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

Correspondence to: Pascale Chelin (pascale.chelin@lisa.u-pec.fr)

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 char-acteristics, 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.

References:

Dammers, E., Vigouroux, C., Palm, M., Mahieu, E., Warneke, T., Smale, D., Langerock,B., Franco, B., Van Damme, M., Schaap, M., Notholt, J., and Erisman, J. W.: Retrievalof ammonia from ground-based FTIR solar spectra, Atmos. Chem. Phys., 15, 12789–12803, https://doi.org/10.5194/acp-15-12789-2015, 2015.

Dammers, E., Shephard, M. W., Palm, M., Cady-Pereira, K., Capps, S., Lutsch, E.,Strong, K., Hannigan, J. W., Ortega, I., Toon, G. C., Stremme, W., Grutter, M., Jones,N., Smale, D., Siemons, J., Hrpcek, K., Tremblay, D., Schaap, M., Notholt, J., andErisman, J. W.: Validation of the CrIS fast physical NH3 retrieval with ground-basedFTIR, Atmos. Meas. Tech., 10, 2645–2667, https://doi.org/10.5194/amt-10-2645-2017,2017.

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 emissionsfrom 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.

Lutsch, E., Dammers, E., Conway, S., & Strong, K. (2016). Long-range Transport ofC5NH3, CO, HCN and C2H6 from the 2014 Canadian Wildfires. Geophysical ResearchLetters, (43), 8286-8297. https://doi.org/10.1002/2016GL070114.

Shephard, M. W. and Cady-Pereira, K. E.: Cross-track Infrared Sounder (CrIS) satel-lite observations of tropospheric ammonia, Atmos. Meas. Tech., 8, 1323–1336,https://doi.org/10.5194/amt-8-1323-2015, 2015.

Someya, Y., Imasu, R., Shiomi, K., and Saitoh, N.: Atmospheric ammonia retrievalfrom the TANSO-FTS/GOSAT thermal infrared sounder, Atmos. Meas. Tech. Discuss.,https://doi.org/10.5194/amt-2019-49, in review, 2019.

Van Damme, M., Clarisse, L., Heald, C. L., Hurtmans, D., Ngadi,Y., Clerbaux, C., Dolman, A. J., Erisman, J. W., and Coheur,P. F.: Global distributions, time series and errorcharacterizationof atmospheric ammonia (NH3) from IASI satellite observations,Atmos.Chem. Phys., 14, 2905–2922, doi:10.5194/acp-14-2905-2014, 2014.

Van Damme, M., Whitburn, S., Clarisse, L., Clerbaux, C., Hurtmans, D., and Coheur, P.-F.: Version 2 of the IASI NH3 neural network retrieval algorithm: near-real-time and re-analysed datasets, Atmos. Meas. Tech., 10, 4905–4914, https://doi.org/10.5194/amt-10-4905-2017, 2017.

Van Damme, M., Clarisse, L., Whitburn, S., Hadji-Lazaro, J., Hurtmans, D., Clerbaux,C., & Coheur, P. F. (2018). Industrial and agricultural ammonia point sources exposed.Nature, 564(7734), 99.

Viatte, C., Wang, T., Van Damme, M., Dammers, E., Meleux, F., Clarisse, L., Shephard,M. W., Whitburn, S., Coheur, P. F., Cady-Pereira, K. E., and Clerbaux, C.: Atmosphericammonia variability and link with PM formation: a case study over the Paris area,Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-138, in review, 2019.

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

Correspondence to: Pascale Chelin (pascale.chelin@lisa.u-pec.fr)

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.

Atmospheric ammonia (NH_3) over the Paris megacity: 9 years of total column observations from ground-based infrared remote sensing

Benoît Tournadre[1*], Pascale Chelin[1], Mokhtar Ray[1], Juan Cuesta[1], Rebecca D. Kutzner[1], Xavier Landsheere[1], Audrey Fortems-Cheiney[1**], Jean-Marie Flaud[1], Frank Hase[2], Thomas Blumenstock[2], Johannes Orphal[2], Camille Viatte[3], and Claude Camy-Peyret[4]

[1]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris-Est Créteil, Université de Paris, Institut Pierre Simon Laplace (IPSL), Créteil, France
*currently at: Centre for Observation, Impacts, Energy, Mines ParisTech, Sophia Antipolis, France
**currently at: Laboratoire des Sciences du Climat et de l'Environnement, UMR 8212, CEA/Orme des Merisiers, 91191 Gif sur Yvette, France
[2]Institut für Meteorologie und Klimaforschung (IMK), Karlsruher Institut für Technologie (KIT), Karlsruhe, Germany
[3]Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), UMR CNRS 8190, UPMC, Université Versailles St. Quentin, Institut Pierre Simon Laplace, Paris, France
[4]Institut Pierre Simon Laplace (IPSL), UPMC/UVSQ, Paris, France

Correspondence to: Pascale Chelin (pascale.chelin@lisa.u-pec.fr)

Abstract. In this paper, we present the first multi-year time series of atmospheric NH_3 ground-based measurements in the Paris region (Créteil, 48.79°N, 2.44°E, France) retrieved with the mid-resolution "Observations of the Atmosphere by Solar absorption Infrared Spectroscopy" (OASIS) ground-based Fourier Transform infrared solar observatory. Located in an urban region, OASIS has previously been used for monitoring air quality (tropospheric ozone and carbon monoxide), thanks to its specific column sensitivity across the whole troposphere down to the atmospheric boundary layer. A total of 4920 measurements of atmospheric total columns of ammonia have been obtained from 2009 to 2017, with uncertainties ranging from 20% to 35%, and are compared with NH_3 concentrations derived from the Infrared Atmospheric Sounding Interferometer (IASI). OASIS ground-based measurements show significant interannual, and seasonal variabilities of atmospheric ammonia. NH_3 total columns over the Paris megacity (12 million people) vary seasonally by 2 orders of magnitude, from approximately 10^{15} molecules cm^{-2} in winter to 10^{17} molecules cm^{-2} for spring peaks, probably due to springtime spreading of fertilizers on surrounding croplands.

1 Introduction

Ammonia (NH_3) is a reactive and volatile chemical species present in the atmosphere as a trace gas. As the main alkaline atmospheric molecule (Behera et al., 2013), it plays a major role in the formation of secondary fine particulate matter of ammonium salts and thus in particle air pollution (Seinfeld and Pandis, 2006). NH_3 is heterogeneously distributed in the atmosphere, depending on local and regional sources (potentially including agriculture, urban traffic, particle-to-gas conversion, sewage, industrial activities) and sinks (wet and dry deposition, gas-to-particle conversion).

In France, atmospheric ammonia (NH_3) is mainly emitted (more than 94%) by agricultural activities (Ringuet et al., 2016, Genermont et al., 2018) via livestock waste and urine, manure spreading and the use of synthetic nitrogen fertilizers. Other minor sources exist, including the combustion of biomass and fossil fuels as well as industrial activity. The source related to motor traffic has increased significantly in recent years, due to the increasing use of catalytic (or non-catalytic) NO_x reduction systems on light and heavy duty vehicles. These devices use an injection of urea or ammonia and can give rise to NH_3 emissions (Chang et al., 2016). The urban area corresponding to the Paris city and its suburbs is the second largest megacity in Europe with more than 12 million people. Ammonia emissions in the Paris region reached nearly 11 kilotons in 2014 of which 93% are attributed to agricultural activities, with a negligible contribution of livestock (DRIEE, 2017). The Paris megacity is located at the administrative region Île-de-France, which includes 49% of agricultural land, with particularly strong activity in the eastern half of the territory. Île-de-France agriculture is mainly dedicated to crops, in particular cereals (with a dominance of wheat), which occupy 67% of the cultivated area. This sector is described as an agricultural belt, with 59% in the Seine-et-Marne department. Urban traffic in the Paris region is estimated to be responsible for 5% of ammonia emissions and industry for 2% (DRIEE, 2017).

Atmospheric ammonia concentrations vary to a large degree during the day, since the atmospheric lifetime of NH_3 is rather short, on the order of hours to a few days (Galloway et al., 2003; Lutsch et al., 2016; Van Damme et al., 2018). Wet and dry depositions dominate the atmospheric sink of this inorganic compound. NH_3 is also a gaseous precursor of fine particulate matter (PM2.5, particles of an aerodynamic diameter less than 2.5 μm). As the main alkaline molecule in the atmosphere, it reacts rapidly with sulfuric (H_2SO_4) and nitric (HNO_3) acids in the atmosphere to form ammonium sulfate or ammonium nitrate (Behera et al., 2013). These ammonium salts may represent more than 50% of the PM2.5 fraction, during peaks of spring air pollution, periods of fertilizer application by agriculture. Concentrations of ammonium nitrate in Île-de-France in the 2009/2010 period can be simulated by the CHIMERE chemistry-transport model with only a small bias (<20%, Petetin et al., 2016). However, comparisons of the precursors' concentrations measured during the FRANCIPOL campaign (May 2010 to February 2011) show an overestimation of nitric acid and an underestimation of ammonia by the CHIMERE model (Petetin et al., 2016). These differences appear to stem in part from the uncertainties associated with ammonia emissions. They suggest large uncertainties in the emissions of the precursors of ammonium nitrate over the Paris region.

Monitoring the atmospheric concentrations of NH_3 is essential for improving air quality models, as well as for quantifying the fluxes characterizing the nitrogen cycle. The measurement of atmospheric ammonia concentrations is not subject to

regulation (in the sense of the European Directives) and is really challenging for several reasons: (i) High temporal and spatial dependence of ambient concentration levels (Allen et al. al., 1988; Sutton et al., 1998); (ii) Rapid conversion of NH_3 between gaseous, particulate and aqueous phases (Warneck, 1988); (iii) Measurement artefacts due to NH_3 reactivity with sampling and measurement systems: NH_4^+-NH_3 conversion, adsorption on surfaces, etc. (Sutton et al., 2008; Von Bobrutzki et al., 2010). This is why there are only a few measuring stations for which atmospheric ammonia concentrations are measured with a time resolution finer than a month. Most of the existing observation networks are designed to evaluate long-term trends and are therefore based on sampling techniques accumulating during several weeks (passive samplers, denuders or liquid bubblers) and off-line analysis in the laboratory.

Other in situ methods enable to estimate surface atmospheric concentrations of NH_3 (e.g. by cavity ring-down spectroscopy (CRDS) techniques (Sun et al., 2015)) or even in the lower atmosphere (airborne campaigns (Leen et al., 2013, Shephard et al. al., 2015, Sun et al., 2015)). Hourly measurements are very rare at present, and are mainly available during intensive short-term measurement campaigns and are limited to a small number of measurement sites of several established networks such as the European Monitoring and Evaluation Programme (EMEP) (EMEP/EEA, 2016) used by the French Centre interprofessionnel technique d'études de la pollution atmosphérique (CITEPA) (CITEPA, 2015) or the Dutch National Air Quality Monitoring Network (LML: Landelijk Meetnet Luchtkwaliteit) of the Netherlands (Volten et al., 2012).

