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Comment on acp-2022-419

Anonymous Referee #2

Referee comment on "Quantifying the importance of vehicle ammonia emissions in an urban area of northeastern USA utilizing nitrogen isotopes" by Wendell W. Walters et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-419-RC2, 2022

This study presented very interesting results on the ammonia and ammonium concentrations and isotopic compositions at an urban site, highlighting the importance of urban ammonia emission to the regional atmospheric composition. The year-long observation provides valuable information for evaluating the ammonia emission inventory which is currently under strong debate. In addition, this paper presented detailed observation about the isotopic compositions of both NH3(g) and NH4(p), emphasizing that the isotopic fractionations between these species are significant and highly variable. In general, this manuscript is well written and easy to follow. However, some part of the discussion could use a little bit more clarification. I suggest a minor revision.

Lines 246-248: as you mentioned in the previous section, pNH4 is highly correlated with nitrate and sulfate aerosols in the atmosphere, meaning the partitioning between NH4 and NH3 should be mostly controlled by the atmospheric composition. In another word, the amount of pNH4 should be determined by multiple factors, such as the total emission of NHx, NOx and SO2 concentration in the atmosphere, and maybe water content. So, simply based on the observation that pNH4 concentration are similar among these sites, I would not argue "[pNH4+] may be more regional representative than [NH3] due to its extended atmospheric lifetime relative to NH3".

Figure 1a: for such a small figure, perhaps it is better if you can only show the sites discussed in this figure and remove places like Boston and New Haven as they are not talked about in this paper.

Lines 286-299: I would recommend a more detailed discussion here as it presents interesting results of the isotopic fractionation between the two species, at least moving Figure S2 into the main text and discuss a little bit more about why the seasonal cycle occurred.

I would argue against the role of R4 in explaining the variable isotopic fractionation. NH3 has a very high pKa (9.26), and aerosol water is usually acidic (at least pH<8), so in aqueous aerosols, NH3(aq) is almost non-existent, almost 100% NH4+. So, only R2 and R3 should be important, and the equilibrium fractionation factor should be somewhere between 31 to 34 permil. The lower isotopic fractionation in the summer may be more related to 1) lower isotopic fractionation factor observed by Kawashima and Ono (2019), and 2) a more important role of kinetic isotopic fractionation.

Line 400: discussing how the relative contribution change by season without considering the change in concentration can be misleading. For example, the relative contribution of vehicle emission is lower in the summer and higher in the winter – however once you fold in the concentrations of NHx, you can see the contribution of vehicle emission (in ug/m3) may not change that much. I would recommend the authors revise Figure 8 to include the concentration information, so it is clear for the readers to see the variations of each source, as a sanity check.

In addition, using the source appointment results, the authors should discuss how it is different from NEI2014. It is clear that our observation showed strong discrepancy vs. emission inventory. For example, emission inventory suggests higher emission in the winter, considering lower mixing height winter, the NHx concentration should be significantly higher than summer, but we see the opposite trend. Isotopic evidence should at least tell us if the seasonal trends of the sources in the emission inventory agree with our observations.