.6 | | 0.31 ± 0.33 |
| Livingston et al. (2009)[23] | 41 (Tier 0, Tier 1, TLEV, LEV, ULEV, SULEV) | dynamometer (FTP) | FTIR | 41 ± 46 | | |
| | | dynamometer (UC) | FTIR | 58 ± 48 | | |
| | | dynamometer (SC03) | FTIR | 24 ± 16 | | |
| | | dynamometer (US06) | FTIR | 76 ± 82 | | |
| | | dynamometer (M090) | FTIR | 32 ± 28 | | |
| Heeb et al. (2008)[21] | 10 (Euro 3) | dynamometer (EDC) | CIMS | 16 ± 12 | | |
| | 10 (Euro 4) | dynamometer (EDC) | CIMS | 10 ± 7 | | |
| Karlsson (2004)[32] | 5 | dynamometer (NEDC) | SIMS | 8.3 ± 7.2 | | |
| | | dynamometer (FTP) | SIMS | 17.3 ± 14.0 | | |
| Durbin et al. (2004)[19] | 12 (LEV, ULEV, SULEV) | dynamometer (FTP) | TDL | 10.7 | | |
| | | dynamometer (US06) | TDL | 52.0 | | |
| Durbin et al. (2002)[17] | 39 (Tier 0, Tier 1, LEV, ULEV) | dynamometer (FTP) | FTIR | 33.6 ± 32.9 | 0.41 ± 0.12 | |
| Vieira-Filho et al. (2016)[33] | gas-dominated | tunnel | $H_2SO_4$ absorption | 44 ± 22 | | |
| Chang et al. (2016)[8] | 85% gasoline | tunnel | $H_2SO_4$ absorption | 28 ± 5 | | |
| Liu et al. (2014)[24] | 88.2% gasoline | tunnel | CLD | 230 ± 14 | 1.79 ± 0.14 | |
| Kean et al. (2009)[16] | ~99% gasoline | tunnel | IC | 49 ± 4 | 0.40 ± 0.02 | |
| Kean et al. (2000)[15] | ~99% gasoline | tunnel | IC | 78 ± 6 | 0.64 ± 0.04 | |
| Fraser and Cass (1998)[14] | >90% gasoline | tunnel | colorimetric | 61 | | |
| Bishop et al. (2015)[13] | LDV | remote sensing | dispersive UV | | 0.43–0.80 | |
| Bishop et al. (2010)[12] | LDV | remote sensing | dispersive UV | | 0.49–0.79 | |
| Burgard et al. (2006)[35] | LDV | remote sensing | dispersive UV | | 0.50 ± 0.01 | |
| Baum et al. (2001)[34] | LDV | remote sensing | dispersive UV | 34 ± 11 | 0.35 ± 0.03 | 0.32 |
| Zavala et al. (2006)[36] | LDV | on-road chasing | TILDAS | | | 0.12 ± 0.07 |
| Sun et al. (2017)[9] | LDV in the U.S. | on-road chasing | open-path TDL | | | 0.27–0.40 |
| | LDV in China | on-road chasing | open-path TDL | | | 0.36–0.56 |

**In order to directly collect vehicle-emitted $NH_3$ and $NO_x$ for isotopic analysis, we recently conducted detailed measurements of $NH_3$ and $NO_x$ emissions from 6 Euro 2 to Euro 5 light-duty gasoline vehicles in Xiamen City, China (see pictures below). Results show that the average concentrations of NOx are at least two orders of magnitude higher than that of**

**$NH_3$ (this is not a new finding because numerous studies have already proven it).**



**Similarly, in order to directly collect $NH_3$ and $NO_x$ emitted from coal-fired power plants (CFPP), we also conducted detailed measurements of $NH_3$ and $NO_x$ emissions at two typical CFPPs in China (see field photos below). Although ammonia slip is a common issue with selective catalytic reduction technology used in CFPP for removal of nitric oxide, the mass concentration of ammonia (typically 3−5 mg $NH_3$ $m^{-3}$) in flue gases is 2 or 3 orders of magnitude smaller than that of $NO_x$.**

Line 125: Additional inorganic ion concentration measurements are mentioned. Was $NO_2^-$ also measured? If so, was the concentration significant compared to $NO_3^-$. It will also be measured in

the isotope analysis and will contribute to the $^{15}$N-$NO_3^-$ value reported. Was $NO_2^-$ removed before $^{15}$N-$NO_3^-$ analysis?

