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 #2

Referee: In situ data records of NH3, especially over a long period, are very rare. This paper presents a nine year dataset of NH3 total column measurements from an FTIR located in a suburb of Paris. This is a valuable resource for validating NH3 satellite data and for determining the relationships between satellite and surface measurements. That the data is from one of the largest cities in Europe makes it especially relevant, given that the fraction of the world's population living in urban areas is increasing significantly, with all the attendant air quality problems. The paper provides both a mostly very clear description of the data and the results of a comparison against the IASI ANNI-NH3-v2.2R product, along with analyses of the seasonal variability captured by the FTIRNH3 and correlations between the FTIR data and measured PM2.5 amounts.

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.

Referee: I have many of the same comments posted by Reviewer#1, and will refer to them in the next few paragraphs.

Comment 2: The authors need to confirm that the PROFIT retrievals only provides a scaling factor.

Authors: Clarified. We confirm that a scaling factor retrieval is used (in Section 2.2) for all the NH3-OASIS time series and state it clearly in the text (in Section 2.2, lines 11-12 page 6) "A scaling factor of a climatological vertical profile of NH3 is adjusted in order to minimize the difference between measured and simulated spectra, so the degree of

freedom for the ammonia retrievals is 1". We also added information about the MIPAS a priori profile in Section 2.3 of the revised paper (lines 19-20 page 6) "A climatological a priori profile of NH3 that assumes fixed vertically homogenous NH3 concentrations (0.1 ppb) in the troposphere is taken from the MIPAS project (Remedios et al., 2007).".

As the first reviewer stated, this type of retrieval can be strongly influenced by the a priori profile shape; therefore showing a plot of the selected a priori profile and comparing it against the a priori profiles used in the papers listed is an excellent idea. The authors did test a different a priori, but did not state which one and without the plot we suggest it is not possible to ascertain how different it is from the selected a priori.

Authors: Clarified. A different a priori profile, that is closed to those used in NDACC-FTIR retrievals for Bremen and Lauder, was also tested and described in Section 2.3 of the revised paper (lines 27-29 page 6) "Another a priori was tested with higher concentrations of NH3 in the atmospheric boundary layer (with fixed concentrations up to 900 m then decreasing NH3 concentrations until 4 km).". While it reduces the spectral fit residual by 60%, it shows the same variabilities 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.

Comments 3 and 4: here I partially disagree with the first reviewer: if the PROFFIT algorithm does not retrieve a profile it cannot provide an averaging kernel (AK); the IASI product also does not generate an AK for each observation, though some AKs are available (see van Damme et al., 2014). The authors could use an optimal estimation algorithm (possibly the FORLI code (van Damme et al., 2014)) on a subset of the data in order to obtain an AK that could provide at least a sense of the vertical sensitivity of the OASIS-NH3, then compare it to the IASI AK. I leave it to the editor to decide if this exercise is required. It would certainly be useful for interpreting the results.

Authors: Agreed and test performed. In order to estimate the full averaging kernels matrix, we have implemented a profile retrieval approach and tested it on a subset of the data. This corresponds to the new section 3.3 and the new Figure 10 (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."

Comment 5: The section on PM2.5 is poorly written and not very informative; it should either be expanded and rewritten or eliminated.

Authors: Agreed and withdrawn. In the revised version, the section 3.3 on PM2.5 has been eliminated because NH3 diurnal variation observed by OASIS and its impact on ammonium particles will be analyzed in details in a next 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." As a consequence, the previous Figure 10 was suppressed.

Comment 6: Here I strongly agree that a section on diurnal variability observed by OASIS-NH3 would be very interesting and useful, since there are large uncertainties in the diurnal cycle. However, it appears the authors will present this analysis in a separate paper. Can they confirm?

Authors: Clarified. We can confirm 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.

Comment on Figure 7: Can the authors explain why the slopes increase with increasing dmin, until about 120 km, then decrease again?

Authors: Clarified. We can assume that until about 120 km, we include, step by step, areas close to agricultural regions such as Picardie (Amiens city) and Champagne (Reims city) with higher NH3-IASI amounts as seen in the map: Global ammonia point sources as seen by IASI satellite instruments, provided by L. Clarisse and M. Van Damme in https://www2.ulb.ac.be/cpm/NH3-IASI.html (Clarisse et al., 2019; Van Damme et al., 2018). Beyond 120 km, we would expect more horizontal heterogeneity of the NH3 sources and abundances and therefore the slope decreases accordingly. This is clarified in the RM (lines 9-12 page 10) as "The regression slope increases until 120 km for dmin and decreases beyond. This might be linked to the fact that the main surrounding agricultural regions (e.g. Picardie and Champagne) are located until about 120 km away from OASIS, and therefore NH3 sources (Clarisse et al., 2019; Van Damme et al., 2018), and these sources are more heterogenous beyond this distance.".

