RC3 of "Measurement report: Evolution and distribution of NH3 over Mexico City from ground-based and satellite infrared spectroscopic measurements"

Reviewer 2

General Comments

This study aims to constrain the spatial and temporal distribution of total ammonia columns in the Mexico City Metropolitan Area (MCMA) using ground-based FTIR spectrometers (from two sites) and satellite-based IASI observations. The study finds meaningful differences between the two surface sites (particularly in the diurnal cycle), illustrates the spatial heterogeneity in NH3 column concentrations within the MCMA using IASI data, and highlights annual NH3 trends across both datasets. The study also uses a back-trajectory cluster analysis to suggest a large portion of the measured NH3 is local and urban in nature, with significant contributions from non-agricultural sources. The study is well-written and highlights important conclusions, namely the need for a re-evaluation of NH3 sources in the MCMA region. It is a useful contribution to the literature and provides a basis for more targeted work in this region. That said, the paper provides a somewhat limited discussion of a few key methods and conclusions that are central to its interpretation. With this in mind, I provide the following comments below and recommend that these issues be addressed prior to publication in ACP.

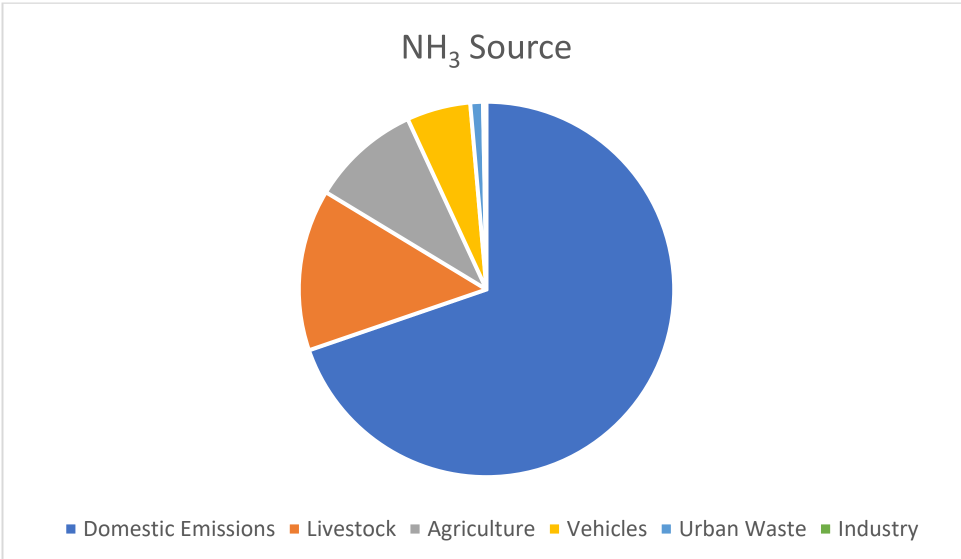
The authors would like to thank the reviewer for this positive review and all the suggestions to improve this work. We address each comment below and in the revised manuscript.

Specific Comments

Impact of Human Emissions

The authors allude to the importance of human emissions in the region (even providing a back-of-the envelope estimate). However, based on this very estimate, human emissions appear to be 3 orders of magnitude lower than the total regional NH3 flux. It thus seems unlikely that these sources are 'meaningful', but they are presented in this study as being an important underappreciated source. The authors also discuss the importance of local and urban sources multiple times in the study, citing human emissions as one of these sources. However, given the relatively small contribution of human emissions to the total flux, it stands to reason that there are other 'main' urban and local sources that should be prioritized over human emissions in order to develop accurate inventories. It would thus be a very useful contribution if the authors could quantitatively or qualitatively prioritize the relative importance of these underappreciated sources (fires, waste treatment, humans, pets, etc.) and discuss how their estimates differ from the current inventory estimates.