**In these six cloudwater samples, $NO_2^-$ concentrations were below the detection limit (1.11 ppb) of our IC system; that is less than 1% of the $NO_3^-$ and $NH_4^+$ concentrations. We thus are certain that their interference with the $^{15}$N-$NO_3^-$ analysis is negligible.**

Line 197: State the significance of the correlation using p-value. The authors don't refer to the very strong correlation coefficient between $NO_3^-$ and $NH_4^+$ although this could help argue for the similar primary source (BB).

**Thanks for the suggestion. Indeed, there is a strong correlation between $NO_3^-$ and $NH_4^+$ in our study. Although BB is an important source of $NH_3$ and $NO_x$, we cannot conclude per se that both $NO_3^-$ and $NH_4^+$ primarily derived from BB just based on their strong correlation. Because a large fraction of $NO_3^-$ and $NH_4^+$ is chemically bound, they naturally show a strong correlation in aerosols or cloudwater.**

Line 205: change "biomass-burring" to "biomass-burning"

**Corrected accordingly.**

Line 207: Are these $^{15}$N averages concentration-weighted? The weighted average could be a better representation of the overall source contribution.

**Given that the limited data set and considering the comments provided by Prof. Yingjun Chen and referee #2, we've added more discussion on transformation than source.**

Line 223: The discussion comparing 15N-NH3/4 in gas, cloudwater, rain, and particulates may be overstated due to the small sample size. The authors should at least remind the reader that this is a small sample set and these comparisons are preliminary. Also, the authors can now compare to the Vega et al., fog water values.

**Agreed. In the revised MS, we've deleted "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". Instead, we added "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**

**cloudwater is vital for understanding the anthropogenic influence on nitrogen deposition in the study region." at the end of this paragraph.**

**Moreover, we've added "*Recently, Vega et al. (2019) reported the $\delta^{15}$N (-8 ± 2‰) and $\delta^{18}$O (71 ± 3‰) values of $NO_3^-$ in fog water at a forest site in Sweden. The relatively higher $\delta^{15}$N values in our study (-2.35‰) suggest more $NO_x$ emitted from combustion processes. While the much higher $\delta^{18}$O values in Vega et al. (2019) indicate a greater contribution from $O_3$ in sub-Arctic environments.*"**

Line 231: "This can most likely be attributed to the preferential absorption 14N-NH3 associated with washout during precipitation." Is there a reference to this? Is this trend

observed in literature?

**This trend was observed in the reference below, which we've added in the revised MS to support our statement:**

**Zheng, X. D., Liu, X. Y., Song, W., Sun, X. C., and Liu, C. Q.: Nitrogen isotope variations of ammonium across rain events: Implications for different scavenging between ammonia and particulate ammonium, Environ. Pollut., 239, 392-398, doi:10.1016/j.envpol.2018.04.015, 2018.**

Line 250: The authors discuss equilibrium fractionation but do not address the kinetic fractionation that is predicted to have an opposite fractionation effect (" = 28‰ (Pan et al., 2016). The authors should make the reader aware of this pathway and discuss why they assumed it is insignificant if they are not taking it into account when investigating the 15N data.

**Thanks for the suggestion. We added "In addition, the isotopic fractionation from the conversion of $NH_3$ to $NH_4^+$ was simplified in this study, and it was not possible to incorporate all of the possible equilibrium and kinetic fractionation scenarios" in the revised MS.**

**Recently, we operated in tandem an online gas and aerosol composition monitor and a custom-made automated drop collector for hourly measurements of the $NH_3$ and aerosol $NH_4^+$ concentrations and the collection of absorption solutions, respectively. We performed lab-in-the-field experiments, with different levels of $NH_3$ contamination of the ambient air from an urban $NH_3$ point source. Phase-resolved $\delta^{15}$N values of $NH_x$ were determined at hourly resolution to provide observational constraints on the N isotope effects during $NH_3$-$NH_4^+$ gas-to-aerosol conversions.**

