Interactive comment on "Atmospheric ammonia (NH3) over the Paris megacity: 9 years of total column observations from ground-based infrared remote sensing" by B. Tournadre et al.

Review of Tournadre et al. in AMT

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Atmospheric ammonia (NH3) over the Paris megacity: 9 years of total column observations from ground-based infrared remote sensing

Anonymous Referee #1

Referee: As I mentioned in my previous review, the paper presents an extensive and highly usable data record of FTIR-NH3. Without any doubt it will be very helpful for future air quality evaluation and model and satellite validations. There are not many locations in the world with such an extensive and long term NH3 record, and only a few with instruments with the capability to measure the total column of NH3 at high temporal resolution. The revised paper shows a lot of improvement and I only have a few minor comments and suggestions.

Authors: First of all, we would like to thank the referee for his/her constructive and useful comments which served us as a guideline for compiling and improving the second revised version of the manuscript. All minor comments and edits are addressed as detailed below.

Minor comments.
1. Page 6, line 16, as you mention the fits are pretty good with a stdev of 2%. The green arrows point out the main absorption features of ammonia. These however also show that at those line positions the fit is the worst. While partially a result of the lower resolution, a similar thing was seen in Dammers et al., 2015, Fig.3. Potentially add a small discussion point about the uncertainty in the line parameters. The authors already sort of remark this on Page 11 Line 9.

Authors: Clarified.
The PROFFIT retrieval algorithm is a well-recognized method within the NDACC community and the present work on NH$_3$ is based on the HITRAN 2008 spectroscopic database. For the intensities of the relevant lines of the ν_2 band used in our retrieval, an uncertainty index of 4 is generally given (i.e. between 10% and 20%). A paper by Down et al. 2013 compares several experimental sources for NH$_3$ intensities in the region 770-1200 cm^{-1} with a consistency better than ~4%. The best theoretical total band intensity for the ν_2 band is reported as 2.26 × 10^{-17} cm^{-1}/(molecule cm^{-2}) as compared to the total band intensity of 2.21 × 10^{-17} cm^{-1}/(molecule cm^{-2}) in HITRAN 2014, i.e. a difference of 2 % consistent with the uncertainty quoted previously. This systematic uncertainty is certainly contributing to a small fraction of the retrieval uncertainty on the NH$_3$ column given in the

present paper. The residuals of the fit as seen in Figure 2 and Figure 3 are smaller than 2 % and some residuals do present some correlation with NH_3 lines. However, the effect is within the stated uncertainty of the retrieved column amount. Several effects are intermixed in the simultaneous retrieval of NH_3 together with CO_2 and H_2O, the lines of which have to be fitted properly. Uncertainty on air-broadening coefficients of NH_3 and their temperature dependence and also the line-mixing effects should have also a contribution. So the residuals shown in the figures are to be considered as typical and can vary from one fit to the other.

To have a compromise about these complex question concerning spectroscopy, we propose these updated sentences (Page 6, Lines 31-34 and Page 7, Line 1) in the second revised version. "The total errors are dominated by the combination of uncertainties in the spectroscopic parameters (including also the interfering species), the noise in the spectra and the hypotheses on the retrieval (*a priori* profile of NH_3, forward model uncertainties). They are comparable to those estimated by Dammers et al. (2015) for a high resolution ground-based station at Bremen (Germany). In complement to these, according to a review paper on NH_3 spectroscopic parameters (Down et al., 2013) the uncertainty of 20% on line intensities is probably a worst case estimate."

2. Page 6, Line 29-33. If I understand correctly the fit improves by 60%! (Or do the authors mean that the fit mismatch increase by 60 %?) When using the sloped apriori profiles, and shows an increase in the NH3 abundances. What is the reason for not switching to these aprioris? Even though the seasonal/temporal patterns do not change, this offset/ratio will change the comparison with IASI.

Authors: Clarified. This a priori profile is just one possibility and is empirically chosen. We are currently developing a new version of the OASIS-NH_3 retrieval algorithm. Among the different changes, we will change the a priori profile in order to reduce both the spectral fit and the retrieval error (as compared to IASI data for example). We are currently testing several a priori profiles, issued by chemistry-transport models for example, in order to find the best one. These changes will lead to a new version of the OASIS dataset that will be presented in a future publication.
The following sentence in the current version of the paper mentions this coming work (Page 12 Lines 20-21) "Tests of different a priori NH_3 profiles will also be performed for reducing the spectral residuals between measured and simulated spectra while providing accurate retrievals of NH_3 abundances."