Response: We found an update of the inventory for 2018 (SEDEMA, 2021) and there were some changes in the different sources, with the main difference in the "area sources". They reported 46931 tonnes of NH_3/yr, with 0.3% of NH_3 emissions in Mexico City come from "point sources" such as industry, 5.5% from "mobile sources" such as vehicles, and 94.2% from "area sources" including urban waste (1.09%), agriculture (9.44%), livestock (13.92%), domestic emissions (69.73%), and controlled fires (0.01%). As described in the previous sentence, the domestic emissions category was implemented as the most significant contributor to NH_3 sources in Mexico City, and the percentage attributed to agriculture and livestock also increase significantly, in agreement with this work. Given the information presented in this measurement report, it is not possible to specifically and quantitatively assign the relative importance of each one of the underappreciated sources, however, as the updated emissions inventory presented, domestic emissions, including the emissions from domesticated animals, are a significant contributor to NH_3 and are becoming more relevant as can be observed in the pie chart below. In Mexico, the estimated number of dogs and cats in the whole country is around 23 million and 70% are homeless (GACETA: LXIV/1PPO-56/86584, 2022). The authors believed that the fires are another NH_3 source that is still underestimated in the inventory, as was shown with the Altzomoni enhancement. Further improvements in the estimated emissions are still needed.



We implemented this new information in the revised manuscript by updating the percentages as well as the references below.

GACETA: LXIV/1PPO-56/86584: https://www.senado.gob.mx/64/gaceta_del_senado/documento/86584, last access: 2 September 2022.

SEDEMA Secretaría del Medio Ambiente de la Ciudad de México: Inventario de Emisiones de la Zona Metropolitana del Valle de México 2018. Dirección General de Gestión de la Calidad del Aire, Dirección de Proyectos de Calidad del Aire. Ciudad de México. URL: http://www.aire.cdmx.gob.mx/descargas/publicaciones/flippingbook/memoria-inventario-emisiones-2018/memoria_inventario_emisiones_2018.pdf, 2021.

IASI retrieval and validation

Since the IASI retrieval scheme does not produce averaging kernels, could the authors expand the discussion in Section 2.2 to include a more in-depth overview of the underlying uncertainties and sensitivity constraints in the retrieval? Could the authors also please provide a more detailed description of the ANNI that estimates NH3 column concentrations based on the various input parameters (e.g., a list of all the parameters considered, the uncertainties associated with each parameter, the uncertainties associated with the ANNI transformation itself). A brief discussion in the main-text of the differences in the dynamic range of the data used to train the ANNI vs. the data inputs in this study would also be helpful. Could the authors also please build o n the above request to expand on potential reasons for the IASI column underestimation relative to the surface instruments? This is important in order to appropriately interpret the broader IASI spatial patterns.

Response: We expanded Section 2.2 by adding more information regarding the ANNI-NH_3 retrieval process, including more details about the input parameters, sensitivity, uncertainty, and previous comparisons with ground-based FTIR measurements. The potential reasons for the IASI column underestimation were addressed in the response for RC1 and are also included in the revised manuscript as follows:

"The IASI-NH_3 retrieval products are based on Artificial Neural Networks (ANNI) that link the Hyperspectral Range Index (HRI), a calculated dimensionless index that represents the amount of NH_3 in the column, to other input parameters such as temperature, pressure, water vapor profiles, and parametrized vertical profiles of NH_3 to derive the NH_3 total column. The algorithm maps the HRI to the NH_3 total column using a trained neural network; the uncertainty of each NH_3 column can be estimated by the propagation of the input parameters' uncertainties. However, large HRI values (more than 3 σ) are associated to a confident detection of NH_3 (Van Damme et al., 2014, 2017; Whitburn et al., 2016). The current spectral range for the retrieval process is set to 812-1126 cm^{-1} to increase the sensitivity of NH_3 and reduce interferences (Van Damme et al., 2021). The retrieval scheme does not produce averaging kernels, however, previous studies comparing the IASI-NH_3 product with ground-based FTIR measurements have demonstrated good agreement (e.g., Dammers et al., 2016,2017; Lutsch et al., 2019; Tournadre et al., 2020; Yamanouchi et at., 2020). In addition, under conditions of high NH_3 and when the thermal contrast is large, IASI has maximum sensitivity to NH_3 in the boundary layer (Clarisse et al., 2010). An error estimate is provided with each individual IASI observation; for this work IASI observations with errors less than 100% were used. IASI's average detection limit for NH_3 under large thermal contrast is about 3 ppbv, and can be as low as 1 ppbv under conditions of well-mixed NH_3 throughout a thick boundary layer (Clarisse et al., 2010)."

We added the reference below.