**Our high-resolution time-series isotopic data suggest that an (isotope) equilibrium can be reached very rapidly, even at the time scale of hours. In turn, equilibrium N isotope fractionation during gas-to-particle conversion of $NH_3$ to $NH_4^+$ may dominate the overall N isotope fractionation in the ambient atmosphere already soon after the $NH_3$**

**volatilization/emission, with a net $\Delta^{15}\delta_{\mathrm{NH}_4^+-\mathrm{NH}_3}$ on the order of 20‰. <u>Given that the sampling period of our study (and most of previous studies) was longer than an hour, the influence of KIE can probably be neglected.</u> We clarify this in the revised MS.**

Line 268: When taking into account the literature range and overlap of fertilizer and livestock waste emission 15N-NH3 values and the fact that both sources originate from source pools (waste and fertilizer N) with similar 15N values and are the product of similar fraction effects, is it realistic to treat these as separate sources rather than just an overall agricultural source?

**We fully understand the consideration by referee #3. Although livestock waste and N-fertilizer application can be classified into agricultural source and they have relatively low $\delta^{15}$N-NH$_3$ values, the $\delta^{15}$N values of NH$_3$ that is emitted are distinctly different. Due to the nature of volatilization, their $\delta^{15}$N-NH$_3$ values are lower than that of vehicle and biomass burning. However, there are several other factors to influence the $\delta^{15}$N-NH$_3$ values. For example, ammonium in animal waste and N fertilizer have drastically different $\delta^{15}$N values.**

**Another important point is that the NH$_3$ emissions from vehicle and biomass burning also have very different $\delta^{15}$N values. For vehicles, the activity of the three-way catalytic converters is responsible for the production of NH$_3$ in automobile exhaust. NH$_3$ formation has been attributed to the reactions of nitric oxide with hydrogen gas produced from a water-gas shift reaction between carbon monoxide and water.**

Line 301 and 39: OH oxidation is mentioned as the dominate pathway. The wording here should be changed since the results do not indicate it is dominate. Also, it would be expected that OH is the dominate pathway during this sampling period, why do the authors think it wasn’t in this particular case?

**Following the suggestion by referee #1, we’ve moved the description from L301 to L319 to the method section.**

Prof. Yingjun Chen

General Comments:

In this study, the authors analyzed stable nitrogen and oxygen isotope ratios timeseries of a biomass burning event at a mountaintop site in eastern China to investigate the sources and formation processes of nitrogenous species in cloudwater. A theoretical approach to calculate N isotope effects is used. While extensive studies of nitrogen containing aerosol isotopic compositions have been conducted worldwide, this study represents the first attempt to isotopically explore what happens to nitrogenous species in cloudwater. My major concern is relatively short discussion regarding their data and results. I will be glad to recommend a final publication after the following questions can be addressed.

**We appreciate the favorable comments. The discussion regarding the results has been expanded in the revised MS (see details below).**

1. I am not questioning the novelty of this work, but the authors should put more efforts to clearly describe the novelty of their study in the abstract or introduction section.

**Thanks for the suggestion. We've highlighted the novelty of our work in the sections of introduction (we added relevant papers) and abstract (see the revised version below). In the original MS, the importance of our work was only reflected by the interpretation of tropospheric cloud formation. Now we realize that while dry and rain deposition of nitrate and ammonium are regularly assessed, cloudwater or fog water deposition is often overlooked. But in fact, cloudwater deposition can significantly contribute to atmospheric nitrogen inputs to nitrogen-limited ecosystems. Therefore, cloudwater or fog water should be considered in deposition estimates of inorganic nitrogen and major ions. If cloudwater or fog water deposition is not accounted for, ion wet deposition may be greatly underestimated. The revised abstract is shown below. We have adapted the text accordingly.**

**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 cloudwater. 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, cloudwater deposition is often underappreciated. 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 simultaneously measured for the first time the isotopic compositions (mean ± 1σ) of cloudwater nitrogen species ($\delta^{15}N\text{-}NH_4^+ = -6.53 \pm 4.96‰$, $\delta^{15}N\text{-}NO_3^- = -2.35 \pm 2.00‰$, $\delta^{18}O\text{-}NO_3^- = 57.80 \pm 4.23‰$), 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%). 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 cloudwater is vital for understanding the anthropogenic influence on nitrogen deposition in the study region.***

2. Since the isotope data reported in the MS are the first of its kind, thus the authors should discuss more about the data in section 3.2.

