

We appreciate the helpful comments and feedback from Reviewer #1, which have helped improve our manuscript. We have carefully considered the recommendations of Reviewer #1 to shorten the manuscript, which was also suggested by Reviewer #2. To this end, we have shortened our introduction, moved the description of our denuder and filter preparation, handling, and extraction protocol to the supplement, and removed our discussion of the elevated vehicle [NH₃], which distracted from our main point of characterizing the isotopic composition of vehicle derived NH₃. Overall, these changes have shortened the manuscript by ~150 lines.

Reviewer #1 also pointed out that perhaps we should consider reporting the results of passive vs active collection for $\delta^{15}\text{N}(\text{NH}_3)$ characterization in a separate manuscript. We respectfully disagree with this suggestion and feel that this is an important result for this study, as pointed out by Reviewer #2. Specifically, this comparison helps put our measurements into context with previous studies that have reported very different $\delta^{15}\text{N}(\text{NH}_3)$ values derived from vehicle emissions. Our observation that a large $\delta^{15}\text{N}(\text{NH}_3)$ offset exists between active and passive sampling techniques reconciles differences in our measurements with previous literature reports and highlights the need for the reactive nitrogen isotope community to consider using robust, laboratory and field verified techniques shown to be accurate in characterizing $\delta^{15}\text{N}$. This is an incredibly important point that cannot be stressed enough. Therefore, we did not remove our comparison between active and passive NH₃ collection in the revised manuscript. Below we provide a point-by-point response to specific comments raised by Reviewer #1.

Specific Comments:

Comment: I think the title is somewhat misleading. You don't really constrain the vehicle ammonia emissions using N isotopes. The title as is suggests a source apportionment study, which is not the case. It should read: "Characterizing the isotopic composition of ammonia from vehicle plumes" or something like that.

Response: Thank you for this comment. We have changed the title in the revised manuscript to "Characterizing the Spatiotemporal Nitrogen Stable Isotopic Composition of Ammonia in Vehicle Plumes" to reflect the content of this work better.

Comment: Your abstract makes no mention of the comparison between active and passive collection techniques, which supports my previous point that you could remove that from your manuscript and have it in a separate paper. It reads as a sideways discussion in the present format and distracts the reader from the main findings. I am not saying it is not interesting and useful, just that it could be its own paper.

Response: We appreciate the comment, but we believe this comparison is an important finding and should be included in this manuscript, which is also aligned with the opinion of Reviewer #2. Thank you for pointing out that we did not mention this comparison in our abstract, which was an oversight, and also brought up by Reviewer #2. In the revised manuscript, we have changed the abstract to draw attention to the comparison between active and passive sampling, adding the following sentences, "Our recommended vehicle $\delta^{15}\text{N}(\text{NH}_3)$ signature is significantly different

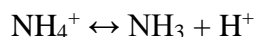
from previous reports. This is due to a large and consistent $\delta^{15}\text{N}(\text{NH}_3)$ bias of approximately -15.5 ‰ between commonly employed passive NH_3 collection techniques and the laboratory-tested active NH_3 collection technique.” Additionally, we have restructured our section headings to help reduce the comparison between active and passive sampling to read as a sideways discussion. We have removed the subsection division in the results and discussion section between (1) Active NH_x Collection using a Denuder-Filter Pack and (2) Comparison Between Active and Passive Collection. We feel that this reduces the complicated subsection grouping and creates more streamlined results and discussion sections in the revised manuscript.

Comment: L37-39: I thought soil acidification is mostly due to HNO_3 . How can an alkaline compound like NH_3 cause acidification?

Response: There are numerous processes in which NH_3 can cause soil acidification that has been well-documented, including plant uptake and assimilation, nitrification, and NH_3 volatilization. The uptake and assimilation of NH_4^+ results in a net release of H^+ as NH_4^+ is deprotonated during this process. Nitrification associated with the oxidation of NH_4^+ to NO_2^- and subsequent oxidation to NO_3^- will also lead to the net release of H^+ :



Finally, during NH_3 volatilization, the pH of the soil surface will decrease as H^+ is released when NH_4^+ is converted to NH_3 :



To clarify how $\text{NH}_3/4$ can lead to acidification we have revised the sentence in question to the following, “Deposition of NH_3 and its secondary product, particulate ammonium (pNH_4^+), have critical environmental consequences, including soil acidification (via plant assimilation, nitrification, and NH_3 volatilization), eutrophication, and decreased biodiversity in sensitive ecosystems,” and included an additional reference that does an excellent job reviewing soil acidification (Bolan, N.S., Hedley, M.J., White, R.E. Processes of soil acidification during nitrogen cycling with emphasis on legume based pastures. *Plant and Soil*, 134(1), 53-63, 1991.