An innovative and very promising alternative for monitoring atmospheric ammonia is infrared remote sensing. This approach exploits the ammonia absorption spectral signatures of thermal infrared radiation measured by Fourier transform infrared spectroscopy (FTIR) instruments. These methods are free from sampling problems and are noticeably less influenced by local sources than in situ observations. Current or until very recent space-based NH_3 data are available from the IASI sounder (Infrared Atmospheric Sounding Interferometer, onboard the Metop satellites, Clerbaux et al, 2009; Clarisse et al., 2009), TES (Tropospheric Emission Spectrometer embedded on the Aura satellite, Shephard et al., 2015, TES's mission was ended in January 2018, after nearly a 14-year career of discovery), CrIS (Cross-track Infrared Sounder embedded in the Suomi National Polar-Orbiting Partnership satellite, Shephard and Cady-Pereira, 2015 ; Dammers et al., 2017), TANSO/FTS (Thermal And Near-infrared Sensor for carbon Observation-Fourier Transform Spectrometer on the Greenhouse Gases Observing SATellite (GOSAT), Someya et al., 2019) and AIRS (Atmospheric Infrared Sounder, Warner et al., 2016, here, a grating spectroscopy instrument installed on the Aqua satellite). These measurements allow the retrieval of total columns of NH_3, vertically integrated concentrations between the Earth's surface and the top of the atmosphere. In particular for the IASI instrument, observation processing algorithms have evolved considerably in recent years (Van Damme et al 2014, 2015; Whitburn et al. 2016), a data product that we call hereafter NH_3-IASI. These currently available satellite data also feature indicators of the quality of the space-based observations and retrievals, and have been validated (Dammers et al., 2016). Even though the observations from space remain complex due to the weak absorption of this species, the availability of a global distribution of NH_3 twice a day (for example over Europe) is an important achievement.

In addition, the high-resolution FTIR solar stations of the Network for the Detection of Atmospheric Composition Change (NDACC) measure, from the ground, the total ammonia columns but are also capable of providing information on its vertical

distribution (Dammers et al., 2015). Spectroscopic measurements from the ground have been used for decades in the validation of satellite measurements. The diurnal variability is observed directly from the ground, with a temporal resolution of a few minutes. The high temporal resolution of these ground-based solar measurements can help to understand the nature of ammonia sources, especially in urban environments where there is a crucial lack of observations of this short-lived and spatially highly disperse pollutant. A better knowledge of NH_3 emissions and associated atmospheric processes thus requires extended observational networks able to assess high temporal and spatial variabilities of the atmospheric content of ammonia. Such networks are still to be built, especially in France where NH_3 measurements are extremely rare.

In this study, we present the first multi-year time series of atmospheric NH_3 ground-based measurements over a European megacity (Paris), retrieved with the moderate-cost mid-resolution OASIS (Observations of the Atmosphere by Solar absorption Infrared Spectroscopy) FTIR solar observatory located in the Paris suburbs (Créteil, France). Given its good sensitivity to surface pollutant concentrations, it has been used previously for monitoring urban pollution (tropospheric ozone and carbon monoxide) (Viatte et al., 2011; Chelin et al., 2014). A total of 4920 measurements of NH_3 total columns have been obtained between 2009 and 2017, with uncertainties ranging from 20% to 35% (one standard deviation) using the retrieval code PROFFIT (Hase et al., 2004) adapted for our medium spectral resolution and based on the NDACC stations' methodology. The data are compared with NH_3 concentrations from IASI measurements for verifying consistency with the NH_3-OASIS retrievals.

The paper is organized as follows. First, we present in detail the NH_3-OASIS data by describing the site, the retrieval strategy and uncertainties (Section 2). A comparison between the NH_3-OASIS columns and the NH_3-IASI satellite data is provided in Section 3.1, while Section 3.2 gives the atmospheric NH_3 time-series focusing on seasonal variability. Finally, in Section 3.3, we examine the correlation between atmospheric ammonia measured by OASIS and surface PM2.5 concentrations at a daily scale.

2 Ground-based FTIR NH_3 data: description and characterization

2.1 The FTIR-OASIS observatory

The OASIS ("Observations of the Atmosphere by Solar Infrared Spectroscopy", 48.79° N, 2.44° E, 56 m above sea level) observatory is located in the Paris region, which is a European megacity (12 million inhabitants) surrounded by a large rural region and relatively flat terrain (Figure 1). It routinely performs solar absorption measurements since 2009 under clear-sky conditions, using a mid-spectral resolution spectrometer (BRUKER Vertex 80, with a spectral resolution of 0.06 cm^{-1}, maximum optical path difference of 12 cm). In order to carry out air quality research, we have assessed the capability of a medium-resolution FTIR solar absorption spectrometer for monitoring pollutants, especially O_3 and CO. We have demonstrated that OASIS is able to continuously monitor tropospheric ozone over Créteil with good accuracy and sufficient information content (Viatte et al., 2011). A 5-year analysis of ozone in the lower troposphere and carbon monoxide has also

been made (Chelin et al., 2014). Given the moderate cost and compactness of OASIS, deployment of analogous systems nearby or in large megacities might be useful in support of satellite and air quality studies in other regions of the world.

The observatory comprises an automatized cupola (Sirius 3.5 "School Model" observatory, 3.25 m high and 3.5 m in diameter) in which the upper part (a dome equipped with a mobile aperture) rotates to track the sun. The alt-azimuthal solar tracker in OASIS is the A547N model manufactured by Bruker Optics, using bare gold-coated mirrors which are less sensitive to corrosion and pollution than the original Al mirrors. Infrared solar absorption spectra are nominally recorded on a deuterated-triglycine-sulfate (DTGS) detector using a potassium bromide (KBr) beamsplitter, in order to cover the spectral region from 700 to 11000 cm^{-1} (0.9 to 14.3 μm) without any optical filter, so that column abundances of many different atmospheric trace gases can be retrieved simultaneously.

2.2 Ground-based NH_3 retrievals

The ammonia spectral signatures used in this study are observed in the 10.6 μm spectral region and belong to the ν_2 vibrational band (Dhib et al., 2007). To achieve a sufficiently high signal-to-noise ratio, each spectrum is produced by co-adding 30 scans at the highest spectral resolution, resulting in one interferogram recorded over a period of approximately 10 min. Each coadded interferogram is Fourier-transformed for obtaining a spectrum without further numerical apodization (i.e. unapodized/boxcar apodization). Carbonyl sulfide (OCS) cell measurements are regularly performed to verify the alignment of the instrument (Chelin et al., 2014). Ammonia absorption lines from the ν_2 vibrational band are also used for satellite-based estimates (Clarisse et al., 2009; Whitburn et al., 2016) and in the first retrievals of ammonia from high-resolution ground-based NDACC FTIR stations (Dammers et al., 2015). Atmospheric transmission spectra from two spectral microwindows are used in this work (926.3-933.9 cm^{-1} and 962.5-970 cm^{-1}). They are slightly larger than those for the Bremen and Lauder NDACC stations (Dammers et al., 2015) because of the coarser spectral resolution of OASIS atmospheric spectra (0.06 cm^{-1}). 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. The main interfering species in these windows are H_2O, CO_2, O_3, which are simultaneously retrieved together with NH_3. Minor interfering species are HNO_3, SF_6, C_2H_4, and CFC-12. Figure 2 shows an example of a measured spectrum on the 21 March 2012 with contributions of all main species, here calculated using the spectral atlas of Meier at al. (Meier et al., 2004). The strong spectral signatures of ammonia are seen in both microwindows, even when observed with the medium spectral resolution of the Vertex 80 spectrometer. Note that the NH_3 concentrations of this day were particularly higher than on average, resulting in very strong NH_3 features.

The retrievals are performed using the PROFFIT 9.6 code (Hase et al., 2004) widely used by the NDACC community to retrieve trace gases from high-resolution FTIR measurements, but adapted for the medium resolution. The software is capable of including spectral channeling in the fitting process and for the estimation of error budgets. Channeling is caused by the presence of optical resonators as e.g. filters or windows, in the measurement beam. Here, the ability of the code to

handle spectral channeling in the fit is of relevance, because we intend to quantify a minor absorber and some channeling was detected in the measured spectra. For this purpose, the channeling frequency is determined from a Fourier transform of the residual of an auxiliary fit. A neighbouring spectral section containing few absorption lines and wide enough to encompass many cycles of the channeling signal is selected for this purpose. For the chosen frequency, a sine and a cosine amplitude are subsequently included in the fit of the NH_3 target windows. Daily temperature and pressure profiles for the meteorological variables are obtained from the Goddard Space Flight Center NCEP (National Center for Environmental Prediction). For radiative transfer calculations, profiles at 44 altitude levels, from 50 m up to 70 km, are set. Spectroscopic data are taken from the HITRAN 2008 database (which does not include ad-hoc changes on line parameters added in HITRAN 2012, Rothman et al., 2009), except for CO_2 lines from the HITRAN 2012 database (Rothman et al., 2013). As for satellite retrievals and in consistency with the moderate spectral resolution of OASIS, we derive total columns of NH_3 from each radiance spectrum. A scaling factor of a climatological vertical profile of NH_3 is adjusted in order to minimize the difference between measured and simulated spectra, so the degree of freedom for the ammonia retrievals is 1. 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, as measured between 960 and 990 cm^{-1} covering lines of a weak CO_2 band. Figure 3 shows a measured spectrum (black line), the corresponding simulated spectrum (red line) and the difference between observation and simulation (blue line) in both microwindows. The fits are excellent with a standard deviation of 2% in both microwindows.

2.3 A priori profiles and uncertainty

A climatological a priori profile of NH_3 that assumes vertically homogenous NH_3 concentrations (0.1 ppb) in the troposphere is taken from the MIPAS project (Remedios et al., 2007). The a priori profiles of the interfering species (H_2O, CO_2, O_3) are taken from the Whole Atmosphere Community Climate Model (WACCM version 6) (Chang et al., 2008). We consider the posteriori errors calculated by PROFFIT 9.6. This calculation is based on the error estimation method by Rodgers (2000). For the uncertainty in the NH_3 line parameters, we assume values as stated in the HITRAN 2008 database (Rothman et al., 2009). We assume a conservative value of 20% for the integrated intensities and of 10% for the pressure broadening coefficients. The total errors are dominated by uncertainties in the spectroscopic parameters, and are equivalent to those estimated by Dammers et al. (2015) for a high resolution ground-based station at Bremen (Germany). Table 1 summarizes the results of total errors according to the different ammonia total columns, which vary from 20% to 35%. Another a priori was tested with higher concentrations of NH_3 in the atmospheric boundary layer (with fixed concentrations up to 900 m then decreasing NH_3 concentrations until 4 km). 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 NH_3 abundances by 20% with respect to that using an homogenous a priori).