**Agreed. Referee #3 already recommended a recent publication (Vega et al., 2019) regarding the N and O isotopic data of fog water. See comment above.**

6. The authors assess the contributions of potential sources and processes with exact numbers. I suggest the authors to discuss more about the uncertainties of these results.

**Agreed. We've expanded the discussion regarding the uncertainties of the results in the revised MS. Please refer to the discussion section in the MS with track changes for details (after the reply letter).**

Specific comments:

1. Line 52-56: the authors should double-check the references used here.

**All the references used here were double-checked.**

2. Line 127-129: brief introduction about the chemical analysis is need.

**Agreed. See comment above. In the revised MS, we've added details on the method.**

3. Line 205: "burring" should be changed as "burning".

**Corrected accordingly.**

4. Please note that Ô´ S represents isotope enrichment factor. Keep a consistent expression in the text.

**Revised accordingly.**

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

Yunhua Chang[1, 2], Yanlin Zhang[1*], Jiarong Li[2], Chongguo Tian[3], Linlin Song[4], Xiaoyao Zhai[1], Wenqi Zhang[1], Tong Huang[1], Yu-Chi Lin[1], Chao Zhu[2], Yunting Fang[4], Moritz F. Lehmann[5], and Jianmin Chen[2*]

[1]Yale-NUIST Center on Atmospheric Environment, Nanjing University of Information Science & Technology, Nanjing 210044, China.

[2]Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP[3]), Department of Environmental Science & Engineering, Institute of Atmospheric Sciences, Fudan University, Shanghai 200433, China.

[3]Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China.

[4]CAS Key Laboratory of Forest Ecology and Management, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China.

[5]Aquatic and Isotope Biogeochemistry, Department of Environmental Sciences, University of Basel, Basel 4056, Switzerland.

[*]Corresponding authors: Yanlin Zhang (dryanlinzhang@outlook.com) and Jianmin Chen (jmchen@fudan.edu.cn).

## Abstract

~~The interpretation of~~Predicting tropospheric cloud formation and subsequent nutrient~~s~~ deposition ~~rests~~ relies 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~~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~~n~~ important role in tropospheric cloud formation. ~~Besides, while~~While dry and wet (mainly rainfall) deposition of $NH_4^+$ and $NO_3^-$ are regularly assessed, cloudwater deposition is often underappreciated~~overlooked~~. 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 simultaneously measured for the first time the isotopic compositions (mean ± 1σ) of cloudwater nitrogen species ($\delta^{15}N\text{-}NH_4^+ = -6.53 \pm 4.96‰$, $\delta^{15}N\text{-}NO_3^- = -2.35 \pm 2.00‰$, $\delta^{18}O\text{-}NO_3^- = 57.80 \pm 4.23‰$), 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 $\delta^{15}N\text{-}NO_3^-$ values suggest that $NO_x$ emissions from transportation may have exceeded emissions from coal combustion. $\delta^{18}O\text{-}NO_3^-$ 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%). Although ~~our very~~the limited sample set used her~~s~~e results in ~~could introduce~~a relatively large ~~great~~ uncertainty ~~on the~~with regards to ~~calculation of~~the origin of cloud-associated nitrogen

~~cloudwater~~ deposition, the high concentrations of inorganic nitrogen ~~suggest~~imply that clouds ~~may be~~represent an important source of nitrogen, especially for nitrogen-limited ecosystems in remote areas. Further simultaneous and long-term sampling of aerosol, rainfall, and cloudwater~~,~~ is~~are~~ vital for understanding the anthropogenic influence on nitrogen deposition in ~~this region~~the study region.