Comment: L47: Helpful if you could indicate here NH_3 atmospheric lifetime.

Response: Thank you for pointing this out. We have revised this sentence to include the NH_3 atmospheric lifetime to the following, “While agricultural activities are known to dominate the emission of NH_3 , accounting for over 60 % of the global inventory (Bouwman et al., 1997), there are significant spatiotemporal variabilities due to its short atmospheric lifetime that is on the order of a several hours to a day (Paulot et al., 2016) and its multitude of emission sources (e.g., Hu et al., 2014).”

Comment: L48-49: The Templer group in Boston has more recent studies highlighting large vehicle contributions to urban NH₃ budget. Check out the Decina et al., papers, particularly relevant since you drove to Boston for this study

Response: We have added the following reference to the end of this sentence in the revised manuscript, “Decina, S. M., Templer, P. H., Hutyra, L. R., Gately, C. K. and Rao, P.: Variability, drivers, and effects of atmospheric nitrogen inputs across an urban area: emerging patterns among human activities, the atmosphere, and soils, *Sci. Total Environ.*, 609, 1524–1534, 2017.”

Comment: L61: Can you quantify here the contribution as a % at the global scale?

Response: To help shorten the manuscript, we have removed this sentence in the revised manuscript. We point out that vehicle emissions are an important urban source of NH₃, “In urban regions, vehicle derived emissions have been identified as a major NH₃ source (Decina et al., 2017; Gong et al., 2011; Li et al., 2006; Livingston et al., 2009; Meng et al., 2011; Nowak et al., 2012; Sun et al., 2014, 2017). Recently, vehicle NH₃ emissions have been suggested to be a key driver of N deposition in urban and urban-affected regions (Fenn et al., 2018).”

Comment: L65: Once again, check the work lead by the Templer group in Boston about N deposition in urban areas

Response: Thank you for this comment. We have included additional references to Decina et al., 2017 and Decina, S. M., Hutyra, L. R. and Templer, P. H.: Hotspots of nitrogen deposition in the world’s urban areas: a global data synthesis, *Front. Ecol. Environ.*, 18(2), 92–100, 2020.

Comment: L66-67: how are “fuel-combustion” and “vehicle” source different? Isn’t the latest included with the first?

Response: The original use of “fuel-combustion” was to refer to stationary fuel-combustion, such as electricity and heating generation. To improve clarity, we have changed “fuel-combustion” to “stationary fuel-combustion” in the revised manuscript.

Comment: L90-91 Didn’t you just say that these techniques were shown to not accurately capture the $\delta^{15}\text{N-NH}_3$, based on work by Skinner et al.,? This seems contradictory.

Response: Thanks for the comment, and we have removed this sentence in the revised manuscript.

Comment: L. 158: How long is the inlet line?

Response: No inlet sampling line was used for the employed denuder-filter pack (ChemComb Speciation Cartridge), as the cartridges were directly exposed to ambient air as stated in section 2.2, “The samplers were directly exposed to ambient air without the use of an additional inlet tubing to prevent the loss of NH₃.” The inlet described in Line 158 of the original manuscript refers to the air inlet of the ChemComb Speciation Cartridge, where ambient air is first introduced into the sampler. This piece is approximately 4 cm long, which has been indicated in the revised manuscript in Section 2.2, “The PTFE coated air inlet (~4 cm).”

Comment: L.209: Did you characterize the potential inlet loss, and induced fractionation on NH₃, to see if it was indeed negligible?

Response: Thank you for pointing this out, as we also feel that it is very important to consider potential inlet losses of reactive species to accurately characterize isotopic compositions, which had been previously largely ignored. In a previous study, we have conducted extensive laboratory experiments to document such potential sampling artifacts (Walters, W.W., Hastings, M.G. Collection of ammonia for high time-resolved nitrogen isotopic characterization utilizing an acid-coated honeycomb denuder. *Anal. Chem.*, 90, 8051-8057, 2018). We evaluated the potential of the ChemComb inlet to induce fractionation by comparing NH₃ collections with (1) honeycomb denuders housed in the ChemComb Cartridge and (2) a gas scrubbing impinger that does not have an inlet (control), in which the NH₃ line was directly scrubbed in an acid solution. We found no statistical difference in $\delta^{15}\text{N}(\text{NH}_3)$ between the ChemComb sampler and the control, suggesting that inlet loss as a potential source of $\delta^{15}\text{N}(\text{NH}_3)$ fractionation was negligible. This result is also in agreement with Koutrakis et al., 1993 that reported no evidence for significant loss of NH₃ induced via the PTFE-coated sampling inlet. We have added the following sentence to the revised manuscript in Section 2.2 to demonstrate that we have considered the potential influence of the sampling inlet on inducing $\delta^{15}\text{N}(\text{NH}_3)$ fractionation, “The PTFE coated inlet has been shown to lead to a negligible loss of NH₃ and induce insignificant $\delta^{15}\text{N}(\text{NH}_3)$ fractionation (Koutrakis et al., 1993; Walters and Hastings, 2018).”