3 Results

3.1 Seasonal variability of NH_3 ground-based data

Figure 4 shows the multi-year time series of NH_3 total columns derived from FTIR ground-based OASIS measurements retrieved from all the 4920 available spectra in 2009–2017, resulting from 234 measurement days. Table 2 gives a summary of statistics of the retrieved NH_3 measurements versus the four seasons. Individual measurements with an overall mean total column of 0.84 10^{16} molecules NH_3 cm^{-2} and a standard deviation of 0.86 10^{16} molecules NH_3 cm^{-2} indicate a large variability in the observations. They highlight peak abundances in spring (March-April-May), more precisely in March. The amplitude of the spring peaks varies throughout the years, with maxima in March 2012, reaching about 9 10^{16} molecules NH_3 cm^{-2}. The occurrence of the highest NH_3 concentrations in March is particularly noticeable: all measurements are above 2 10^{16} molecules NH_3 cm^{-2}, which corresponds to the mean of data plus one standard deviation over the springtime period (March/April/May). They are measured for this calendar month, for almost every year (2011 (2 days), 2012 (11 days), 2014 (6 days), 2015 (4 days), 2016 (4 days) and 2017 (1 day)). March 2012 is therefore a month particularly polluted in terms of atmospheric NH_3. In addition to many days with more than 2 10^{16} molecules NH_3 cm^{-2}, a peak reaching the quadruple of that threshold on March 21, 2012, represents the maximum retrieved ammonia total column.

The seasonal variability is analysed in Figure 5 in terms of monthly averages over the 2009-2017 period. The mean NH_3 column in March is 1.65 10^{16} molecules NH_3 cm^{-2}, which is two times higher than the overall mean total column over the 4920 measurements in 9 years.

As for many other regions, NH_3 seasonality is well marked, with high values that might be connected with the timing of agricultural manure spreading. As shown by both approaches of Ramanantenasoa et al. (2018) for 2005-2006, mineral fertilizers are mainly used in the Île-de-France region because they are major arable crop (especially cereals) farming areas. They account for 59% of NH_3 emissions according to CADASTRE_NH3 framework based on the process-based Volt'Air model (Garcia et al., 2011; Garcia et al., 2012). These fertilizers are mostly spread during springtime. In Bremen, NH_3 atmospheric total columns have a similar seasonal cycle with highest levels during spring. The maximum values occur around April, which is consistent with temporal emission patterns for manure application reported for this region (Dammers et al., 2015). Note that for example, highest levels in Bremen were observed during springtime with total columns reaching up to 9.3 10^{16} molecules NH_3 cm^{-2}, which is close to the maximum peak observed by OASIS in March 2012.

One can observe also in Figure 4 significant concentrations in June (2017), July (2010, 2012, 2013, 2014, 2015 and 2017) and in August 2016, with another threshold of 1.5 10^{16} molecules NH_3 cm^{-2}, which corresponds roughly to the mean of data plus one standard deviation over the summer time period (June/July/August). This shows a second seasonal peak for the summer period. On the contrary, during winter months (December-January-February) the NH_3 total columns have a pronounced minimum (mean total column of 0.12 10^{16} molecules NH_3 cm^{-2} and a standard deviation of 0.12 10^{16} molecules NH_3 cm^{-2}). It is worth noting that fewer observations are available during this season due to frequent overcast conditions.

This evolution during early winter and, to a lesser extent, summer are also observed in the Bremen measurements, emphasizing some similarities between both the Paris and Bremen station environments. Such seasonal behavior is not only found in Europe but also in other megacities as Seoul (Korea), where surface ammonia concentration exhibit higher values during spring and in the warm season (summer), while dropping to a minimum in the cold season (winter) (Phan et al., 2013). One possible explanation is the increased volatility of ammonia in agricultural soils and ammonium particles (in the atmosphere in aqueous or solid phase) under warm meteorological conditions.

3.2 Comparison between NH_3-OASIS and NH_3-IASI

The validation of the satellite products of IASI (Van Damme et al., 2014) is limited by the scarcity of long-term series of atmospheric ammonia measurements. A first attempt to validate IASI-NH_3 measurements was made with correlative data from surface in-situ and airplane-based measurements (Van Damme et al., 2015). They confirmed consistency between the NH_3-IASI dataset and the available in-situ observations and showed promising results for validation by using independent airborne data from the CalNex campaign (California Research at the Nexus of Air Quality and Climate Change). Nevertheless, that study was limited by the availability of independent measurements and suffered from representativeness issues for the satellite observations when comparing to surface concentration measurements. Recently, Dammers et al. (2016) reported a first step in the validation of NH_3-IASI products, comparing ammonia columns with high-resolution FTIR measurements from several NDACC stations around the world. They concluded that IASI reflects similar pollution levels and seasonal cycles as shown by FTIR observations and the best correlation (R = 0.83 and a slope of 0.60) was obtained with the NDACC Bremen station. Bremen is located in the northwest of Germany, which is characterized by intensive agriculture. It is most suitable for comparisons with IASI given the very high atmospheric concentrations of NH_3 observed there. Compared to this work over Bremen, our analysis is the first comparison of ground-based NH_3 measurements performed in a megacity (Paris) with NH_3-IASI and covers nine years of data. In this study, we consider NH_3 total columns retrieved from the IASI-A instrument (aboard the Metop-A platform) observations along with those retrieved from the IASI-B instrument (aboard the Metop-B platform) observations, IASI-B data being available only for the period from 8 March 2013. 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. The sensitivity of IASI retrievals to surface concentrations of NH_3 is also limited, and the time of IASI overpasses (early morning and early evening) are not coincident with the typical early afternoon peaks of NH_3 concentrations.

For the comparison, only morning overpass (AM) satellite observations (i.e. 09:30 local time) are considered here, as they are generally more sensitive to NH_3 owing to more favorable thermal contrast at daytime (Van Damme et al., 2014), and for better temporal coincidence (OASIS observations are only carried out during daytime). The satellite data have a circular footprint of 12 km diameter at nadir and an ellipsoid shaped footprint of up to 20 km×39 km at the outermost angles

(Clarisse et al., 2009). We use raw observations from 1 January 2009 to 31 December 2016, from the most recent version of IASI NH_3 retrievals (the near-real-time neural network retrieval version 2 with reanalysed meteorological inputs called ANNI-NH3-v2.2R, Van Damme et al., 2017).

Note that, the lifetime of atmospheric NH_3 is rather short, on the order of hours not being uncommon (Galloway et al., 2003; Lutsch et al., 2016; Van Damme et al., 2018), up to a few days, due to efficient deposition and fast conversion to particulate matter. Thus, NH_3 concentrations vary strongly as function of emission strengths and meteorological conditions (such as temperature, precipitation, wind, vertical mixing in the atmospheric boundary layer).

In order to minimize differences associated with the temporal variability of NH_3, we only consider NH_3 measurements from OASIS performed within +/- 30 min with respect to the IASI morning overpass. The spatial coincidence criterion is 15 km between the center of IASI pixels and OASIS. 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). We also exclude NH_3-IASI data with relative errors higher than 100%, except those with absolute errors lower than 5.10^{15} molecules cm^{-2}

Figure 6 shows a scatterplot comparison between NH_3-OASIS and NH_3-IASI data. We obtain a very good correlation of R = 0.79 and a slope of 0.73 for a total of 52 coincidences. These results are similar to those from a comparison between a ground-based FTIR at Bremen and NH_3-IASI look-up table version: R = 0.83 and a slope of 0.60 for a total of 53 coincidences (Dammers et al., 2016) and NH_3-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). Here for Paris, we used stricter spatiotemporal collocation criteria for the comparison, as we have more data than the Bremen study. For this correlation, we calculated the absolute differences (AD) between satellite (y axis) and FTIR-OASIS NH_3 total columns (x axis), which are defined here as:

$$\mathrm{AD} = (NH_3\text{-}IASI)\ column - \left(NH_3\text{-}OASIS\right)\ column \quad (1)$$

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}**.** This reveals a very good consistency between NH_3-IASI and NH_3-OASIS, this last one being analyzed during 9 years (2009-2017) in section 3.1.

We further investigate the representativeness of the OASIS site for the Île-de-France region by comparing NH_3-OASIS data with that from IASI at different distances from the ground-based site. We use 15-km-wide rings (Figure 7) centered on the OASIS observatory and increasing the minimal distance (d_{min}) of the rings from OASIS observatory with a 1-km step. The 15-km width of the rings is chosen to minimize the impact of ammonia spatial variability and to consider a sufficient number of coincidences for statistics. The minimal distance (d_{min}) varies from 0 km up to 400 km. Figures 8 and 9 show respectively the correlation and regression slope as a function of d_{min} using a maximum allowed sampling time difference of 30 min. The numbers on the right axis of each of the figures show the number of coincident observations used in the comparison. An increasing d_{min} shows a decreasing correlation (blue lines) and a changing slope (increasing with distance up to 120 km, then decreasing). One can distinguish three different regimes in the plot of Fig. 8. For d_{min} between 0 and 12 km, highest

correlations are seen with R varying from 0.84 down to 0.57, then between 12 km and 120 km, R is around 0.6 despite lots of noise and then we get decreasing correlations for d_{min} between 120 km and 400 km. This comparison underlines that measurements from OASIS observatory provide information about atmospheric NH_3 variability on a regional scale, up to 120 km away from the site, but might also be affected by more local processes and/or emissions.

For d_{min} between 0 and 12 km, regression slopes vary between 0.73 and 0.81 revealing an underestimation of observed columns by IASI compared to OASIS (Fig. 9), already mentioned by Dammers et al. (2016) when evaluating IASI with some high resolution NDACC stations. 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 regression slope increases until 120 km for d_{min} 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 NH_3 sources (Clarisse et al., 2019; Van Damme et al., 2018), and these sources are more heterogenous beyond this distance.

3.3 Vertical distribution of sensitivity of the NH3-OASIS approach

As mentioned in section 2.2, the NH_3-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 NH_3 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 NH_3 provided by OASIS measurements, we have performed a few tests using a NH_3 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 NH_3 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 NH_3 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 Conclusions and perspectives

Ground-based infrared remote-sensing is undoubtedly a promising and powerful spectroscopic technique to retrieve ammonia columns, even using FTIR instruments with moderate spectral resolution such as OASIS. Recording one spectrum over a period of approximately 10 minutes, the OASIS instrument can provide over 40 spectra per day over the Paris region and allows the observations of the diurnal cycle of ammonia. In this paper, we presented the first multi-year time series (2009-2017) of atmospheric NH_3 total column measurements from ground-based infrared remote-sensing over the Paris megacity. NH_3 total columns vary seasonally by 2 orders of magnitude, approximately from 10^{15} molecules cm^{-2} in winter to 10^{17} molecules cm^{-2} for spring peaks. Error estimations show random errors of about 10 % and systematic errors less than 25 % for individual observations, mainly due to uncertainties in spectroscopic parameters.

