Interactive comment on “Atmospheric ammonia (NH_3) over the Paris megacity: 9 years of total column observations from ground-based infrared remote sensing” by B. Tournadre et al.

Review of Tournadre et al. in AMT

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

Anonymous Referee #1

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

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

Minor comments.

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

Authors: Clarified.
The PROFFIT retrieval algorithm is a well-recognized method within the NDACC community and the present work on NH_3 is based on the HITRAN 2008 spectroscopic database. For the intensities of the relevant lines of the ν_2 band used in our retrieval, an uncertainty index of 4 is generally given (i.e. between 10% and 20%). A paper by Down et al. 2013 compares several experimental sources for NH_3 intensities in the region 770-1200 cm^{-1} with a consistency better than ~4%. The best theoretical total band intensity for the ν_2 band is reported as 2.26×10^{-17} cm^{-1}/(molecule cm^{-2}) as compared to the total band intensity of 2.21×10^{-17} cm^{-1}/(molecule cm^{-2}) in HITRAN 2014, i.e. a difference of 2 % consistent with the uncertainty quoted previously. This systematic uncertainty is certainly contributing to a small fraction of the retrieval uncertainty on the NH_3 column given in the

present paper. The residuals of the fit as seen in Figure 2 and Figure 3 are smaller than 2 % and some residuals do present some correlation with NH_3 lines. However, the effect is within the stated uncertainty of the retrieved column amount. Several effects are intermixed in the simultaneous retrieval of NH_3 together with CO_2 and H_2O, the lines of which have to be fitted properly. Uncertainty on air-broadening coefficients of NH_3 and their temperature dependence and also the line-mixing effects should have also a contribution. So the residuals shown in the figures are to be considered as typical and can vary from one fit to the other.
To have a compromise about these complex question concerning spectroscopy, we propose these updated sentences (Page 6, Lines 31-34 and Page 7, Line 1) in the second revised version. “The total errors are dominated by the combination of uncertainties in the spectroscopic parameters (including also the interfering species), the noise in the spectra and the hypotheses on the retrieval (*a priori* profile of NH_3, forward model uncertainties). They are comparable to those estimated by Dammers et al. (2015) for a high resolution ground-based station at Bremen (Germany). In complement to these, according to a review paper on NH_3 spectroscopic parameters (Down et al., 2013) the uncertainty of 20% on line intensities is probably a worst case estimate.”

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

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

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

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

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

Authors: Clarified. We understand the fact that IASI data are derived from a statistical approach providing in some cases negative values. However, we chose to exclude all values with too high uncertainty (>100%) and without physical meaning such as negative ones. We prefer to avoid highly uncertain retrievals. The large majority (98%) of NH_3-IASI retrieval corresponding to small NH_3 abundances are screened by the retrieval error filter. Therefore, excluding negative values has a negligible effect on the comparison of IASI and OASIS datasets.

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

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

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

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

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

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

Minor edits

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

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

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

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

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

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

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

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

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

8. Page 4, Line 20-21: The part about section 3.3 needs to be rewritten as it still point to the previous version of the paper.
Authors: Agreed. We apologize for this error in the introduction with the former section 3.3. A consistent sentence with section 3.3 has been added in the second revised paper (Page 4 Lines 26-27) "Finally, in Section 3.3, a few tests are performed using a NH_3 profile retrieval scheme applied to OASIS spectra with a Tikhonov-Phillips regularization, showing the vertical sensitivity to NH_3 provided by OASIS measurements. "

9. Page 5, Line 27, mention the green arrows in the figure.
Authors: Added. We have mentioned in comma (Page 5 Line 32) that the strong spectral signatures of ammonia are pointed out by green arrows in Figures 2 and 3 "The strong spectral signatures of ammonia (pointed out by green arrows in Figures 2 and 3). We also added one sentence about green arrows in each caption of Figures 2 and 3.

10. Page 11 Line 2, add "a" between "FTIR instruments" and "moderate spectral resolution".
Authors: Added. The suggested change has been included.

References

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

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

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

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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 $0.1\ 10^{16}$ molecules cm^{-2} in winter to $10\ 10^{16}$ 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 (including agriculture, urban traffic, particle-to-gas conversion, sewage, industrial activities) and sinks (wet and dry deposition, gas-to-particle conversion) (Galloway et al., 2003; Behera et al., 2013; Chang et al., 2016; Van Damme et al., 2018).

