# Interactive comment on “Atmospheric ammonia ($NH_3$) 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: 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 paper is easy to read but could use some restructuring and editing of the text. The sections on the FTIR retrieval and the comparison with IASI are interesting, but section 3.3 seems added on and could be removed without too much impact to the manuscript. For example PM2.5 is barely mentioned in the introduction. While comparing FTIR-NH3 to pm2.5 is interesting, a more complete analysis and interpretation using a model will be needed if the authors want to keep the section.

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 the revised version of the manuscript. All comments are addressed as detailed below. We agree with the restructuration of the paper, editing and withdrawing section 3.3 about particles, as done in the revised manuscript (RM) of the paper.

**Major comments.**

1. The retrieval fits are performed over a very wide window. While the authors claim that this is needed, have tests been performed for smaller windows? Past results with the more high resolution FTIR have shown problems with very wide windows, which was one of the reasons to use smaller micro windows (Dammers et al., 2015). The FTIR used by the UNAM team in Mexico City is also a VERTEX and they have reported succesfull fits with smaller windows (Dammers et al., 2017). A comparison of Figure 2 and 3 (maybe merge the figure?) shows that the strongest signatures in the residual correlate well with the location of the strongest NH3 lines. While the fits with an SD of 2% are excellent, compared to the weak absorption feature of NH3 this can still result in a large offset of

the NH3 total columns. If possible add a % based fit and take a look at the % deviation around the NH3 lines (maybe mark the locations like in Figure 2).

Authors: Clarified. The choice of using large microwindows aims at retrieving gas abundances from the intensity contrast between the target gas signature and the surrounding continuum. If the spectral range for the determination of the continuum is too limited, the ability of correctly reconstructing the target gas amount is likely decreasing, while the result that fit residuals are reduced when the spectral window is restricted to lesser number of points is not necessarily linked to a better quality of the retrieval of the gas abundance. In former times, computational burden was enforcing the use of narrow microwindows in practical work, with the hardware available today this constraint is less relevant. The approach of using narrow microwindows is still used in some cases. More recent fit strategies developed for example for TCCON apply rather broad microwindows for their primary target species (molecular oxygen, carbon dioxide, and methane). This choice can induce problems also if the background continuum over the entire selected spectral window used cannot be modelled down to the spectral noise level for spectroscopic or instrumental reasons (see discussion on this matter in Kiel et al, 2016). Obviously the optimum strategy is to include an empirical smooth background continuum fit, which preserves as much information on the contrast between target spectral lines and surrounding continuum, while still allowing for compensation of background continuum variation beyond our rigorous spectral modelling capability. We decided to maintain the broad microwindows, but the referee's comment induced some further testing on the applied background fit, as a result from this investigation, we decided to fit an empirical background with four degrees of freedom instead of the linear background we used before (the background fitting model used by PROFFIT is approximately equivalent to cubic splines).

In the RM, we didn't merge Figures 2 and 3 because we thought it is not necessary for clarity but we marked the NH3 line locations with arrows close to the fits. We clarify this issue on large microwindows as follows (lines 21-23, page 5) "The choice of using large microwindows aims at retrieving $NH_3$ abundances from the intensity contrast between the target gas signature and the surrounding continuum. We account for this last one by fitting an empirical background polynomial function with respect to wavelength, with four degrees of freedom.".

Kiel, M., D. Wunch, P. O. Wennberg, G. C. Toon, F. Hase, and T. Blumenstock: Improved retrieval of gas abundances from near-infrared solar FTIR spectra measured at the Karlsruhe TCCON station, Atmos. Meas. Tech., 9, 669-682, doi:10.5194/amt-9-669-2016, 2016

Referee: In the text the authors mentioned that HITRAN 2008 was used. Dammers et al 2015 and most of the NDACC FTIR teams used HITRAN 2012 in combination with a few CO2 line adjustments. This can potentially improve the spectral fits.