Comment: L.214: Any chance the denuders could trap a portion of the particulate phase as well on top of the gas phase?

Response: Thank you for raising this point. Particulates do not contribute to the final measurement from the denuder extracts due to the system design of the denuder-filter pack and operation conditions. We have added the following to the revised manuscript in section 2.2 to elaborate on this point, “Briefly, ambient air is drawn into the sampler and reactive gases are removed under laminar flow conditions such that radial mixing can only be achieved via diffusion-based processes. Particulates, with their much lower diffusion velocity compared to gases, cannot migrate to the walls of the denuder during the residence time within the unit and are collected on a downstream filter pack. The samplers are also held vertically to limit the potential for gravitational settling of particles onto the denuder surfaces, such that particulates do not contribute to the denuder extract (Ali et al., 1989).”

Comment: L214: Can you give quantify your detection limits?

Response: Thank you for this comment. Limits of detection are based on off-line ion quantification as described in Section 2.3 in the revised manuscript. We have added the limit of detection (LOD) quantification for NH_4^+ , NO_2^- , NO_3^- , and SO_4^{2-} in section 2.3, “The limit of detection (LOD) of the quantified ions were no higher than 0.5, 0.2, 2.0, and 1.5 $\mu\text{mol}\cdot\text{L}^{-1}$ for $[\text{NH}_4^+]$, $[\text{NO}_2^-]$, $[\text{NO}_3^-]$, and $[\text{SO}_4^{2-}]$, respectively”. To improve the clarity of the manuscript, we have moved the sentence on Line 214 in the original manuscript to after the instrumentation LOD was discussed in the revised manuscript.

Comment: L.219: pNO_3^- , but what about pNH_4^+ ?

Response: Thank you for raising this point. Nylon filters will quantitatively capture pNO_3^- but a significant fraction of pNH_4^+ will volatilize off this type of filter (see Walters, W.W, Blum, D.E., Hastings, M.G. Selective collection of particulate ammonium for nitrogen isotopic characterization using a denuder-filter pack sampling system, *Anal. Chem*, 91, 7586-7594, 2019 & Yu, X., Lee, T., Ayres, B., Kreidenweis, S.M., Malm, W., Collett, J.L. Loss of fine particulate ammonium from denuded nylon filters. *Atmos Environ*, 40, 4797-4807, 2006). However, a backup acid-coated filter will quantitatively capture any volatilized pNH_4^+ (Walters et al., 2019). We note that we had originally planned to quantify the inorganic anions collected on the filters in all measurement campaigns, which is why we planned to utilize both Nylon and citric acid coated filters. However, we found the extracted anion concentrations to be below our detection limits, such that this data was not reported for the stationary and mobile US measurements. If quantification of pNH_4^+ is the main goal (for concentration or isotopic analysis), a single acid-coated filter downstream from an acid-coated denuder should suffice, as we have pointed out in Walters et al., 2019.

We clarified this sentence in the revised manuscript to the following, “However, due to potential loss of semi-volatile NH_4NO_3 , all subsequent campaigns utilized a Nylon filter (Cole-Parmer, 0.8 μm pore, 47 mm diameter) which has been shown to collect and retain pNO_3^- quantitatively (Yu et al., 2005). A significant fraction of pNH_4^+ collected on denuded Nylon filters may volatilize (Yu et al., 2006), such that a backup acid-coated (5 % citric acid (w/v) in water) cellulose filter (Whatman, 8 μm pore, 47 mm diameter) is used to capture any volatilized NH_3 from the collected particles and/or NH_3 breakthrough during conditions of denuder saturation (Walters et al., 2019).”

Comment: L.241: What do you use ethanol for?

Response: This was used to wet the hydrophobic Teflon filter surface. We have clarified this sentence in the revised manuscript, “The PTFE filters were pre-wetted with 500 μL of ethanol to wet its hydrophobic surface before extraction.” We note that this text was moved to the Supplement (Text S1) in the revised manuscript to shorten the manuscript length.

Comment: L.380: Does it mean that the urban background NH₃ has the isotopic composition of vehicle emissions?

Response: Thank you for this comment. I think concluding that urban background $\delta^{15}\text{N}(\text{NH}_3)$ is the same as vehicle emissions based on wind direction analysis at the near-highway stationary site would be incorrect since the measurement location is near a major NH₃ emission source. We have pointed this out in the revised manuscript, “Overall, the $\delta^{15}\text{N}(\text{NH}_3)$ values were not found to be significantly different when the monitoring site was upwind or downwind of I-95, with averages of 7.6 ± 1.4 ‰ (n=3) and 7.1 ± 1.8 ‰ (n=51), respectively (p>0.05), which is likely due to the proximity of the sampling location to airmasses significantly influenced by vehicle emissions.”