## 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; 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 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

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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). This is different for the O isotopes. $NO_3^-$ production ~~is initiated by~~involves the oxidation of NO. The first step in the overall process is the conversion of NO into $NO_2$, e.g., ~~which can occur by~~through the oxidation by either ozone ($O_3$) or peroxy radicals (Michalski et al., 2011). ~~The stable oxygen isotopic composition of atmospheric $NO_3^-$ is a powerful proxy for assessing whatthe oxidation pathways are important forduring conversion converting of nitrogen oxides into $NO_3^-$ (Michalski et al., 2011). Large~~ Significant $^{18}O$ enrichments and excess $^{17}O$ (i.e., clear evidence for -mass independent ~~composition~~fractionation) are observed in atmospheric $NO_3^-$ collected across the globe (e.g., Michalski et al., 2005; Hastings et al., 2003). ~~These~~Such diagnostic isotope ~~enrichments and~~signatures, as well as -their variability in space and time have been linked to the ~~magnitude of~~extent of $O_3$ oxidation (Michalski et al., 2011). ~~In other words~~Put another way, the oxygen isotope composition of $NO_3^-$ ($\delta^{18}O-NO_3^-$) is largely determined by chemical reactions rather than the source, and it~~as~~ it is primarily modulated by the ~~atmospheric~~ O-atom exchange (Michalski et al., 2011).~~reactions~~ in the atmosphere~~of the oxygen isotope.~~ Therefore, $\delta^{18}O-NO_3^-$ 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). ~~To our knowledge, there are no reports on the N and O isotopic composition of nitrogenous species in cloudwater.~~

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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 (Hastings et al., 2003)

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

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:

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

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):

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

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). $\delta^{18}$O-X is the O isotopic composition of X. The range of $\delta^{18}$O-$H_2O$ 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

$$1000\left({}^{m}\alpha_{X/Y}-1\right)=\frac{A}{T^4}\times10^{10}+\frac{B}{T^3}\times10^{8}+\frac{C}{T^2}\times10^{6}+\frac{D}{T}\times10^{4} \qquad (4)$$

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-$NO_3^-$ 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‰.

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 that BB events leave in the N pool of clouds. Integrating cloudwater nitrogenous species isotope data ($\delta^{15}$N-$NH_4^+$, $\delta^{15}$N-$NO_3^-$ and $\delta^{18}$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. Although numerous studies have been conducted ~~in terms of~~that ~~measuring~~ involved the ~~the~~ chemical ~~components of~~characterization of fog water or cloudwater, to our knowledge, there are no reports on the N (and O) isotopic composition of both $NO_3^-$ *and* $NH_4^+$ in cloudwater.

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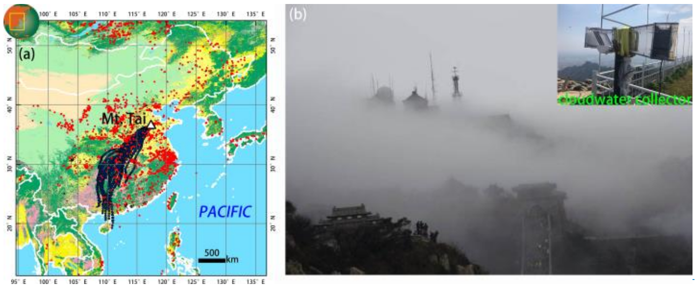
## 2 Materials and Methods

### 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 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 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).