3. Page 8, Line 5-6, maybe remove the "possible" as it's well-known that temperature increases volatility and in many cases seems the reason for higher NH3 temperatures in summer.

Authors: We prefer to keep the adjective "possible" because we would like to be careful with ammonia volatility since not only temperature can impact its abundance, such as the soil properties (soil pH,...) or the properties of the fertilizer applied (organic manure or mineral fertilizer)…

4. Page 9, line 11-12. Excluding negative values will bias the IASI "mean" high, especially in the lower range of the concentrations where the sensitivity is a strong factor. As it's a statistical retrieval, negative values are somewhat to be expected when sensitivity is low, and should average out towards zero (in case of no ammonia).

Authors: Clarified. We understand the fact that IASI data are derived from a statistical approach providing in some cases negative values. However, we chose to exclude all

values with too high uncertainty (>100%) and without physical meaning such as negative ones. We prefer to avoid highly uncertain retrievals. The large majority (98%) of NH_3-IASI retrieval corresponding to small NH_3 abundances are screened by the retrieval error filter. Therefore, excluding negative values has a negligible effect on the comparison of IASI and OASIS datasets.

This aspect is clarified in the revised manuscript (Page 9 Lines 22-24) as "The majority of IASI retrievals corresponding to weak NH_3 abundances are screened out by the relative error criterion, thus the exclusion of negative values has a negligible effect in the comparisons.".

5. Page 9, Lines 19-24. What are the matching mean total columns and relative differences? Most of the values (Fig 6.) seem to be in the range of 0-1.5x1016 molecules cm-2. So 0.78 would be around 50%. Considering IASI's and the FTIR products uncertainty that's about the range we expect for this lower range of total columns. Add some discussion on how these values compare to the uncertainties of the products. Similarly add a short reflection to the conclusions/perspectives.

Authors: Clarified. We think that there is a misunderstood about the range of mean bias between NH3-IASI and NH3-OASI. Indeed in the last version, we mentioned that "The average of the absolute differences is -0.78 10^{15} molecules cm^{-2}, with a root mean squared error (RMSE) equal to 4.86 10^{15} molecules cm^{-2} and a standard deviation of error (STDE) equal to 4.84 10^{15} molecules cm^{-2}". So mean bias is -0.08 10^{16} molecules cm^{-2} which represents 10% of the average of the values (Fig 6.) in the range of 0-1.5 10^{16} molecules cm^{-2} and 4 time less than NH_3-OASIS total retrieval errors of about 20% to 35%. Concerning the matching mean total columns: the average of NH3-IASI is 0.70 10^{16} molecules. cm^{-2} and that for NH3-OASIS is 0.78 10^{16} molecules.cm^{-2}.

So, to avoid the confusion and for consistency, we put each NH_3 total column in 10^{16} molecules.cm^{-2} in the second revised version of the manuscript and added the following statement (Page 10 Lines 2-4) "The mean absolute difference is a factor 10 smaller than the average values of the NH_3 abundances (0.78 10^{16} and 0.70 10^{16} molecules cm^{-2} respectively for OASIS and IASI) and also smaller than OASIS total retrieval errors (20 to 35 %)."

6. Page 12, line 6-7. The manuscript already describes the use/test of a different (sloped) a-priori. Shortly reflect on those results?

Authors: Agreed. We have added the additional sentence in the second revised version of the manuscript to mention those tests (Page 12 Lines 21-23) "First tests with a different a priori profile for NH_3 show a significant reduction of the residuals between the radiance spectra measured by OASIS and those simulated by PROFFIT."

Minor edits
1. Page 2, Line 5, remove "potentially" as its well established what the sources are.
Authors: Agreed. The adverb "potentially" has been suppressed.

2. Page 2, line 6, add a reference for the sources.

Authors: Agreed. Four references already cited in the text have been included related to ammonia sources and sinks.
(Galloway et al., 2003; Behera et al., 2013; Chang et al., 2016; Van Damme et al., 2018).

3. Page 2, Line 21, potentially add a reference to the recent paper by Dammers et al which includes lifetime estimates for NH3 point sources.
Authors: Added. The suggested reference has been included.