Comment: L.395-401: I understand that you can't estimate f(NH₃) accurately, but why can't you calculate the concentration of pNH₄⁺ here? Were the Nylon filters also saturated? There is not mention of that aspect it, and it should be expanded on.

Response: The Nylon filters were likely not “saturated”, but pNH₄⁺ collected on Nylon filters are subject to significant volatilization, as we have mentioned in section 2.2. Thus, we cannot quantitatively determine the NH_x speciation as pNH₄⁺ extracted from the Nylon filter likely contains a negative artifact. The extracted pNH₄⁺ extracted from the acid-coated filter represents both NH₃ breakthrough due to denuder saturation as well as some component of pNH₄⁺ volatilization. We have further clarified why we can't quantitatively determine pNH₄⁺ in section 3.2 of the revised manuscript, “Thus, our NH_x measurements are expected to be accurate, but there could be uncertainty in the NH_x speciation, because the NH₄⁺ extracted from the acid-coated denuder and Nylon filter will have a low bias due to denuder saturation and pNH₄⁺ volatilization, respectively, and NH₄⁺ extracted from the acid-coated filter will derive from both NH₃ breakthrough and NH₃ volatilized from the Nylon filter.”

Comment: L.409: An introduction sentence about what ISORROPIA is would be nice.

Response: In the revised manuscript, we have further elaborated on ISORROPIA as followed, “NH_x speciation was also estimated using ISORROPIA, which is a gas-aerosol equilibrium partitioning model (Fountoukis and Nenes, 2007; Nenes et al., 1998).”

Comment: L.421: I think it would be useful and interesting to provide, maybe in the SI, the isotopic composition for each component, especially the nylon-collected pNH₄⁺. And maybe expand on the different isotopic compositions of NH_x and pNH₄⁺, if such is the case (and I expect it to be).

Response: Thank you for this comment as this is an interesting point and one of the original goals of attempting to collect and speciate between NH₃ and NH₄⁺ simultaneously. However, due to our

NH_x speciation problems in the tunnel measurements from NH₃ denuder saturation (as we have well-documented in section 3.2), it is impossible to relate the NH₄⁺ extracted from the acid-coated denuder, Nylon filter, and acid-coated filter to their atmospheric component due to numerous sampling artifacts. Therefore, we do not think it would be a good idea to discuss the δ¹⁵N(NH₄⁺) from the varying sampling media and attempt to relate them to NH₃ and pNH₄⁺, and this was the reason we presented the results in section 3.2 as δ¹⁵N(NH_x). As requested, we have included a figure in the Supplement (Fig. S6) that shows the varying δ¹⁵N values of NH₄⁺ extracted from the acid-coated denuder, Nylon filter, and acid-coated filter in the revised manuscript. In section 3.2 of the revised manuscript, we added the average δ¹⁵N values of the varying sampling media, “The measured δ¹⁵N from NH₄⁺ extracted from the acid-coated denuders, Nylon filters, and acid-coated filters averaged 6.0±5.6 ‰ (n=21), 1.0±10.7 ‰ (n=21), and -20.0±10.1 ‰ (n=21) (Figure S6).” Additionally, we note, “These δ¹⁵N differences to some degree reflect differences in the δ¹⁵N of ambient NH₃ and NH₄⁺ but are difficult to interpret due to the ambiguity in NH_x speciation.” Since we have strong evidence that we captured 100% of NH_x, but did not accurately speciate NH_x, we focus our discussion in the text on δ¹⁵N(NH_x).

Comment: L.431: Section title should be revised; it is the same as the previous section title

Response: Thank you for pointing this out. We have provided the correct subtitle name, “Mobile On-Road NH₃ Survey in Northeastern US” in the revised manuscript.

Comment: L.481: Please recall here what are elevated NH₃ concentrations.

Response: Thank you for this comment. In the revised manuscript, we removed our discussion of the elevated vehicle [NH₃] to reduce the manuscript length and to draw attention to our δ¹⁵N results, which is the main focus of this work.

Comment: L.521-523: Maybe recall that your f(NO₃) is approximate in this case.

Response: Thank you for pointing this out. We believe Reviewer #1 is referring to f(NH₃) and not f(NO₃), and have included that the f(NH₃) in our tunnel measurements were an approximation in the revised manuscript, “The temporal tunnel variability is not likely to be driven by f(NH₃) partitioning influences as the estimated f(NH₃) was not found to be significantly different between periods the tunnel was open or closed (p>0.05), indicating a significant change in NH₃/pNH₄⁺ partitioning did not occur during these periods.”