Lutsch, E., Strong, K., Jones, D. B. A., Ortega, I., Hannigan, J. W., Dammers, E., Shephard, M. W., Morris, E., Murphy, K., Evans, M. J., Parrington, M., Whitburn, S., Van Damme, M., Clarisse, L., Coheur, P. F., Clerbaux, C., Croft, B., Martin, R. V., Pierce, J. R., and Fisher, J. A.: Unprecedented Atmospheric Ammonia Concentrations Detected in the High Arctic From the 2017 Canadian Wildfires, J. Geophys. Res. Atmos., 124, 8178–8202, https://doi.org/10.1029/2019JD030419, 2019.

Back-trajectory analysis

Please briefly expand Section 2.3 and Section 3.3 to provide more information on the specifics of the back-trajectory cluster analysis such that it can be reproducible by a third-party reader of this paper. Please also provide a brief discussion on how sensitive your results were based on the number of clusters assumed, clustering technique, etc.

Response: We expanded Sections 2.3 and 3.3 by adding more information about the methodology and the results, as follows:

"Section 2.3

To determine the primary sources of NH_3 measured at the UNAM station and to assess the dominant atmospheric transport pathways during the events with the largest hourly means of the NH_3 columns in the time series, trajectory cluster analysis (Reizer and Orza, 2018) was applied. Eight-hour back-trajectories were selected to capture the air masses passing over the MCMA. Using the UNAM station as the receptor, back-trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2015; Draxler et al., 1997) at different altitudes above the UNAM station level (2280 m.a.s.l.). The HYSPLIT model can be run online at the following link https://www.ready.noaa.gov/HYSPLIT.php. The wind data used for the back-trajectories was derived from the NCEP North American Mesoscale (NAM) analysis product at 12 km and 1 hour of spatial and temporal resolution respectively. The cluster analysis is an embedded routine in HYSPLIT and is based on the Ward's agglomerative hierarchical clustering algorithm (Ward, 1963). Finally, the Total Spatial Variance (TSV) method (Draxler et al., 2021), included in HYSPLIT, was used to fit the number of clusters that represent the data.

Section 3.3

A cluster analysis was applied using eight-hour back-trajectories 100 m above UNAM station to identify the main transport pathways for air masses arriving at this station that correspond to the highest average hourly NH_3 total columns (Figure 7d). The 100 m cluster was considered the most representative because NH_3 is mostly concentrated near the surface. The TSV method was able to represent the primary trajectories at 100 m above UNAM with only three clusters"

We added the reference below.

Ward, J: Hierarchical Grouping to Optimize an Objective Function. Journal of the American Statistical Association; 58, 301, 236-244, doi:10.1080/01621459.1963.10500845, 1963.

Minor Comments

Line 71: 'come from'

Response: Done in RC1

Line 74: Suggest restructuring this sentence to – 'The inventory also attributes a meaningful NH3 contribution (%) to a range of different population activities (e.g., X,Y,Z) and feces from domesticated animals'

Response: Done

Line 89: '.. , all classified as ..'

Response: Done in RC1

Line 178: 'The entire period …' – Please restructure this sentence

Response: We have modified this sentence in the revised manuscript as: "The average NH3 total columns for the entire period (1.46± 0.64 $x10^{16}$ molecules/cm^2 at UNAM and 1.87 ± 2.40 $x10^{15}$ molecules/cm2 at Altzomoni) are listed and …"

Line 206: '.. conversion to ammonium, as was observed …'

Response: Done

Line 314: ‘Comparisons between the seasonal and temporal variability of NH3 over …’

Response: Done

Line 317: ‘However, IASI-NH3 shows a …’

Response: Done

Line 318: ‘The temporal evolution is represented using ..’

Response: Done

Line 320: ‘even in Altzomoni, except for 2013 which was …’

Response: Done

Line 321: ‘averaged’

Response: Done

Line 322: ‘molecules/cm2), yields a 62% increase in Mexico City over the course of a decade, in agreement with the trend of …..’

Response: Done and complemented with a comment in RC1 A “, yields a 62 % increase over a decade for Mexico City, in agreement with”

Line 332: Please restructure for clarity

Response: We have modified this sentence in the revised manuscript as:

“However, the individual back-trajectories that comprise the red cluster (the thin black lines in Figure 7d), indicate that most of the NH_3 detected at UNAM comes from a variety of local sources and does not originate exclusively from NH_3-enriched air masses transported from the enhancement region to the northeast observed in Figures 7a to 7c.”