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; Dammers et al., 2019). 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 (Bressi et al., 2013; Petit et al., 2014; 2015), 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.

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. A few observations were first reported from space using an advanced IR sounder (Beer et al., 2008) which enables retrievals of atmospheric NH_3. 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 for different trace species (Griesfeller et al., 2006; Strong et al., 2008; Buchholz et al., 2017) and also recently for ammonia (Dammers et al., 2016, 2017). 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). The atmospheric NH_3 time-series focusing on seasonal variability is provided in Section 3.1, while Section 3.2 gives a comparison between the NH_3-OASIS columns and the NH_3-IASI satellite data. Finally, in Section 3.3, a few tests are performed using a NH_3 profile retrieval scheme applied to OASIS spectra with a Tikhonov-Phillips regularization, showing the vertical sensitivity to NH_3 provided by OASIS measurements.

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 (pointed out by green arrows in Figures 2 and 3), 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 the combination of uncertainties in the spectroscopic parameters (including also the interfering species), the noise in the spectra and the hypotheses on the retrieval (a priori profile of NH_3, forward model uncertainties). They are comparable to those estimated by Dammers et al. (2015) for a high resolution ground-based station at Bremen (Germany). In complement to these, according to a review paper on NH_3 spectroscopic parameters (Down et al., 2013) the uncertainty of 20% on line intensities is probably a worst case estimate. 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 a 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 concentrations 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 for those with absolute errors lower than $0.5\ 10^{16}$ molecules cm^{-2}, and retrievals with no physical sense (negative values). The majority of IASI retrievals corresponding to weak NH_3 abundances are screened out by the relative error criterion, thus the exclusion of negative values has a negligible effect in the comparisons.

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:

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

The average of the absolute differences is -0.08 10^{16} molecules cm^{-2}, with a root mean squared error (RMSE) equal to 0.49 10^{16} molecules cm^{-2} and a standard deviation of error (STDE) equal to 0.48 10^{16} molecules cm^{-2}. The mean absolute difference is a factor 10 smaller than the average values of the NH_3 abundances (0.78 10^{16} and 0.70 10^{16} molecules cm^{-2} respectively for OASIS and IASI) and also smaller than OASIS total retrieval errors (20 to 35 %). 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 NH_3-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 has only 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 a 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 0.1 10^{16} molecules cm^{-2} in winter to 10 10^{16} 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 the combination of uncertainties in the spectroscopic parameters (including also the interfering species).

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 for NH_3-OASIS total columns greater than 1.5 10^{16} molecules 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 -0.08 10^{16} molecules cm^{-2} between the two datasets, which represents 10% of the average of the values in the range of 0-1.5 10^{16} molecules cm^{-2}. 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. First tests with a different a priori profile for NH_3 show a significant reduction of the residuals between the radiance spectra measured by OASIS and those simulated by PROFFIT.

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.