Authors: Clarified. We also exchanged the linelists by HITRAN 2012 (which slightly but consistently improves fit quality) but prefer to avoid additional ad-hoc changes on line parameters. This is clarified in the RM as (lines 8-9 page 6) "which does not include ad-hoc changes on line parameters added in HITRAN 2012".

2. The PROFFIT retrieval seems to be based on a scaling method instead of a full physical retrieval (although I can be mistaken, but as far as I can see it is not mentioned in the text) therefore the choice of the NH3 a priori profile shape is quite essential. The authors mention in section 2.3 (this should be moved into 2.2 probably) that they use a climatological ammonia profile. Does this profile vary monthly? Further-more, can some more information (or a figure with the shape) be provided on how it compares to profiles used in other studies/products?, for example the profile used in the IASI-NNv2.X product (Van Damme et al., 2017), the CrIS-NH3 product (Shephard and Cady-Pereira, 2015), and the NDACC-FTIR retrievals (Dammers et al., 2015).

Authors: Clarified. We confirm that a scaling factor retrieval was used (in Section 2.2) for all the NH3-OASIS time series and mention it in the text (line 15, page 10 in the new Section 3.3). We also added information about the MIPAS a priori profile in Section 2.3 (line 19 page 6) of the revised paper.

As mentioned by Van Damme et al. (2014) the choice of profile shape in a column based retrieval can easily vary the results by a factor 2. A similar result seems to be found by the authors as they mention on P6/line 22-24 with a relative different of +20%. What makes the MIPAS profile optimal in this sense? Did the other tested a priori produce worse fits? Authors: A different a priori profile, that is close to those used in NDACC-FTIR retrievals for Bremen and Lauder, was also tested and described in Section 2.3 of the revised paper. While it reduces the spectral fits by 60%, it shows very similar temporal variability with relative differences which are of the same order of magnitude than the ammonia total column error (only +20% relative difference for ammonia total columns retrieved with the new a priori). In that case, results did not vary by a factor of 2.

This is clarified in the RM as (lines 29-33 page 6) "Using this a priori profile reduces the mean squared difference between measured and simulated spectra by about 60%. However, both retrievals with homogenous and sloped a priori profiles show rather similar results, with the same relative evolution in time and differences in absolute terms in the order of magnitude of the total column retrieval error (the use of the sloped a priori profile increases the retrieved NH3 abundances by 20% with respect to that using an homogenous a priori)".

3. The averaging kernel or observational operator are an essential piece of information but are completely missing in the text. The OASIS-NH3 instrument should be superior in its sensitivity to the lower boundary layer compared to satellite measurements. A figure and short discussion of the (total column) averaging kernel can go a long way in helping us understand where the sensitivity of the retrieval lies and why there are differences compared to IASI.

Authors: Agreed. as required by both referees, a paragraph (new section 3.3) and additional Figure 10 about NH3-OASIS sensitivity were added in the revised paper (lines 14-30, page 10): "3.3 Vertical distribution of sensitivity of the NH3-OASIS approach

As mentioned in section 2.2, the NH3-OASIS dataset presented in Figs. 4, 8 and 9 is derived from a scaling factor retrieval scheme whose state vector only has one scalar value associated with the NH3 abundance. Therefore, this approach does not provide an averaging kernel matrix as optimal estimation or Tikhonov schemes do, but only a single value of degrees-of-freedom (DOF) without any information on the vertical distribution of the retrieval sensitivity. In order to estimate the vertical sensitivity to NH3 provided by OASIS measurements, we have performed a few tests using a NH3 profile retrieval scheme applied to OASIS spectra with a Tikhonov-Phillips regularization (as similarly implemented for ozone profiles by Viatte et al., 2011). Figure 10 presents examples of averaging kernel diagonals for NH3 profile retrievals based on OASIS spectra measured on 13 March 2014, at different times of the day and thus different solar zenith angles (SZA). We remark that OASIS measurements may provide information on the abundance of NH3 located around 500 m, with maximum sensitivity for smaller solar zenith angles corresponding to thicker air masses (occurring in the early morning or late afternoon). These OASIS averaging kernel diagonals peak at similar altitudes as those estimated by Dammers et al. (2017) for a high spectral resolution Fourier Thermal Infrared spectrometer at the Pasadena site (peaking around 940 hPa, thus approximately at 600 m above sea level). These altitudes are typically located within the atmospheric boundary layer during springtime and summer, at mid-latitudes where most of the atmospheric $NH_3$ column variability is expected to occur. Additional tests (not shown) using different spectroscopic databases (HITRAN 2008 and HITRAN 2012) change very little the estimation of the sensitivity of the OASIS retrieval."