This study is based on the 9-year NH_3-OASIS time series to order to analyze the seasonal variability of atmospheric NH_3 in the Paris region. The predominance of NH_3 peaks occurring in March is particularly noticeable: all measurements are greater than 2 10^{16} molecules of NH_3 cm^{-2}, which corresponds to the average values of the dataset plus one standard deviation over the springtime period (March/April/May), and are coincident with manure spreading time periods (Ramanantenasoa et al., 2018). Mineral fertilizers are mainly applied in the Île-de-France region because they are major arable crop (especially cereals) farming areas, which may volatilize and can generate high ammonia concentrations under sunny conditions. This study also finds high summer values greater than 1.5 10^{16} molecules NH_3 cm^{-2}, which corresponds roughly to the average value of the dataset plus one standard deviation over the June/July/August time period. This is likely linked to an increase in the volatility of ammonia under warm meteorological conditions.

Satellite remote-sensing instruments such as Infrared Atmospheric Sounding Interferometer (IASI) on board the Metop platforms provide global distributions of atmospheric NH_3 relying on valuable information (Van Damme et al., 2018). We have compared NH_3-IASI data with our measurements from OASIS over the 2009-2016 time period. We show a very good correlation of 0.79 and a mean bias of -0.78 10^{15} molecules cm^{-2} between the two datasets. Besides the space instrument's lower sensitivity to the surface ammonia concentrations, spatial heterogeneity of ammonia within the IASI footprint can lead to lower values. Furthermore, OASIS observatory measurements of NH_3 are representative of the variability at a 100-km regional scale.

This study also illustrates that ground based stations like OASIS may play a key role for validating current (e.g. IASI) and future satellite observations (e.g. Infrared Atmospheric Sounder Interferometer - New Generation - IASI-NG - and Meteosat Third Generation-InfraRed Sounder - MTG-IRS) of ammonia in the infrared for a better understanding of the space and time variability of this major source of nitrogen species in the troposphere.

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 NH_3-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. Moreover, future versions of the NH_3-OASIS approach will be based on vertical profile retrieval using a Tikhonov-Philips-type regularisation. 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.

Acknowledgments:

The authors from LISA acknowledge support from University of Paris-Est Créteil and from the OSU-EFLUVE (Observatoire des Sciences de l'Univers-Enveloppes Fluides de la Ville à l'Exobiologie) to make the observatory still operational. IASI is a joint mission of EUMETSAT and the Centre National d'Etudes Spatiales (CNES, France). They acknowledge the support of the Centre National des Etudes Spatiales (CNES) via the project IASI-TOSCA (Terre-Ocean-Surface-Continentale-Atmosphère). The authors also acknowledge the AERIS data infrastructure for providing access to the IASI data in this study and ULB-LATMOS for the development of the NH_3-IASI retrieval algorithms. The authors wish to thank the NASA Goddard Space Flight Center for providing the temperature and pressure profiles from the National Center for Environmental Prediction (NCEP). The research was also funded by DIM Qi2 (Region Île-de-France) for internship financial support and by LEFE-CHAT. Work at IMK is funded by the ATMO program of the Helmholtz Association of Germany Research Centres.

References

Allen, A.G., Harrison, R.M., Wake, M.T., A meso-scale study of the behaviour of atmospheric ammonia and ammonium, Atmospheric Environment, Volume 22, Issue 7, 1347-1353, 1988.

Behera, S. N., Sharma, M., Aneja, V. P., and Balasubramanian, R.:Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies, Environ. Sci. Pollut. R., 20, 8092–8131, doi:10.1007/s11356-013- 2051-9, 2013.

Chang, L., Palo, S., Hagan, M., Richter, J., Garcia, R., Riggin, D., and Fritts, D.: Structure of the migrating diurnal tide in the Whole Atmosphere Community Climate Model (WACCM), Adv. Space Res., 41, 1398–1407, doi:10.1016/j.asr.2007.03.035, 2008.

Chang, Y., Zou, Z., Deng, C., Huang, K., Collett, J. L., Lin, J., and Zhuang, G.: The importance of vehicle emissions as a source of atmospheric ammonia in the megacity of Shanghai, Atmos. Chem. Phys., 16, 3577-3594, https://doi.org/10.5194/acp-16-3577-2016, 2016.

Chelin, P., Viatte, C., Ray, M., Eremenko, M., Cuesta, J., Hase, F., Orphal, J., and Flaud, J.-M., The OASIS observatory using ground-based solar absorption Fourier transform infrared spectroscopy in the suburbs of Paris (Créteil-France), E. Jimenez et al. (eds.), Environment, Energy and Climate Change I:Environmental Chemistry of Pollutants and Wastes, Hdb Env Chem, doi:10.1007/698_2014_270,Springer-Verlag Berlin Heidelberg, 2014.

CITEPA, 2015. Inventaire des émissions de polluants atmosphériques et de gaz à effet de serre en France - Séries sectorielles et analyses étendues - Format SECTEN. Centre Interprofessionnel Technique d'Etude de la Pollution Atmosphérique

Clarisse, L., Clerbaux, C., Dentener, F., Hurtmans, D., and Coheur, P.-F.: Global ammonia distribution derived from infrared satellite observations, Nat. Geosci., 2, 479–483, doi: 10.1038/NGEO551, 2009.

Clarisse, L., Van Damme, M., Clerbaux, C., and Coheur, P.-F.: Tracking down global NH_3 point sources with wind-adjusted superresolution, Atmos. Meas. Tech., 12, 5457–5473, https://doi.org/10.5194/amt-12-5457-2019, 2019.

Clerbaux, C., Boynard, A., Clarisse, L., George, M., Hadji-Lazaro, J., Herbin, H., Hurtmans, D., Pommier, M., Razavi, A., Turquety, S., Wespes, C., and Coheur, P.-F.: Monitoring of atmospheric composition using the thermal infrared IASI/Metop sounder, Atmos. Chem. Phys., 9, 6041–6054, doi:10.5194/acp-9-6041-2009, 2009.

Dammers, E., Vigouroux, C., Palm, M., Mahieu, E., Warneke, T., Smale, D., Langerock, B., Franco, B., Van Damme, M., Schaap, M., Notholt, J., and Erisman, J. W.: Retrieval of ammonia from ground-based FTIR solar spectra, Atmos. Chem. Phys., 15, 12789–12803, doi:10.5194/acp-15-12789-2015, 2015.

Dammers, E., Palm, M., Van Damme, M., Vigouroux, C., Smale, D., Conway, S., Toon, G.C., Jones, N., Nussbaumer, E., Warneke, T., Petri, C., Clarisse, L., Clerbaux, C., Hermans, C., Lutsch, E., Strong, K., Hannigan, J.W., Nakajima, H., Morino, I., Herrera, B., Stremme, W., Grutter, M., Schaap, M., Wichink Kruit, R.J., Notholt, J., Coheur, P.-F., Erisman,

J.W., 2016. An evaluation of IASI-NH_3 with ground-based Fourier transform infrared spectroscopy measurements. Atmos. Chem. Phys. 16, 10351e10368. http://dx.doi.org/10.5194/acp-16-10351-2016.

Dammers, E., Shephard, M. W., Palm, M., Cady-Pereira, K., Capps, S., Lutsch, E., Strong, K., Hannigan, J. W., Ortega, I., Toon, G. C., Stremme, W., Grutter, M., Jones, N., Smale, D., Siemons, J., Hrpcek, K., Tremblay, D., Schaap, M., Notholt, J., and Erisman, J. W.: Validation of the CrIS fast physical NH_3 retrieval with ground-based FTIR, Atmos. Meas. Tech., 10, 2645-2667, https://doi.org/10.5194/amt-10-2645-2017, 2017.

Dhib, M., Ibrahim, N., Chelin, P., Echargui, M.A., Aroui, H., Orphal, J.: Diode-laser measurements of O2, N2 and air-pressure broadening and shifting of NH_3 in the 10 μm spectral region, J. Mol. Spec., 242, 83-89, DOI: 10.1016/j.jms.2007.02.013, 2007.

DRIEE: Plan de protection de l'atmosphère d'Île-de-France, Direction Régionale et Interdépartementale de l'Environnement et de l'Energie, 2017. Last access Jul. 15th, 2018, available at: http://www.maqualitedelair-idf.fr/w2020/wp-content/uploads/2017/03/PPA-7mars.pdf

EMEP/EEA: The European Monitoring and Evaluation Programme EMEP Status Report, 2016.

Fortems-Cheiney, A., Dufour, G., Hamaoui-Laguel, L., Foret, G., Siour, G., Van Damme, M., Meleux, F., Coheur, P.-F., Clerbaux, C., Clarisse, L., Wallash, M. and Beekmann, M.: Unaccounted variability in NH_3 agricultural sources detected by IASI contributing to European spring haze episode, *Geophysical Research Letters*, 43, 5475–5482, doi:10.1002/2016GL069361, 2016.

Galloway, J.N. Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J.; The Nitrogen Cascade, BioScience, Volume 53, Issue 4, 1 April 2003, Pages 341–356, https://doi.org/10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2

Garcia, L., Bedos, C., Genermont, S., Braud, I., Cellier, P.: Assessing the ability of mechanistic volatilization models to simulate soil surface conditions: a study with the Volt'Air model. Sci. Total Environ. 409:3980–3992. https://doi.org/10.1016/j.scitotenv.2011.05.003, 2011.

Garcia, L., Génermont, S., Bedos, C., Simon, N.N., Garnier, P., Loubet, B., Cellier, P. : Accounting for surface cattle slurry in ammonia volatilization models: the case of Volt'Air. Soil Sci. Soc. Am. J. 76:2184. https://doi.org/10.2136/sssaj2012.0067, 2012.

Génermont, S., Ramanantenasoa, M. M. J., Dufosse, K., Maury, O., Mignolet, C., and Gilliot, J.-M., Data on spatio-temporal representation of mineral N fertilization and manure N application as well as ammonia volatilization in French regions for the crop year 2005/06, Data in Brief, Volume 21, , Pages 1119-1124, doi.org/10.1016/j.scitotenv.2018.06.202, December 2018.

Hase, F., Hannigan, J. W., Coffey, M. T., Goldman, A., H¨opfner, M., Jones N. B., Rinsland, C. P., and Wood, S. W.: Intercomparison of retrieval codes used for the analysis of high-resolution, ground-based FTIR measurements, J. Quant. Spectrosc. Rad. Transf., 87, 25–52, 2004.