4. Page 2, line 26, add a reference for the 50% PM2.5 statement.
Authors : Added. In order to state that ammonium salts can represent 50% of PM2.5, we have added (Page 2 Line 27) the three following references (Bressi et al., 2013; Petit et al., 2014; 2015).
So we have added two of them in the bibliography:
Bressi, M., Sciare, J., Ghersi, V., Bonnaire, N., Nicolas, J. B., Petit, J.-E., Moukhtar, S., Rosso, A., Mihalopoulos, N., and Féron, A.: A one-year comprehensive chemical characterisation of fine aerosol ($PM_{2.5}$) at urban, suburban and rural background sites in the region of Paris (France), Atmos. Chem. Phys., 13, 7825-7844, https://doi.org/10.5194/acp-13-7825-2013, 2013.
Petit, J.-E., Favez, O., Sciare, J., Crenn, V., Sarda-Estève, R., Bonnaire, N., Močnik, G., Dupont, J.-C., Haeffelin, M., and Leoz-Garziandia, E.: Two years of near real-time chemical composition of submicron aerosols in the region of Paris using an Aerosol Chemical Speciation Monitor (ACSM) and a multi-wavelength Aethalometer, Atmos. Chem. Phys., 15, 2985-3005, https://doi.org/10.5194/acp-15-2985-2015, 2015.

5. Page 2, line 26-31, while it's interesting to point out uncertainties in the emissions in the Paris regions, the paper no longer discusses the PM2.5 concentrations, and this part can potentially be shorted or removed from the manuscript.
Authors: Agreed. In the second revised version, as required by the referee, the last sentence on PM2.5 has been withdrawn. We kept the other sentences to highlight the need to have accurate ammonia measurements for improving the air quality models.

6. Page 3, line 19: "current or until very recent space-based NH3 data… etc. add a short line as an introduction how the satellites measure (also Infrared based), and link to the first to show that it's possible: Beer et al., 2008.
Authors: Added. A suggested introduction has been included as follows (Page 3 Lines 21-22) with a link to Beer et al. paper "A few observations were first reported from space using an advanced IR sounder (Beer et al., 2008) which enables retrievals of atmospheric NH_3". Then we have added this reference in the bibliography.

7. Page 4, Line 2, add some references of studies that used FTIR to validate satellite measurements.

Authors: Added. Different references have been included concerning validation of satellite products with ground-based IR instruments for different trace species (Griesfeller et al., 2006; Strong et al., 2008; Buchholz et al., 2017) and also recently for ammonia (Dammers et al., 2016, 2017).

8. Page 4, Line 20-21: The part about section 3.3 needs to be rewritten as it still point to the previous version of the paper.

Authors: Agreed. We apologize for this error in the introduction with the former section 3.3. A consistent sentence with section 3.3 has been added in the second revised paper (Page 4 Lines 26-27) "Finally, in Section 3.3, a few tests are performed using a NH_3 profile retrieval scheme applied to OASIS spectra with a Tikhonov-Phillips regularization, showing the vertical sensitivity to NH_3 provided by OASIS measurements. "

9. Page 5, Line 27, mention the green arrows in the figure.

Authors: Added. We have mentioned in comma (Page 5 Line 32) that the strong spectral signatures of ammonia are pointed out by green arrows in Figures 2 and 3 "The strong spectral signatures of ammonia (pointed out by green arrows in Figures 2 and 3). We also added one sentence about green arrows in each caption of Figures 2 and 3.

10. Page 11 Line 2, add "a" between "FTIR instruments" and "moderate spectral resolution".

Authors: Added. The suggested change has been included.

References

Dammers, E., McLinden, C. A., Griffin, D., Shephard, M. W., Van Der Graaf, S., Lutsch, E., Schaap, M., Gainairu-Matz, Y., Fioletov, V., Van Damme, M., Whitburn, S., Clarisse, L., Cady-Pereira, K., Clerbaux, C., Coheur, P. F., and Erisman, J. W.: NH3 emissions from large point sources derived from CrIS and IASI satellite observations, Atmos. Chem. Phys., 19, 12261–12293, https://doi.org/10.5194/acp-19-12261-2019, 2019.

Beer, R., Shephard M. W., Kulawik, S. S., Clough, S. A., Elder-ing, A., Bowman, K. W., Sander, S. P., Fisher, B. M., Payne, V.H., Luo, M., Osterman, G. B., and Worden, J. R.: First satel-lite observations of lower tropospheric ammonia and methanol, Geophys. Res. Lett., 35, L09801,doi:10.1029/2008GL033642,2008.