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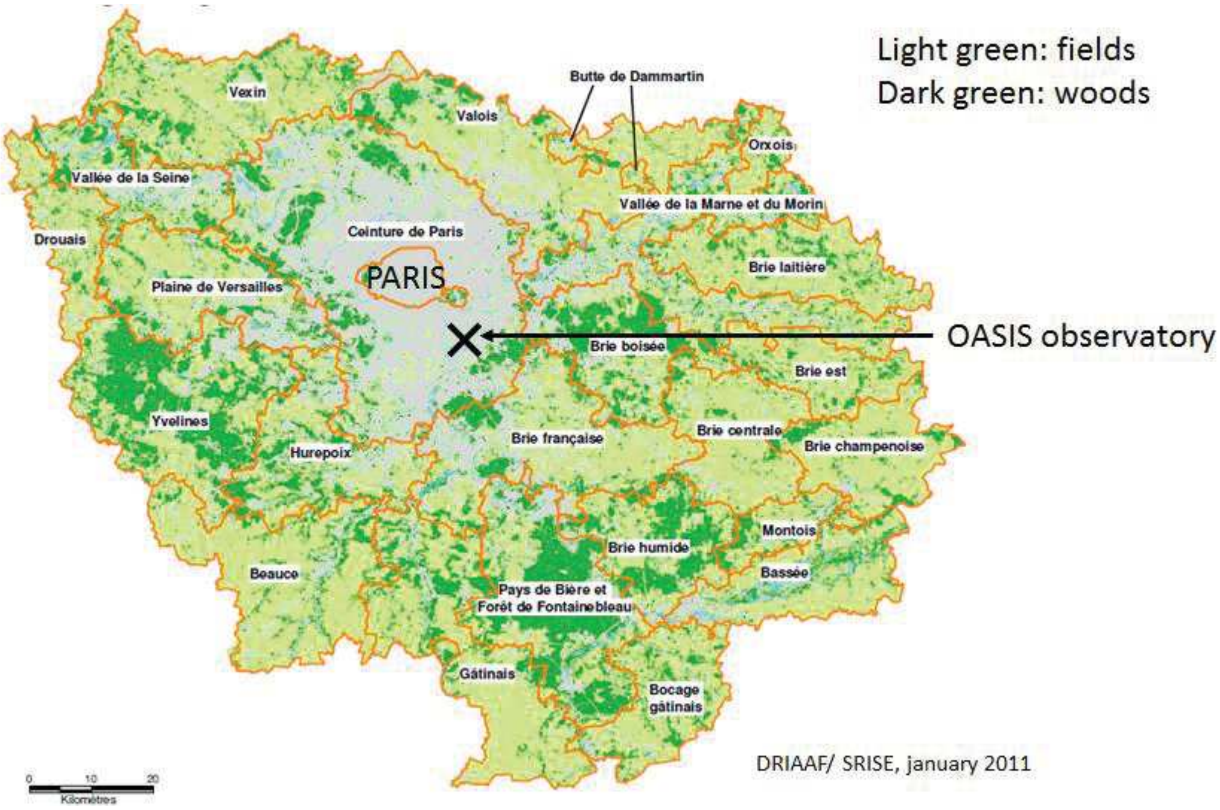


DRIAAF/ SRISE, january 2011

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).

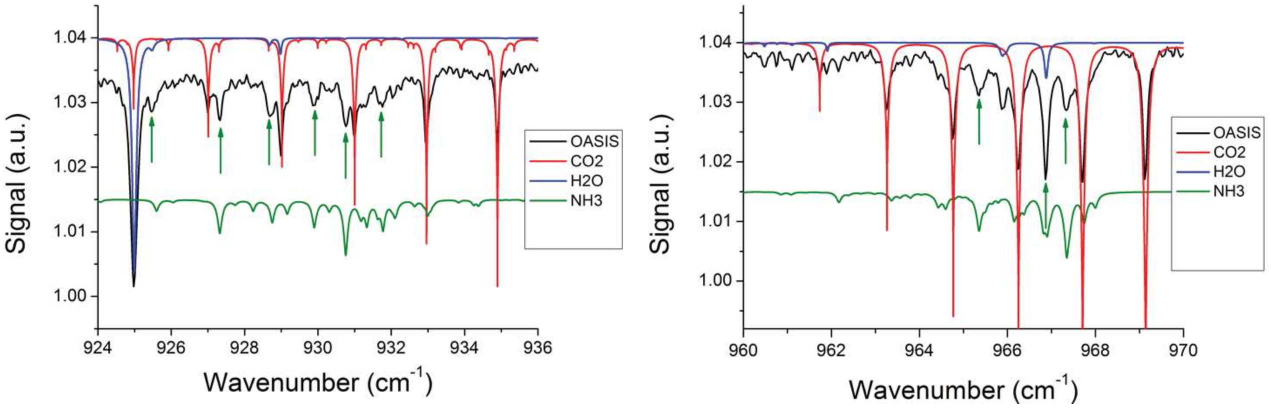


Figure 2: Measured spectrum for both spectral windows obtained with the BRUKER Vertex 80 at Creteil on 21 March 2012, with individual contributions of the main absorbing species represented from the atlas of Meier et al. (Meier et al., 2004) in the first (on the left) and second (on the right) spectral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