Leen, J. B., Yu, X. Y., Gupta, M., Baer, D. S., Hubbe, J. M., Kluzek, C. D., Tomlinson, J. M., and Hubbell, M. R.: Fast in situ airborne measurement of ammonia using a mid-infrared off-axis ICOS spectrometer, Environ. Sci. Technol., 47, 10446–10453, doi:10.1021/es401134u, 2013.

Lutsch, E., Dammers, E., Conway, S., & Strong, K. (2016). Long-range Transport of NH3, CO, HCN and C2H6 from the 2014 Canadian Wildfires. Geophysical ResearchLetters, (43), 8286-8297. https://doi.org/10.1002/2016GL070114.

Meier, A., Toon, G. C., Rinsland, C. P., Goldman, A. and Hase, Frank, A spectroscopic atlas of atmospheric microwindows in the middle infrared, IRF technical report, Swedish Institute of Space Physics, 2004.

Petetin, H., Sciare, J., Bressi, M., Gros, V., Rosso, A., Sanchez, O., Sarda-Estève, R., Petit, J.-E., and Beekmann, M.: Assessing the ammonium nitrate formation regime in the Paris megacity and its representation in the CHIMERE model, Atmos. Chem. Phys., 16, 10419-10440, doi.org/10.5194/acp-16-10419-2016, 2016.

Petit, J.-E., Favez, O., Sciare, J., Canonaco, F., Croteau, P., Močnik, G., Jayne, J., Worsnop, D., and Leoz-Garziandia, E.: Submicron aerosol source apportionment of wintertime pollution in Paris, France by double positive matrix factorization (PMF^2) using an aerosol chemical speciation monitor (ACSM) and a multi-wavelength Aethalometer, Atmos. Chem. Phys., 14, 13773-13787, https://doi.org/10.5194/acp-14-13773-2014, 2014.

Petit, J.-E., Amodeo, T., Meleux, F., Bessagnet, B., Menut, L., Grenier, D., Pellan, Y., Ockler, A., Rocq, B., Gros, V., Sciare, J., and Favez, O., Characterising an intense PM pollution episode in March 2015 in France from multi-site approach and near real time data: Climatology, variabilities, geographical origins and model evaluation, Atmospheric Environment, 155, 2017, 68-84, https://doi.org/10.1016/j.atmosenv.2017.02.012.

Phan, N.-T. Kim, K.-H., Shon, Z.-H., Jeon, E.-C., Jung, K., and Kim, N.-J., Analysis of ammonia variation in the urban atmosphere, Atmospheric Environment, Volume 65, 177–185, 2013, https://doi.org/10.1016/j.atmosenv.2012.10.049.

Ramanantenasoa, M.M.J., Gilliot, J.-M. , Mignolet, C., Bedos, C., Mathias, E., Eglin, T., Makowski, D., and Génermont, S. A new framework to estimate spatio-temporal ammonia emissions due to nitrogen fertilization in France, Sci. Total Environ., 645 (2018), pp. 205-219, doi.org/10.1016/j.scitotenv.2018.06.202

Remedios, J. J., Leigh, R. J., Waterfall, A. M., Moore, D. P., Sembhi, H., Parkes, I., Greenhough, J., Chipperfield, M. P., and Hauglustaine, D.: MIPAS reference atmospheres and comparisons to V4.61/V4.62 MIPAS level 2 geophysical data sets, Atmos. Chem. Phys. Discuss., 7, 9973-10017, https://doi.org/10.5194/acpd-7-9973-2007, 2007.

Ringuet, J., Andre, J.-M., Bouchard, D., Deflorenne, E., Druart, A., Dulhoste, S., Durand, A., Gavel, A., Gueguen, C., Jeannot, C., Langeron, J., Lemaire, A., Mathias, E., Nicco, L., Serveau, L., Taieb, N., Vieira Da Rocha, T., and Vincent, J., Inventaire des émissions de polluants atmosphériques en France au titre de la convention sur la pollution atmosphérique transfontalière à longue distance et de la directive européenne relative aux plafonds d'émissions nationaux, Centre Interprofessionel Technique d'Etudes de la Pollution Atmosphérique, 2016.

Rodgers, C. D.: Inverse Methods for Atmospheric Sounding – Theory and Practice, 2, 256, doi:10.1142/9789812813718, 2000.

Rothman, L. S., Gordon, I. E., Barbe, A., Benner, D. C., Bernath, P . E., Birk, M., Boudon, V., Brown, L. R., Campargue, A., Champion, J. P., Chance, K., Coudert, L. H., Dana, V., Devi, V. M., Fally, S., Flaud, J. M., Gamache, R. R., Goldman, A., Jacquemart, D., Kleiner, I., Lacome, N., Lafferty, W. J., Mandin, J. Y., Massie, S. T., Mikhailenko, S. N., Miller, C. E., Moazzen-Ahmadi, N., Naumenko, O. V., Nikitin, A. V., Orphal, J., Perevalov, V. I., Perrin, A., Predoi-Cross, A., Rinsland, C. P., Rotger, M., Simeckova, M., Smith, M. A. H., Sung, K., Tashkun, S. A., Tennyson, J ., Toth, R. A., Vandaele, A. C., and Vander Auwera, J.: The HITRAN 2008 molecular spectroscopic database, J. Quant. Spectrosc. Rad. Transf., 110, 533–572, doi:10.1016/j.jqsrt.2009.02.013, 2009.

Rothman, L. S., Gordon, I. E., Babikov, Y., Barbe, A., Chris Benner, D., Bernath, P. F., Birk, M., Bizzocchi, L., Boudon, V., Brown, L. R., Campargue, A., Chance, K., Cohen, E. A., Coudert, L. H., Devi, V. M., Drouin, B. J., Fayt, A., Flaud, J. M., Gamache, R. R., Harrison, J. J., Hartmann, J. M., Hill, C., Hodges, J. T., Jacquemart, D., Jolly, A., Lamouroux, J., Le Roy, R. J., Li, G., Long, D. a., Lyulin, O. M., Mackie, C. J., Massie, S. T., Mikhailenko, S., Müller, H. S. P., Naumenko, O. V., Nikitin, A. V., Orphal, J., Perevalov, V., Perrin, A., Polovtseva, E. R., Richard, C., Smith, M. A. H., Starikova, E., Sung, K., Tashkun, S., Tennyson, J., Toon, G. C., Tyuterev, V. G., and Wagner, G.: The HITRAN2012 molecular spectroscopic database, J. Quant. Spectrosc. Rad. Transf., 130, 4–50, doi:10.1016/j.jqsrt.2013.07.002, 2013.

Seinfeld, J.H., and Pandis, S.N., Atmospheric chemistry and physics: from air pollution to climate change, 2nd edn. John Wiley & Sons, New York, 2006.

Shephard, M. W., McLinden, C. A., Cady-Pereira, K. E., Luo, M., Moussa, S. G., Leithead, A., Liggio, J., Staebler, R. M., Akingunola, A., Makar, P., Lehr, P., Zhang, J., Henze, D. K., Millet, D. B., Bash, J. O., Zhu, L., Wells, K. C., Capps, S. L., Chaliyakunnel, S., Gordon, M., Hayden, K., Brook, J. R., Wolde, M., and Li, S.-M.: Tropospheric Emission Spectrometer (TES) satellite observations of ammonia, methanol, formic acid, and carbon monoxide over the Canadian oil sands: validation and model evaluation, Atmos. Meas. Tech., 8, 5189-5211, https://doi.org/10.5194/amt-8-5189-2015, 2015.

Shephard, M. W. and Cady-Pereira, K. E.: Cross-track Infrared Sounder (CrIS) satellite observations of tropospheric ammonia, Atmos. Meas. Tech., 8, 1323–1336, https://doi.org/10.5194/amt-8-1323-2015, 2015.

Someya, Y., Imasu, R., Shiomi, K., and Saitoh, N.: Atmospheric ammonia retrieval from the TANSO-FTS/GOSAT thermal infrared sounder, Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2019-49, in review, 2019.

Sun, K., Cady-Pereira, K., Miller, D. J., Tao, L., Zondlo, M. A., Nowak, J. B., Neuman, J. A., Mikoviny, T., Müller, M., Wisthaler, A., Scarino, A. J., and Hostetler, C. A.: Validation of TES ammonia observations at the single pixel scale in the San Joaquin Valley during DISCOVER-AQ, J. Geophys. Res. Atmos., 120, 5140–5154, doi:10.1002/2014JD022846, 2015.

Sutton, M. A., Milford, C., Dragosits, U., Place, C. J., Singles, R. J., Smith, R. I., Wyers, G. P., Dispersion, deposition and impacts of atmospheric ammonia: quantifying local budgets and spatial variability. Environmental Pollution, 102(1, Supplement 1), 349-361. DOI: 10.1016/S0269-7491(98)80054-7, 1998.

Sutton, M. A., Erisman, J. W., Dentener, F., Möller, D., Ammonia in the environment: From ancient times to the present, Environmental Pollution, 156, Issue 3, 583-604, https://doi.org/10.1016/j.envpol.2008.03.013, 2008.

Van Damme, M., Clarisse, L., Heald, C. L., Hurtmans, D., Ngadi, Y., Clerbaux, C., Dolman, A. J., Erisman, J. W., and Coheur, P. F.: Global distributions, time series and error characterization of atmospheric ammonia (NH_3) from IASI satellite observations, Atmos. Chem. Phys., 14, 2905-2922, https://doi.org/10.5194/acp-14-2905-2014, 2014.

Van Damme, M., Clarisse, L., Dammers, E., Liu, X., Nowak, J. B., Clerbaux, C., Flechard, C. R., Galy-Lacaux, C., Xu, W., Neuman, J. A., Tang, Y. S., Sutton, M. A., Erisman, J. W., and Coheur, P. F.: Towards validation of ammonia (NH3) measurements from the IASI satellite, Atmos. Meas. Tech., 8, 1575–1591, doi:10.5194/amt-8-1575-2015, 2015.

Van Damme, M., Whitburn, S., Clarisse, L., Clerbaux, C., Hurtmans, D., and Coheur, P.-F.: Version 2 of the IASI NH_3 neural network retrieval algorithm: near-real-time and reanalysed datasets, Atmos. Meas. Tech., 10, 4905-4914, https://doi.org/10.5194/amt-10-4905-2017, 2017.

Van Damme, M., Clarisse, L., Whitburn, S., Hadji-Lazaro, J., Hurtmans, D., Clerbaux, C., and Coheur, P.-F.: Industrial and Agricultural Ammonia Point Sources Exposed, Nature, 564, 99–103, https://doi.org/10.1038/s41586-018-0747-1, 2018.

Viatte, C., Gaubert, B., Eremenko, M., Hase, F., Schneider, M., Blumenstock, T., Ray, M., Chelin, P., Flaud, J.-M., and Orphal, J., Tropospheric and total ozone columns over Paris (France) measured using medium-resolution ground-based solar-absorption Fourier-transform infrared spectroscopy, Atmos. Meas. Tech. 4, 2323-2331, doi:10.5194/amt-4-2323-2011, 2011.