4. This brings us to the comparison of OASIS-NH3 to IASI-NH3. The authors reference the results in Dammers et al., 2015 but that study focussed on an older version of IASI, IASI-LUT. Dammers et al., 2017 reports the results using a more recent version of IASI-NH3, IASI-NNv1 (Figure A1). The slope of S=0.96 for that product is a lot better than the reported S=0.6 for the older product. Van Damme et al., 2018 also state that the most recent version of IASI-NN shows even better results and a lower bias for higher total columns, which would mean we can expect a better comparison. One of the reasons can be found in the absence of the use of an averaging kernel to adjust the IASI total columns to the same playing field. The current comparison can be seen as incomplete as its uncertain where the sensitivity of both instruments lie, and potentially we're comparing the NH3 in the mixing layer to half the boundary layer or the effect of a different a priori (shape).

Authors: Clarified. The differences in the sensitivity to NH3 between OASIS and IASI retrievals are clarified in the manuscript. We believe that these differences explain the underestimation of IASI with respect to OASIS, and therefore in a slope of 0.73 to 0.8. This is clarified as (lines 7-9 page 10) "This underestimation may be explained by IASI's lower sensitivity to surface ammonia concentrations, due to the coarse spectral resolution and weak thermal contrast between the surface and the lower troposphere and to the spatial heterogeneity of ammonia within the IASI footprint".
The results of the comparison between the FTIR at Bremen and the new IASI data is mention in the RM as (lines 16-18 page 9) "and NH3-IASI neural network version: R = 0.67 and slope of 0.96 for 802 coincidences from several ground-based FTIR stations (Dammers et al., 2017)".

5. The authors show a initial comparison of OASIS-Nh3 to nearby pm2.5 measurements. While this is interesting it feels somewhat out of place. PM2.5 is barely mentioned in the introduction and only pops up at the end of section 3. Furthermore, most facts are referenced from other studies and the improvement that this study brings, both the high temporal resolution of the FTIR and the vertical total column, are not really used in the analysis. If the authors want to keep the section on PM2.5, an improved

comparison will be needed, with for example the help of a model for interpretation. Thein review study by Viatte et al., 2019 for example, shows similar results with a more extensive analysis of the Ile de France region.

Authors: Agreed. in the revised version, the section 3.3 on PM2.5 has been withdrawn, as NH3 diurnal variation observed by OASIS and its impact on ammonium particles will be analyzed in details in a future separate paper. Only two sentences in the conclusions are kept in order to inform the readers (lines 31-33 page 11 and lines 1-7 page 12) "Since ammonia is a major precursor of PM2.5 over Europe, as shown by e.g. Fortems-Cheiney et al. (2016) during a European spring haze episode, we expect a link between high ammonia concentrations and inorganic salts, such as ammonium nitrate. That period during late 2012 winter (documented by Petit et al. (2014)), was probably the most polluted month of March of the last ten years in Paris region (Petit et al., 2017) with the highest NH3-OASIS total columns in the period 2009-2017 over the Paris region. The link between ammonia concentrations and the formation and volatilization of fine particles such as ammonium salts is beyond the scope of this paper and will be discussed in a future study on the diurnal analysis of total and surface ammonia measurements from Paris region during a high spring pollution event.". Also, the previous Figure 10 was suppressed.