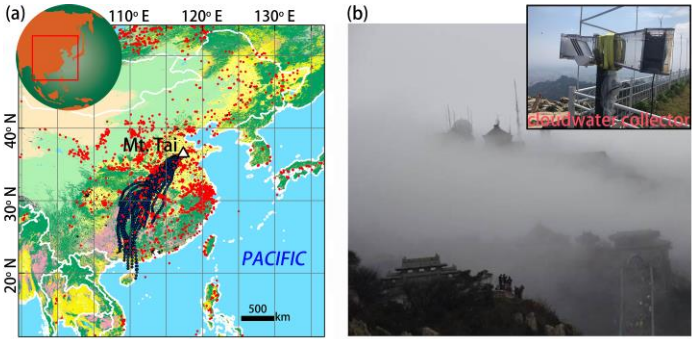


**Figure 1**. (**a**) Location of Mt. Tai (triangle) and twenty-four 48-h back trajectories (black lines) of air masses simulated by the HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT.php) based on the Global Data Assimilation System (GDAS) meteorological data set arriving at Mt. Tai on 1 August 2015 (4:00 UTC) at an altitude 1500-m a.s.l (close to the altitude of our sampling site) ~~(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,~~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$^{TM}$ ICS-5000$^+$ system (ThermoFisher Scientific, Sunnyvale, USA). The IC system was equipped with an automated sampler (AS-DV). Cloudwater sample~~r~~s were measured using an IonPac CG12A guard column and a CS12A separation column, with an aqueous methanesulfonic acid (MSA, 30 mM L$^{-1}$) eluent at a flow rate of 1 mL min$^{-1}$. Detailed information regarding sample processing, pre-treatment, 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, respectively. The analytical errors from duplicate analysis were within 5%~~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 $NH_4^+$ ($\delta^{15}$N-$NH_4^+$) and $NO_3^-$, ($\delta^{15}$N- $NO_3^-$ and $\delta^{18}$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. Standard regressions were made based on the known isotopic values of international standards and the measured standard $\delta^{15}$N values. The slope of the plot of the sample versus the standard $\delta^{15}$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; Chang et al., 2018). The relative contribution of each source in Bayesian theorem is expressed as:

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

where $\theta(\mathrm{data}|\mathrm{f_q})$ and $\mathrm{P(f_q)}$ 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 ($\varepsilon_N$) associated with the kinetic transformation of $NO_x$ to $HNO_3$ (Walters and Michalski, 2015). $\varepsilon_N$ 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 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~~mg L$^{-1}$ (10.1 ~~µg ml~~mg L$^{-1}$ on average), and from 4.9 to 18.0 ~~µg ml~~mg L$^{-1}$ (9.1 ~~µg ml~~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 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-burn~~r~~ing-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~~E~~e~~quations 1-4).

At present, there are no other reports on the isotope ratios of both $NO_3^-$ and $NH_4^+$ in cloudwater, and a comparison is possible only with isotope data from precipitation and aerosol N. Recently, Vega et al. (2019) reported the $\delta^{15}N$ (-8‰ ± 2‰) and $\delta^{18}O$ (71‰ ± 3‰) values of $NO_3^-$ in fog water at a forest site in Sweden. The relatively high~~er~~ $\delta^{15}N$ values in our study (-2.35‰) suggest more $NO_x$ that emitted from combustion processes. ~~While the~~In contrast, the much higher

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$\delta^{18}O$ values in Vega et al. (2019) indicate ~~more~~ a much ~~h~~greater contribution from $O_3$ in sub-Arctic environments. In Fig. 2a, N isotopic differences for $NO_x$ sources are greater (35‰), than for $\delta^{18}O$-$NO_x$. In fact, the oxygen isotope signature of $NO_x$ is mainly ~~determined by~~ chemistry-driven rather than determined 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 $\varepsilon_N$ 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 processes during precipitation (Zheng et al., 2018). We are aware of the fact that our sample/data set used here is limited, resulting in a relatively large uncertainty with regards to the N isotope based source apportionment. However, all $\delta^{15}N$-$NH_4^+$ values in cloudwater samples ~~can be covered by the variation~~fall within the observed range of $\delta^{15}N$-$NH_4^+$ values for~~in~~ fine particles ($PM_{2.5}$), ~~no significant difference in the $\delta^{15}N$-$NH_4^+$ exists between fine particles ($PM_{2.5}$) and cloudwater, indicating~~providing putative evidence that $NH_4^+$ in cloudwater is primarily derived from particulate $NH_4^+$ ~~instead of~~rather than $NH_3$ absorption. ~~Still, great uncertainty on the isotopic comparison of cloudwater with other phases need to be bear in mind due to the small sample size.~~

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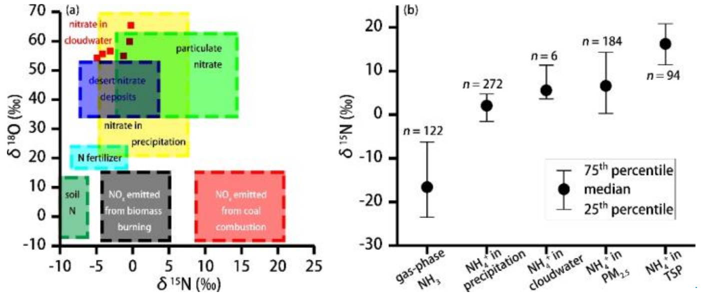