Minor edits and comments (suggested changes are in bold)

Referee: Page 3 Lines 13-16:...infrared remote sensing from satellites.... These methods measure over large footprints rather than at points, but are noticeably....

Authors: Clarified. The statement is meant for remote sensing techniques in general, not only from space.

Current space-based NH3 data are available from the IASI...

Authors: Corrected. The suggested change has been included.

Referee: Line 19:...Partnership, Shephard and Cady-Pereira, 2015, Dammers...

Authors: Reference added. This paper has been added in page 3 as proposed, and in the references.

Line 28:
The authors should contact the IASI team for their estimates of the IASI-NH3 precision and uncertainty.

Authors: Agreed and done. So based on NH3-IASI data from the ANNI-NH3-v2.2R baseline version, used for the comparison, we calculated average and median errors which are 89% and 60%, respectively. These values are now given in Section 3.2 of the revised paper (lines 24-28 page 8) "Average and median errors of these satellite measurements used in this study are 89% and 60% respectively, which are coherent with uncertainties for most of the NH_3-IASI data listed in Van Damme et al. (2014 and 2017), because of small absorption features by ammonia observed with the relatively coarse spectral resolution of IASI as compared to ground-based instruments.

Referee: Page 4 Line 9: . . . located in the Paris suburbs...

Authors: Corrected. The suggested change has been included.

Line 15: Is there any rejection criterion based on weak signals ?

Authors: Clarified. There is no criterion based on weak signals, but on signal-to-noise ration lower than 30, (lines 12-14 page 6) “As the radiance values are rather small below 1000 cm^{-1}, a quality criterion was introduced selecting only spectra with a signal-to-noise ratio higher than 30”

Page 6 Line 13: . . . spectra, so the degree of freedom for the ammonia retrievals is 1.
Authors: Corrected. The suggested change has been included.

Referee: Line 23: . . . differences represented by the error bars...

Authors: Corrected. We have added another expression to clarify our argument.

Referee: Page 7 Line 7: Our analysis is the first comparison of surface NH3 measurements from a megacity with NH3-IASI data and covers seven years of data.

Authors: Added. The suggested sentence has been included.

Referee: Line 26: omit colocation criteria, as it has just been cited above.

Authors: Corrected. The colocation criteria have been suppressed.

Referee: Page 8 Line 6: . . . centered on the OASIS . . .

Authors: Corrected. The suggested change has been included.

Referee: Line 8: . . . the 15 km width of the rings was chosen to minimize the impact of ammonia spatial variability and to maximize . . .

Authors: Corrected. The suggested change has been included.

Referee: Line 11: . . . show the number of coincident . . .

Authors: Corrected. The suggested change has been included.

Referee: Line 21: . . . between the surface and the lower troposphere and to the spatial variability of the IASI footprint.

Authors: Corrected. The suggested change has been included.

Referee: Page 9 Line 27: . . . its impact on the concentrations of fine . . .

Authors: Corrected. The sentence has been modified as follows (lines 2-3, page 12) “The link between ammonia concentrations and the formation and volatilization of fine particles such as ammonium salts “.

Referee: Page 11 Line 11: Besides lower sensitivity to the surface ammonia concentrations, spatial heterogeneity within the IASI footprint can lead to lower values.
Authors: Corrected. The suggested change has been included.

Referee: Line 13-22: These sentences required some rewriting for clarity; my suggestions are below.

This study used the 9 year OASIS-NH3 time series to focus on seasonal variability of atmospheric NH3 in the Paris region. The predominance of NH3 peaks occurring in March is particularly noticeable: all measurements above 2*1016 molecules NH3cm-2 , which corresponds to the mean of data plus one standard deviation over the springtime period (March/April/May), occur in this month, and are well correlated with manure spreading time periods (Ramanantenasoa et al., 2018).The sentence below is confusing. It’s not clear if mineral fertilizers are applied in spring or summer, and if their application contributes to the March or summer peak. Mineral fertilizers are mainly applied in Île-de-France region because there are major arable crop (especially cereals) farming areas, which could generate high ammonia concentrations under sunny conditions, when the solar OASIS measurements are performed. This study also found high summer values above 1.5*1016 molecules NH3 cm-2 ,which corresponds roughly to the mean of data plus one standard deviation over the June/July/August time period, which could be due to increased volatility of ammonia under warm meteorological conditions.

Authors: Corrected. The sentences, that needed rewriting for clarity, have been included as suggested.