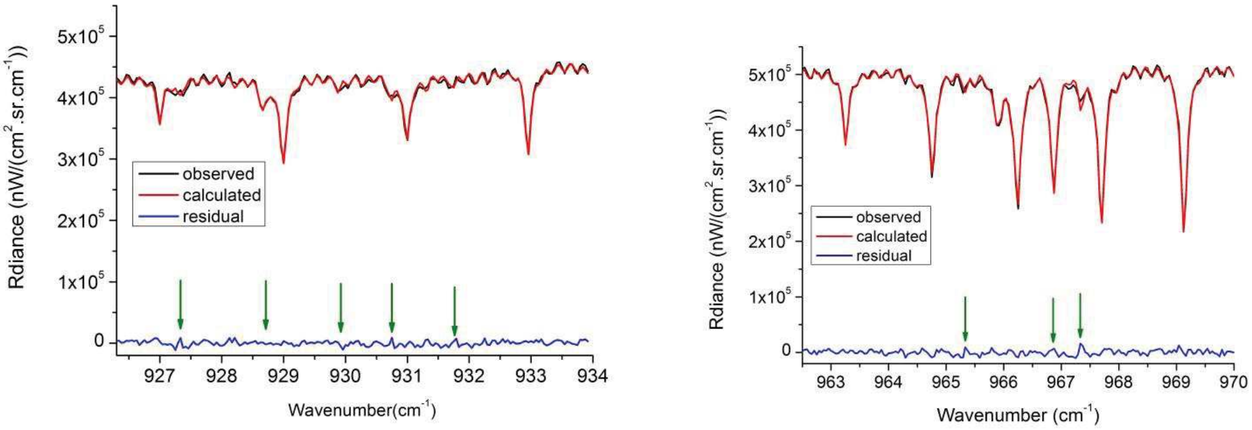


Figure 3: Observed (black line) and calculated spectrum (red line) in radiance unit (nW/(cm^2.sr.cm^{-1})) for both spectral windows measured with the BRUKER Vertex 80 in Creteil on the 21 March 2012 with the fitting residuals (blue line). Green arrows indicate locations of the strong ammonia features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

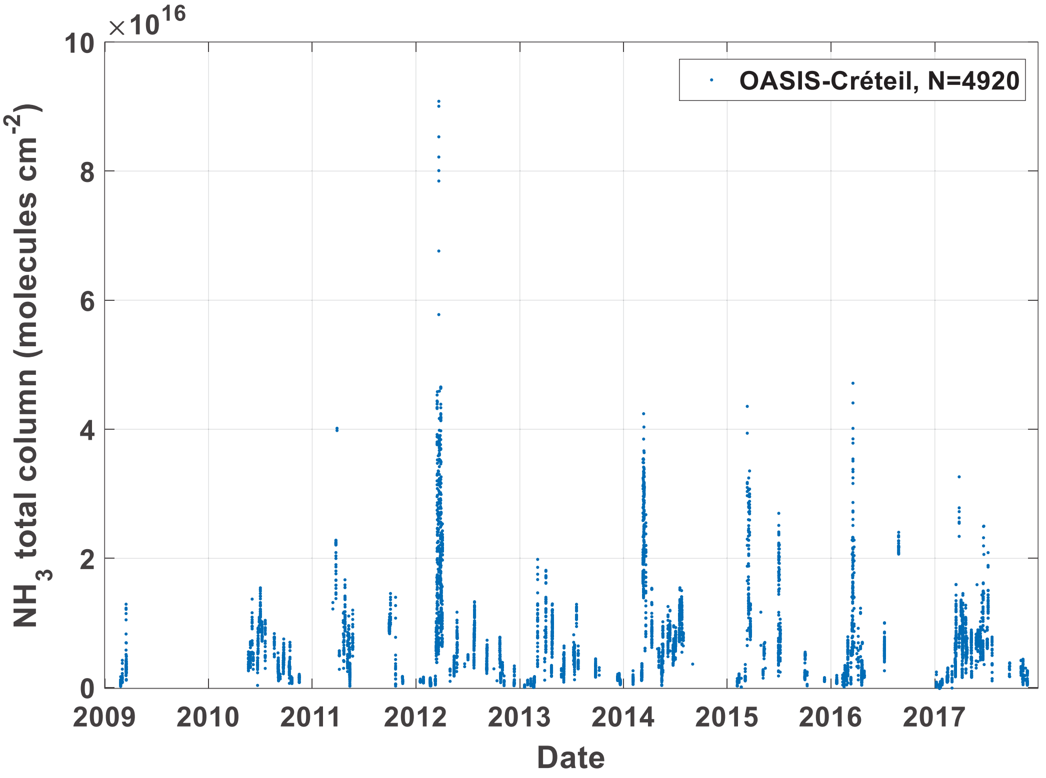


Figure 4: First multi-year time series of NH_3 total columns derived from OASIS measurements over Paris, retrieved from 4920 infrared atmospheric transmission spectra measured during 234 days between 2009 and 2017.