Volten, H., Bergwerff, J. B., Haaima, M., Lolkema, D. E., Berkhout, A. J. C., van der Hoff, G. R., Potma, C. J. M., Wichink Kruit, R. J., van Pul, W. A. J., and Swart, D. P. J.: Two instruments based on differential optical absorption spectroscopy (DOAS) to measure accurate ammonia concentrations in the atmosphere, Atmos. Meas. Tech., 5, 413–427, https://doi.org/10.5194/amt-5-413-2012, 2012.

von Bobrutzki, K., Braban, C. F., Famulari, D., Jones, S. K., Blackall, T., Smith, T. E. L., Blom, M., Coe, H., Gallagher, M., Ghalaieny, M., McGillen, M. R., Percival, C. J., Whitehead, J. D., Ellis, R., Murphy, J., Mohacsi, A., Pogany, A., Junninen, H., Rantanen, S., Sutton, M. A., and Nemitz, E.: Field inter-comparison of eleven atmospheric ammonia measurement techniques, Atmos. Meas. Tech., 3, 91–112, doi:10.5194/amt-3-91-2010, 2010.

Warneck P.: Chemistry of the natural atmosphere, Academic Press, New York, 1988.

Warner, J. X., Wei, Z., Strow, L. L., Dickerson, R. R., and Nowak, J. B.: The global tropospheric ammonia distribution as seen in the 13-year AIRS measurement record, Atmos. Chem. Phys., 16, 5467-5479, https://doi.org/10.5194/acp-16-5467-2016, 2016.

Whitburn, S., Van Damme, M., Clarisse, L., Bauduin, S., Heald, C. L., Hadji-Lazaro, J., Hurtmans, D., Zondlo, M. A., Clerbaux, C., and Coheur, P.-F.: A flexible and robust neural network IASINH3 retrieval algorithm, J. Geophys. Res.-Atmos., 121, 6581–6599, https://doi.org/10.1002/2016jd024828, 2016.

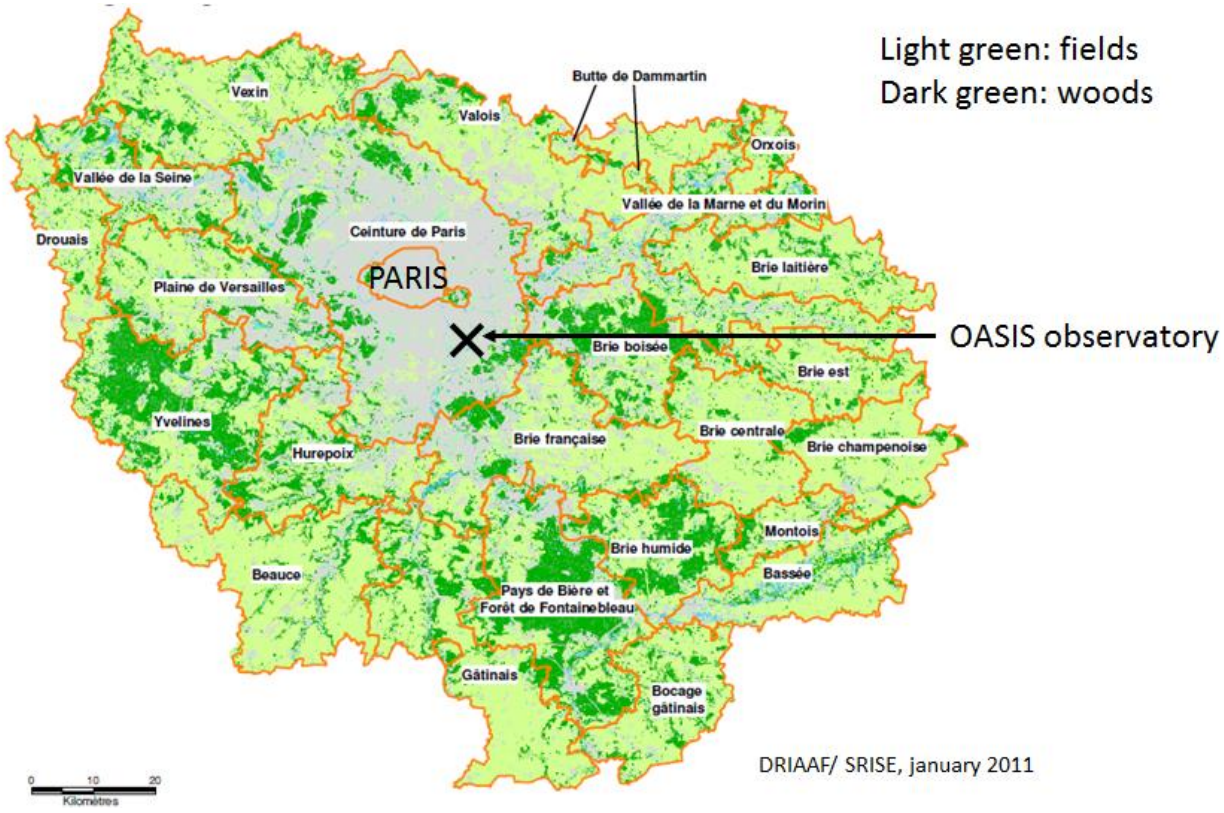

Figure 1: Location of the FTIR OASIS observatory providing NH_3 total columns in Paris region (France). One can see that Paris megacity is very urbanized close to the Paris city, and surrounded by a large rural belt with 49% agriculture surfaces (source Agreste Île-de-France http://agreste.agriculture.gouv.fr/IMG/pdf/R1118C01.pdf).

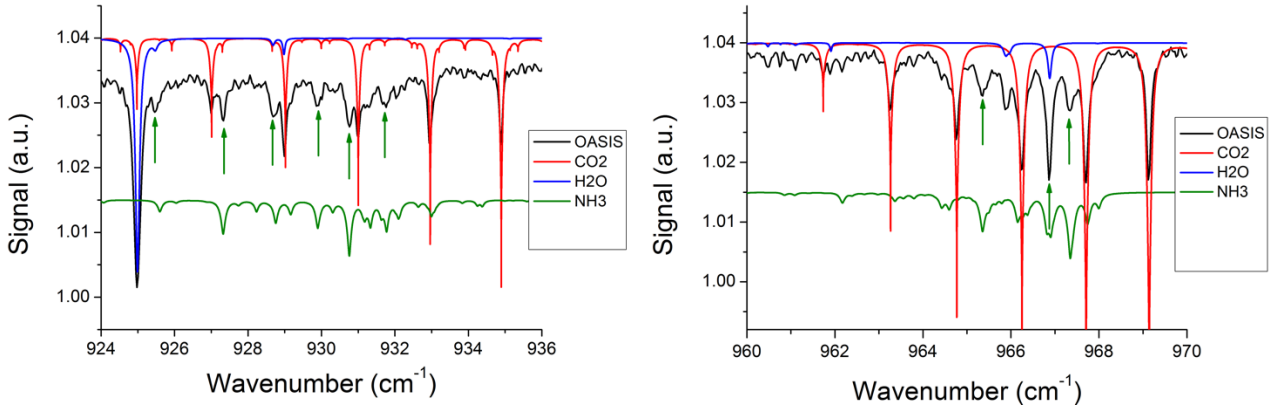

Figure 2: Measured spectrum for both spectral windows obtained with the BRUKER Vertex 80 at Creteil on 21 March 2012, with individual contributions of the main absorbing species represented from the atlas of Meier et al. (Meier et al., 2004) in the first (on the left) and second (on the right) spectral windows.

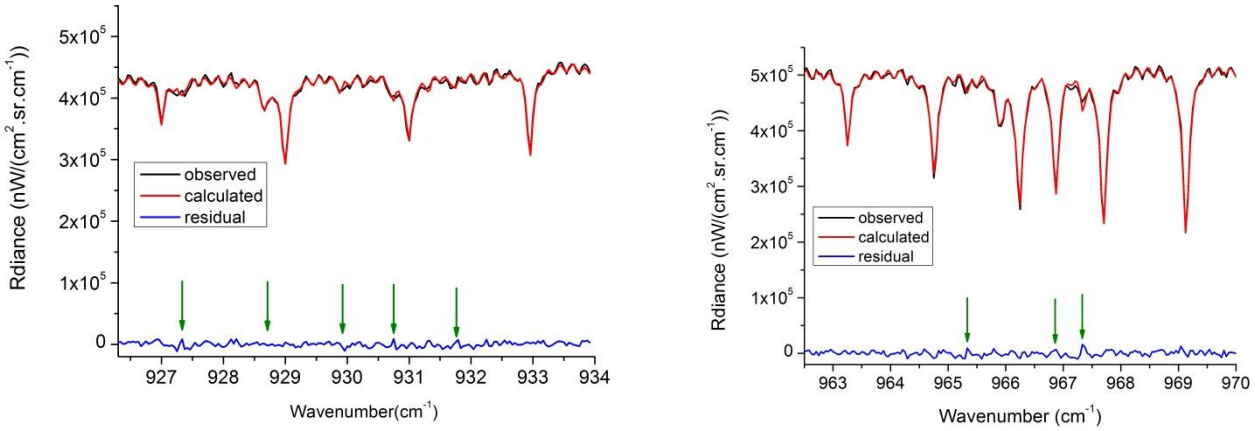

Figure 3: Observed (black line) and calculated spectrum (red line) in radiance unit (nW/(cm^2.sr.cm^{-1})) for both spectral windows measured with the BRUKER Vertex 80 in Creteil on the 21 March 2012 with the fitting residuals (blue line).