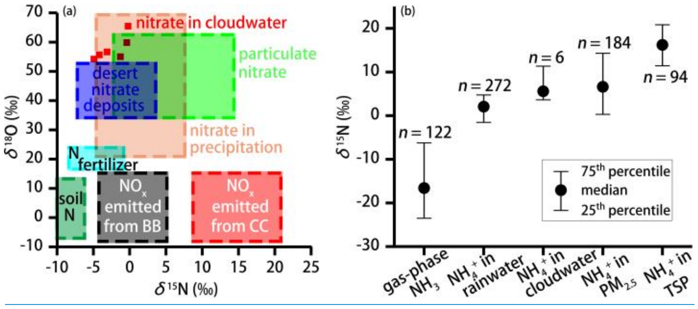
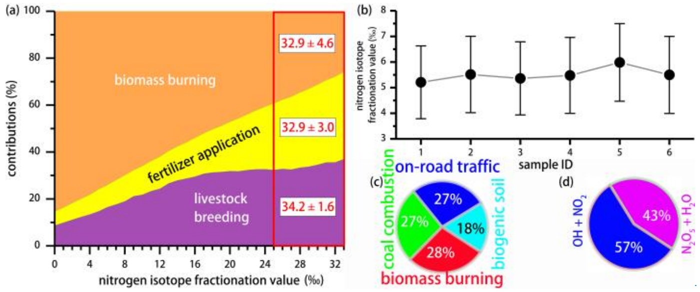


**Figure 2.** (**a**) Observed range of typical $\delta^{18}$O and $\delta^{15}$N values of $NO_3^-$ and $NO_x$ for different sources (adapted from Fenech et al. (2012)). BB and CC represent biomass burning and coal combustion, respectively. The red squares represent nitrate isotope data in cloudwater (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 $\delta^{15}N\text{-}NH_4^+$, 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 $\varepsilon_{NH_4^+-NH_3}$, the measurement of levoglucosan provides compelling evidence that biomass burning represents an important $NH_3$ source, ~~it is evident that biomass burning represents an important $NH_3$ source,~~ independently 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). It is important to note that there was large uncertainty in the evaluation of biomass burning, which was partly ascribed 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 simplified in this study, and it was not possible to incorporate all of the possible equilibrium and kinetic fractionation scenarios.



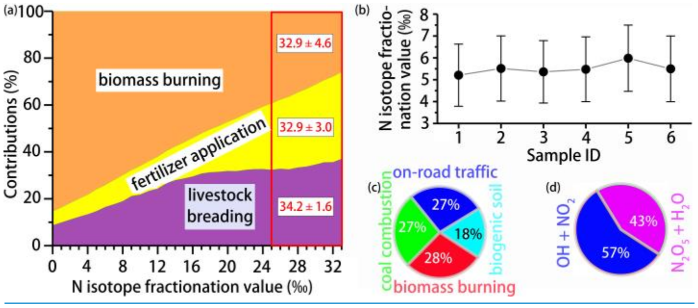


**Figure 3**. (**a**) Source partitioning estimates for $NH_4^+$ in cloudwater as a function of $\varepsilon_{NH_3 \rightarrow NH_4^+}$. The red square highlights the best-guess estimates based on $\varepsilon_{NH_4^+ - NH_3} \geq 25‰$). (**b**) Whisker plot of the N fractionation for the conversation 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**)

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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 computational quantum chemistry (~~-~~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~~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:~~

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

~~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):~~

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

~~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). $\delta^{18}$O-X is the O isotopic composition of X. The range of $\delta^{18}$O-$H_2O$ 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~~

~~$1000\left({}^{m}\alpha_{X/Y}-1\right)=\frac{A}{T^4}\times10^{10}+\frac{B}{T^3}\times10^{8}+\frac{C}{T^2}\times10^{6}+\frac{D}{T}\times10^{4}$ (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-$NO_3^-$ 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 $\gamma$, 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~~In this study, 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~~ processes 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)).

## Acknowledgments

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