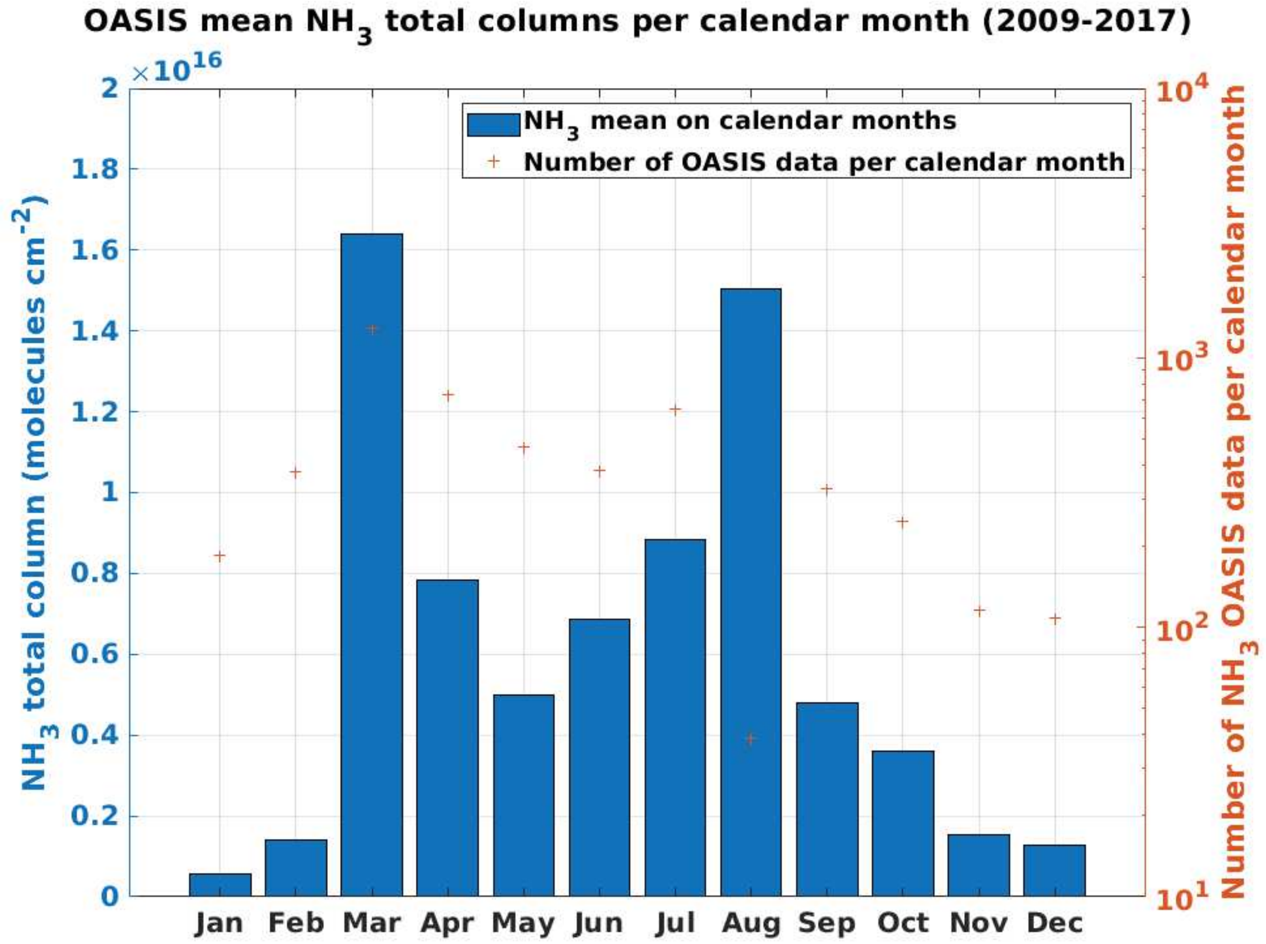


Figure 5: Average annual cycle of monthly NH_3 total columns (molecules cm^{-2}) observed by OASIS over Paris, averaged over the 2009-2017 period. The red crosses represent the number of OASIS data per calendar month on a log scale (right axis).