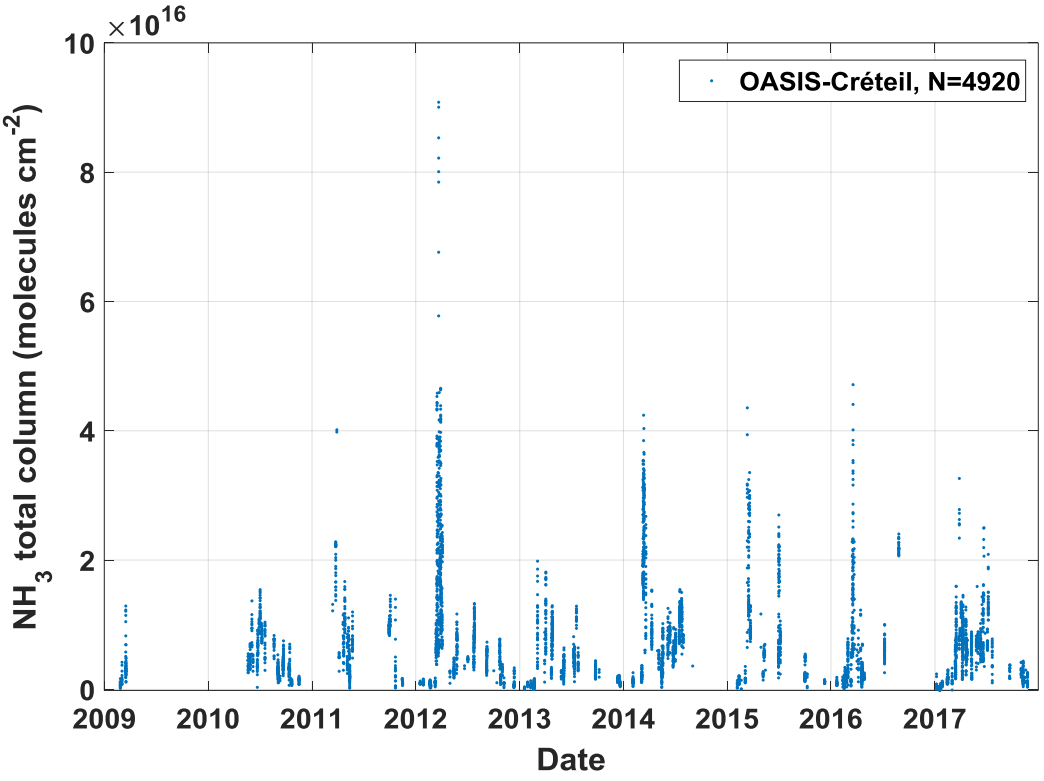

Figure 4: First multi-year time series of NH_3 total columns derived from OASIS measurements over Paris, retrieved from 4920 infrared atmospheric transmission spectra measured during 234 days between 2009 and 2017.

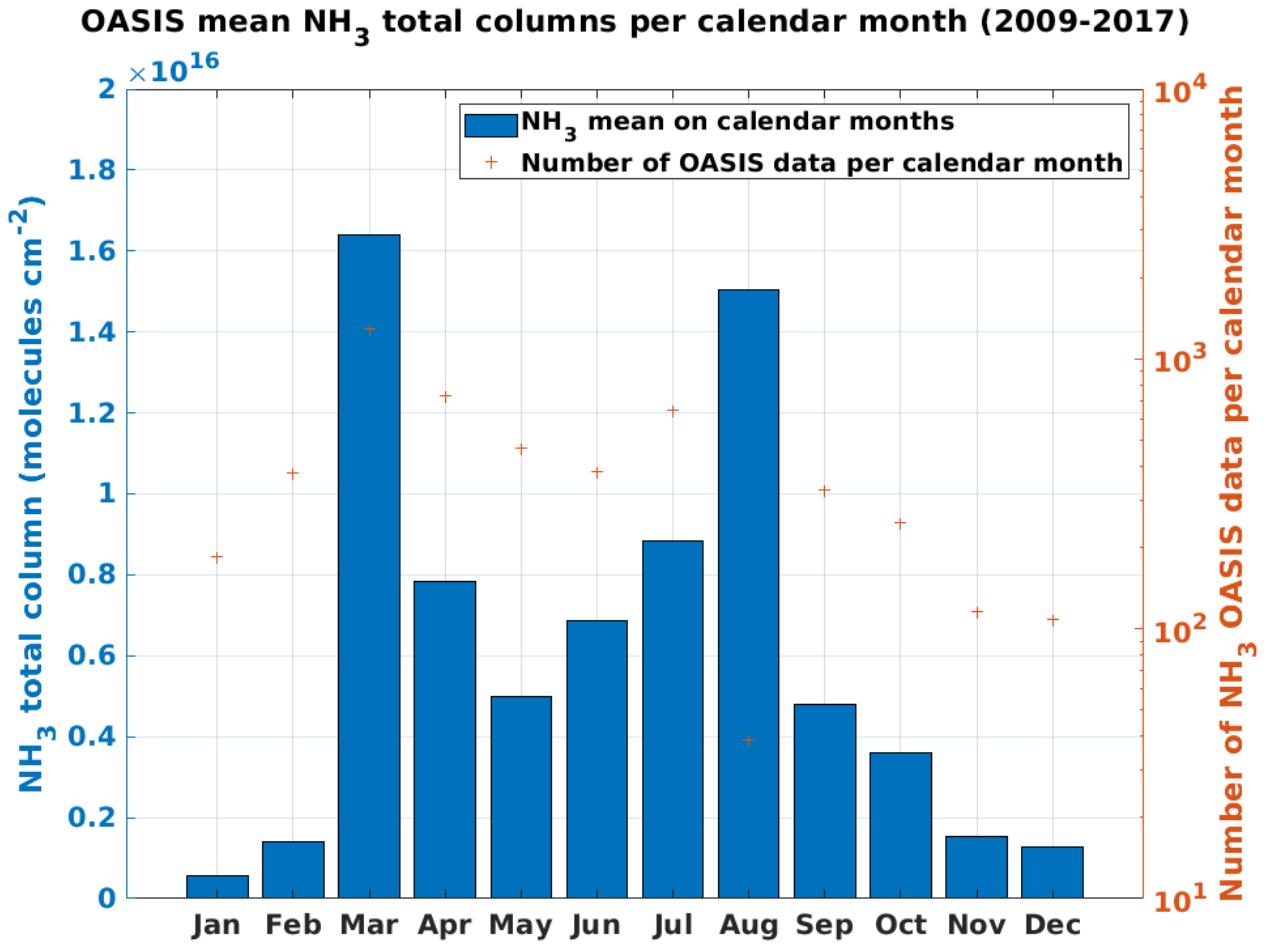

Figure 5: Average annual cycle of monthly NH_3 total columns (molecules cm^{-2}) observed by OASIS over Paris, averaged over the 2009-2017 period. The red crosses represent the number of OASIS data per calendar month on a log scale (right axis).

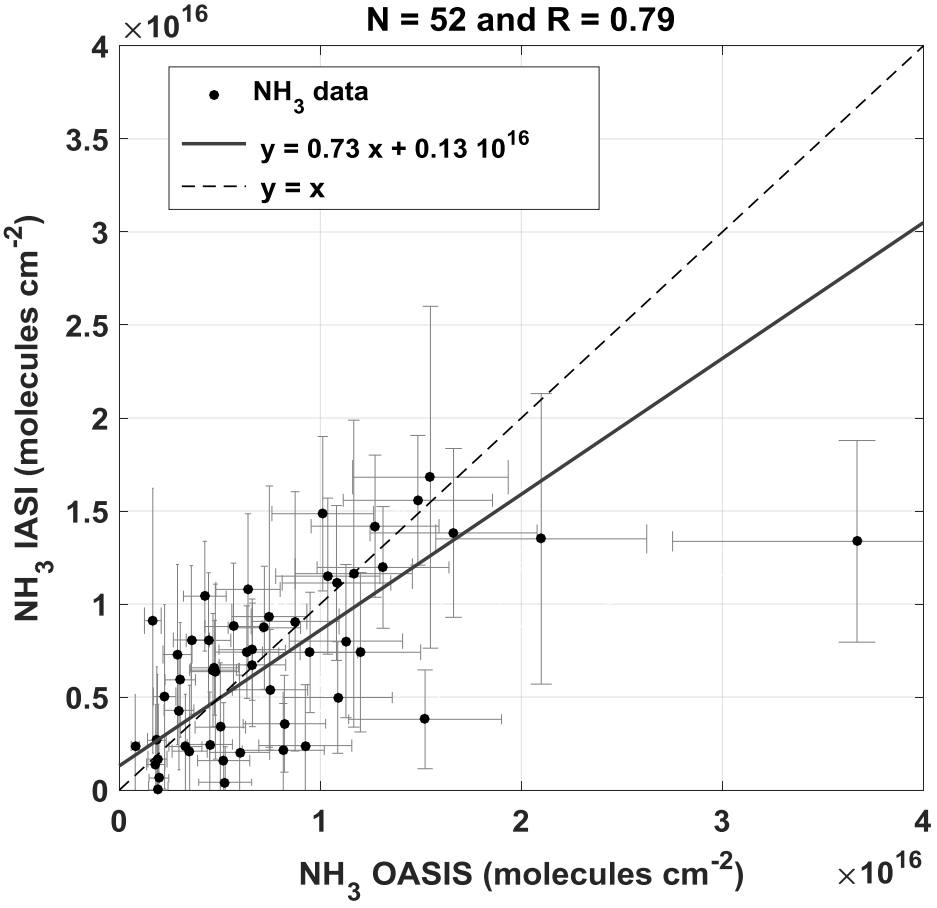

Figure 6: **Correlations between the FTIR/OASIS and IASI NH_3 total columns fulfilling the temporal and spatial coincidence criteria: a time difference smaller than 30 min, and a 15 km radius centered on the ground-based FTIR station. The dashed line is the straight equation with slope 1.**

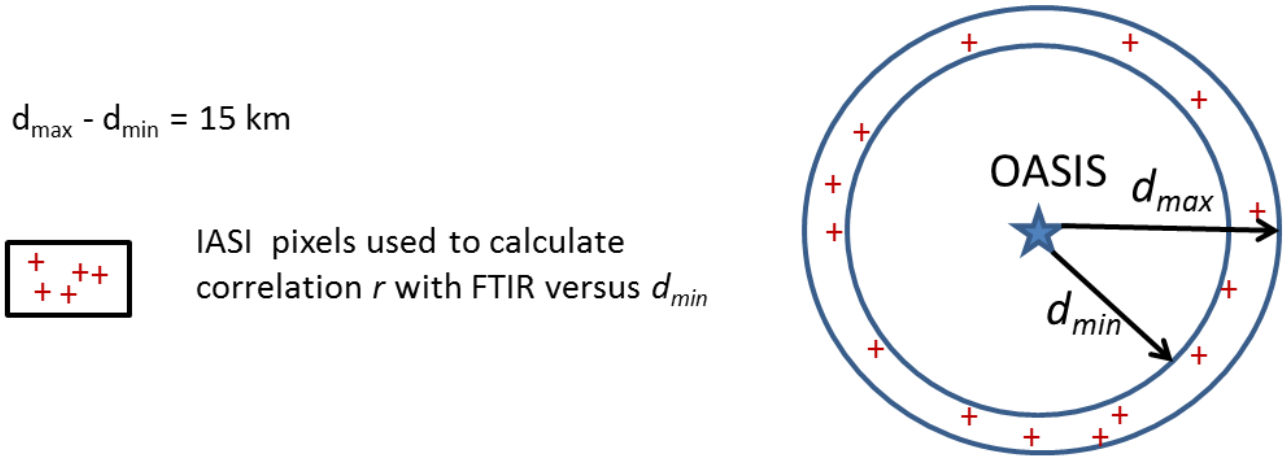

Figure 7: Description of the 15-km rings centred on OASIS observatory that were used to select different IASI pixels for the correlation with FTIR data.

