

***Interactive comment on* “Isotopic Constraints on the Atmospheric Sources and Formation of Nitrogenous Species in Biomass-Burning-Influenced Clouds” by Yunhua Chang et al.**

Anonymous Referee #2

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This study utilizes the isotopic composition of nitrate and ammonium captured in cloud-water 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.

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

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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.

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 more clear 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!).

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 are 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?

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Also, what is assumed for the initial d18O-NO_x 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)

What is the expectation for lifetime of the nitrate and ammonium in this study? Models suggest that the lifetime of NO_x should be $\sim 1 - 1.5$ days 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.

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.

On page 8, line 165-167 it is stated that the raw d15N-NO₃- data was corrected to 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))?

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.

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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.”

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.

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).

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.

Supplement: please consider more recent observations of d15N-NO_x 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.

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