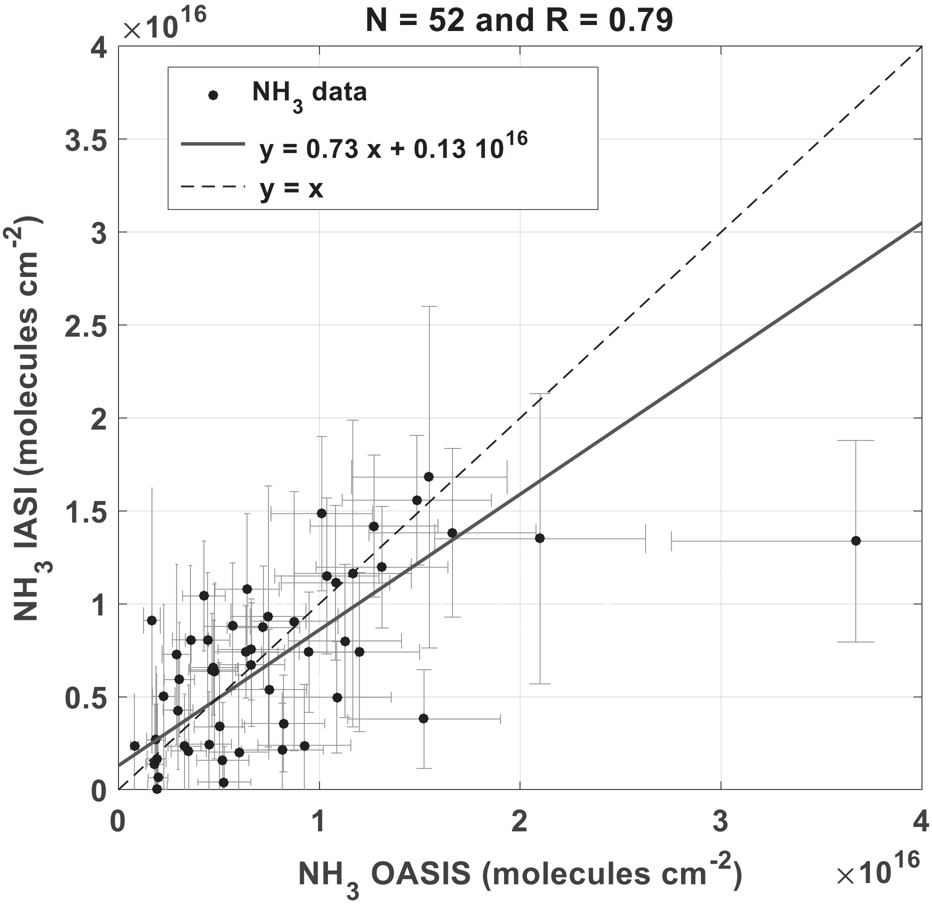


Figure 6: Correlations between the FTIR/OASIS and IASI NH_3 total columns fulfilling the temporal and spatial coincidence criteria: a time difference smaller than 30 min, and a 15 km radius centered on the ground-based FTIR station. The dashed line is the straight equation with slope 1. 5