6. Something that the author could add instead (but not essential to the text!) is an initial analysis of the diurnal variability, which should not take too long to produce. The authors did excellent work on getting such a long data series and have around 5000 measurements spread over 9 years, which accounting for overcast days would mean around 5-10 measurements a day. Spread out every 15 minutes this must show some diurnal variability of the NH3 total column concentrations (for example split by season) and I for one would be very interested to see that instead of a comparison to PM2.5.

Authors: Clarified. We confirm, as asked by Referee #2, that analysis of the NH3 diurnal variation which can be observed by OASIS using a long data series with measurements spread out every 10 minutes in case of continuous sunny conditions, is dedicated to a next separate paper, during spring pollution events over Paris region. See the citation in previous comment.

**Minor comments and edits.**

1. Split section 2 in 2.1 for FTIR, 2.2 with a description of IASI, 2.3 with a description on PM2.5. this will improve the readability and is easier for reference of retrieval characteristics, uncertainties etc.
Authors: Clarified. as section 3.3 on PM2.5 has been withdrawn, we decided not to change section 2 and only describe in details the ground-based remote-sensing measurements.

2. Maybe move section 3.2 up before the comparison with IASI. First completely describe the dataset and variabilities before moving to the comparison with IASI. This can help in the interpretation of any differences between the two.

Authors: Agreed. As suggested by referee #1, section 3.2 moved up before the comparison with IASI helping to interpret any differences between the two remote-sensing data series. Numbers of Figures have consequently been modified.

3. Section 3.1: The authors choose a collocation criteria of 15 km and 30 min while the study that they compare their results with (Dammers et al., 2016) uses 50 km and 90 minutes. Do your results change a lot when using those criteria? Using wider criteria should increase the number of observations, as only 50 measurements out of 5000 initial measurements remain.
Authors: Clarified. We tested a co-location criteria of 50 km and 90 minutes as proposed by Referee #1. We observed that, using these wider criteria, the number of observations is obviously increasing but not so different correlation is found. This is clarified in the RM as (lines 10-11 page 9): "Tests with wider coincidence criteria (50 km and +/- 90 minutes) do not show significant differences (similar correlations are obtained despite a greater number of coincidences)."

**Some smaller edits:**

1. P2 L21, there have been several studies recently covering the lifetime of NH3. If possible reference Lutsch et al., 2016, Van Damme 2018 and Dammers et al., 2019.
Authors: Agreed. More recent studies covering the lifetime of NH3 have been included as mentioned.

2. P3. L 13: add some examples of networks with high temporal resolution measurements (for example LML in the Netherlands, Volten et al., 2013).
Authors: Agreed. The established EMEP and LML networks have been included in the revised paper with the correspondent references.

3. P3. L20: the correct reference for CrIS would be Shephard and Cady-Pereira 2015.GOSAT also has a Nh3 product: Someya et al., 2019.
Authors: Corrected and completed. The correct reference for CrIS (also mentioned by Referee 2) has been added in the revised version and also the GOSAT reference.

4. P3. L28-31, not important for the intro, move to dataset section.
Authors: Agreed. As suggested, lines concerning the precision of NH3-IASI data are moved to dataset section 3.2.

5. P8. L20-21. Although I somewhat agree with the statement, the underestimation can also be caused by other sources. Also the averaging kernel/observational operator has not been applied therefore the results can not be directly compared to the results in Dammers et al., 2016. Explore some further causes of the underestimation (a priori choice) or show some supporting proof that the sensitivity is the cause (which should somewhat be resolved by the use of the averaging kernel).
Authors: Agreed and clarified. As detailed in the answers above, we have performed an analysis of the sensitivity of the $NH_3$-OASIS retrieval (new section 3.3) and also added as possible reason for the underestimation of IASI with respect to OASIS the heterogeneity of $NH_3$ within the IASI footprint. On the other hand, the IASI approach is based on neural networks and it does not provide averaging kernels nor uses a priori profiles that could be compared with those from OASIS.

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