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Atmospheric Chemistry and Physics Discussions

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 #3

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MS No.: acp-2018-1196 Title: Isotopic Constraints on the Atmospheric Sources and Formation of Nitrogenous Species in Biomass-Burning-Influenced Clouds

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 δ15N-NH4+ in cloudwater and second of its kind to measure δ15N-NO3- in cloudwater and apply these values to determine poten-

tial 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.

Comments:

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.

The % deviation associated with the authors' source apportionment model will significantly vary depending on the range in nitrogen emission sources. The authors use δ15N-NH3 signatures of -29.1 $\pm$ 1.7‰ and -50.0 $\pm$ 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 δ15N-NH3 signatures. The authors did an adequate job when compiling the δ15N-NOx source signatures and the mixing model for NH3 would benefit from a similar approach.

The authors dismiss fossil fuel combustion (vehicles and power plants) as an emission source in this study region when discussing contribution to atmospheric NH3 but argue for its significance in this region when discussing NOx source apportionment. For NH3: "Although fossil-fuel combustion, urban waste, and natural soils also represent poten-

tial sources of NH3, 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 NH3 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 NH3 emissions (Li et al., 2016a)." For NOx: "As was expected, biomass burning was the largest contributor (28.2 $\pm$ 2.7%), followed by on-road traffic (27.1 $\pm$ 2.2%), coal combustion (26.8 $\pm$ 3.4%), and biogenic soil (17.9 $\pm$ 3.9%). ". . ..NOx 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 NOx 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 NH3 concentration have been linked to traffic and the authors contribute a significant amount of NOx to vehicles. Also, the authors mention "ultra-low emissions" techniques when referring to NOx contributions and these techniques would include SCR technology in coal combustion plants that lead to NH3 emissions. The authors should clear up their arguments in this section so there aren't contradictory statements or so the readers understands why the arguments seem contradictory.

Line 125: Additional inorganic ion concentration measurements are mentioned. Was NO2- also measured? If so, was the concentration significant compared to NO3-. It will also be measured in the isotope analysis and will contribute to the δ15N-NO3- value reported. Was NO2- removed before δ15N-NO3- analysis?

Line 197: State the significance of the correlation using p-value. The authors don't refer to the very strong correlation coefficient between NO3- and NH4+ although this

could help argue for the similar primary source (BB).

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

Line 207: Are these δ15N averages concentration-weighted? The weighted average would be a better representation of the overall source contribution.

Line 223: The discussion comparing δ15N- 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., fogwater values.

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?

Line 250: The authors discuss equilibrium fractionation but do not address the kinetic fractionation that is predicted to have an opposite fractionation effect (ε = 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 δ15N data.

Line 268: When taking into account the literature range and overlap of fertilizer and livestock waste emission δ15N-NH3 values and the fact that both sources originate from source pools (waste and fertilizer N) with similar δ15N 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?

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?

References:

Elliott, E.M., Yu, Z., Cole, A.S. and Coughlin, J.G., 2019. Isotopic advances in understanding reactive nitrogen deposition and atmospheric processing. Science of The Total Environment, 662, pp.393-403.

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Vega, C.P., Mårtensson, E.M., Wideqvist, U., Kaiser, J., Zieger, P. and StrÖm, J., 2019. Composition, isotopic fingerprint and source attribution of nitrate deposition from rain and fog at a Sub-Arctic Mountain site in Central Sweden (Mt Åreskutan). Tellus B: Chemical and Physical Meteorology, pp.1-19.

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