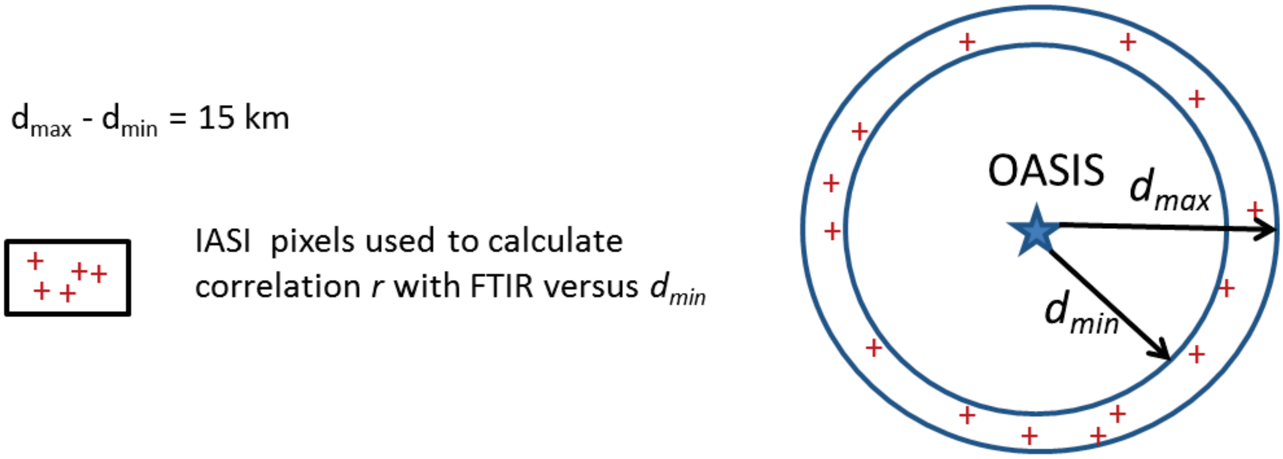


Figure 7: Description of the 15-km rings centred on OASIS observatory that were used to select different IASI pixels for the correlation with FTIR data.

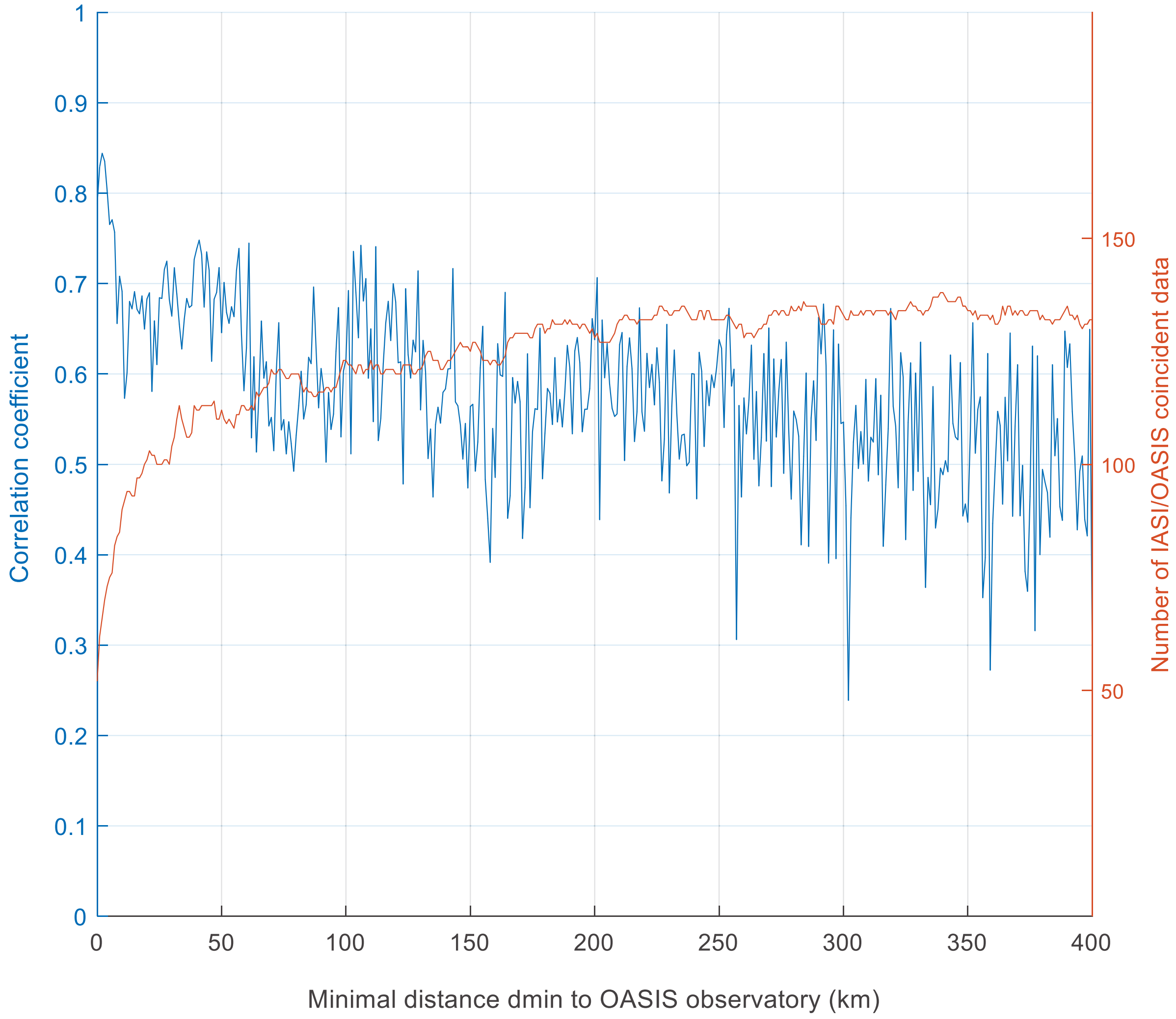


Figure 8: Correlation coefficients R (blue lines, left axis) between IASI and ground-based FTIR observations with temporal sampling difference smaller than 30 min, as a function of *dmin* to OASIS observatory, considered for the calculation of the 15 km wide rings. The data (orange lines, right axis)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