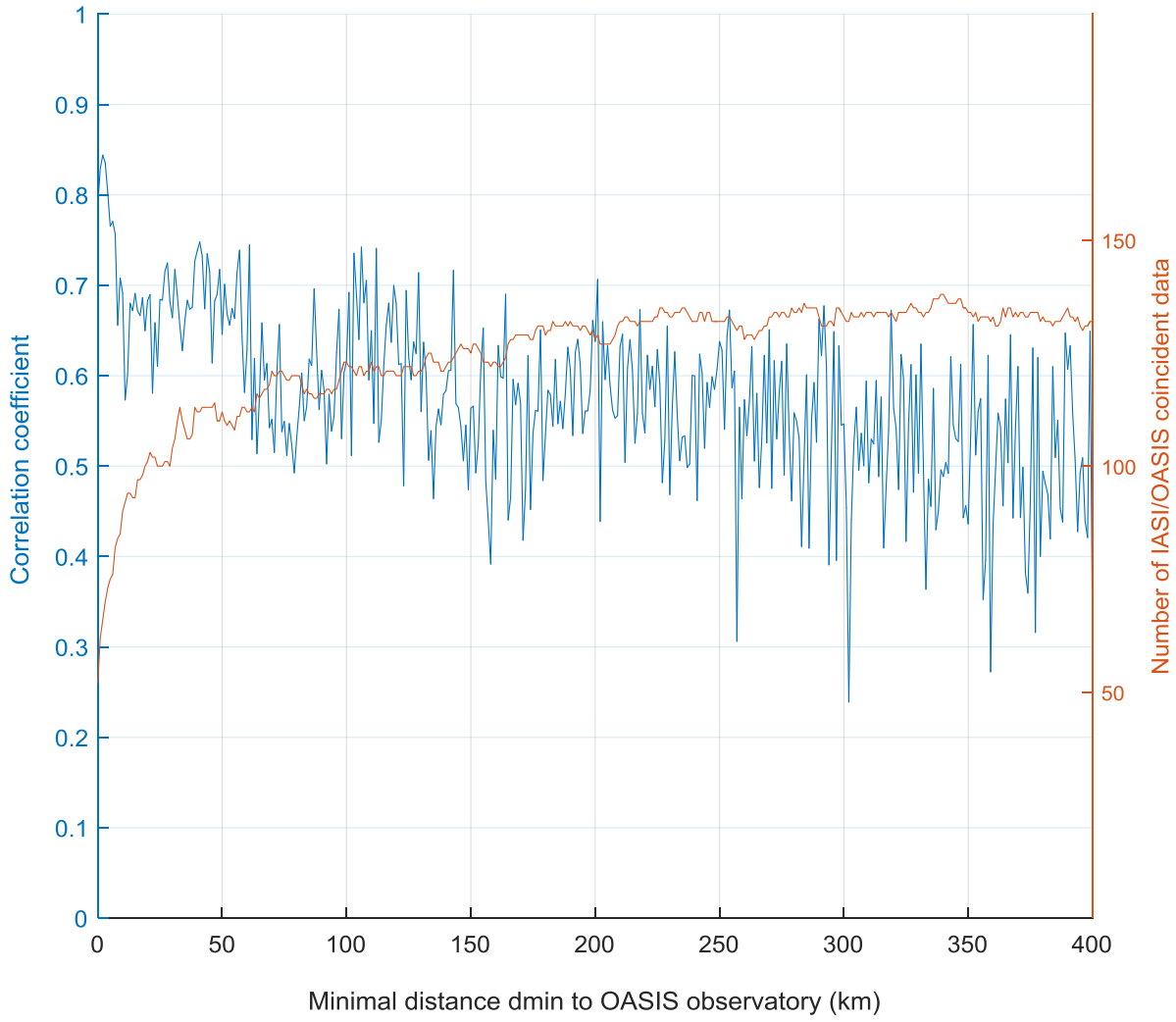

Figure 8: Correlation coefficients R (blue lines, left axis) between IASI and ground-based FTIR observations with temporal sampling difference smaller than 30 min, as a function of *dmin* to OASIS observatory, considered for the calculation of the 15 km wide rings. The data (orange lines, right axis) show the total number of IASI/OASIS coincident observations.

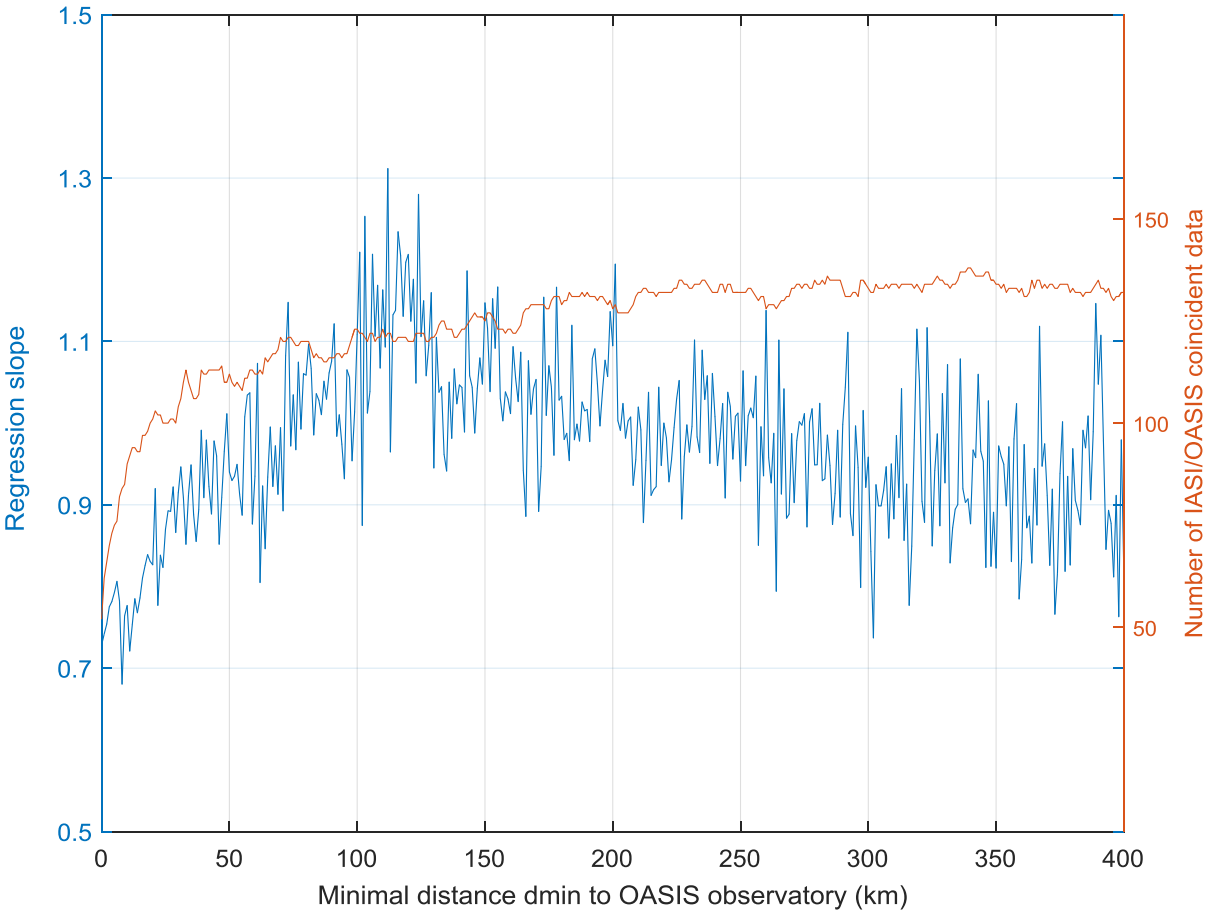

Figure 9: Regression slope (blue lines, left axis) between IASI and ground-based FTIR observations with temporal sampling difference smaller than 30 min, as a function of *dmin* to OASIS observatory, considered for the calculation of the 15 km wide rings. The data (orange lines, right axis) show the total number of IASI/OASIS coincident observations.

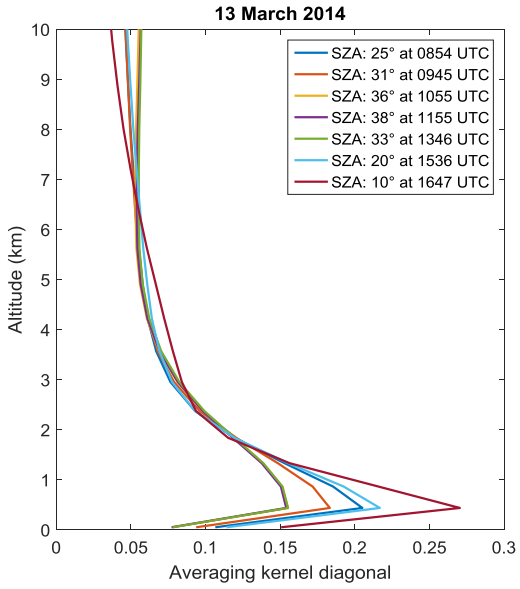

Figure 10: Typical NH_3-OASIS averaging kernel diagonal elements, illustrated on the 13 March 2014 at different times of the day and Solar Zenith Angles (SZA in degree) and using spectroscopic data from the HITRAN 2008 (HIT08) database (except for CO_2 lines).

NH_3 error	NH_3 column (molecules.cm^{-2})		
	average winter NH_3 (0.12×10^{16})	average NH_3 (0.84×10^{16})	max NH_3 (9.1×10^{16})
Random error (%)	23.3	6.7	1.8
Systematic error (%)	22.6	20.8	20.0
Total error (%)	32.4	21.8	20.1

Table 1: Random and systematic errors according to NH_3 total columns. The total errors, combining the systematic and random errors vary from 20% up to 35%. Note that 9.1 10^{16} molecules cm^2 is the maximum ammonia column measured over Paris during the 2009-2017 period (exactly in March 2012).

Season	No.	Mean ($\times 10^{16}$ molecules.cm^{-2})	Median ($\times 10^{16}$ molecules.cm^{-2})	Standard deviation ($\times 10^{16}$ molecules.cm^{-2})
MAM	2486	1.17	0.83	1.03
JJA	1070	0.84	0.73	0.44
SON	691	0.38	0.31	0.28
DJF	673	0.12	0.09	0.12
all year	4920	0.84	0.62	0.86

Table 2: Statistics of the retrieved NH_3-OASIS measurements depending on the season (MAM for March/April/May, JJA for June/July/August, SON for September/October/November, DJF for December/January/February), and for all the calendar year. (No.: Number of spectra, Mean, Median and Standard deviation). Total columns are given in 1 $\times 10^{16}$ molecules cm^{-2}.