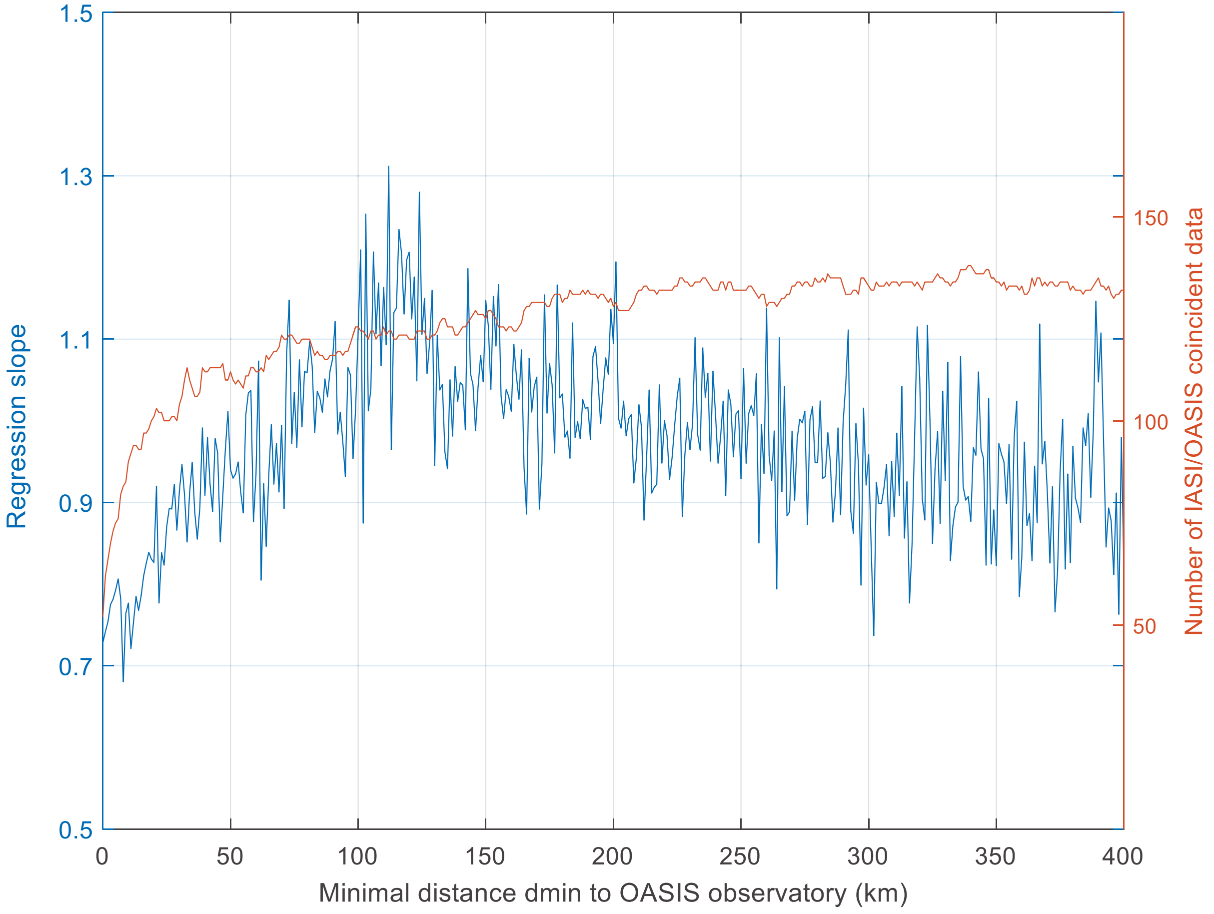


Figure 9: Regression slope (blue lines, left axis) between IASI and ground-based FTIR observations with temporal sampling difference smaller than 30 min, as a function of *dmin* to OASIS observatory, considered for the calculation of the 15 km wide rings. The data (orange lines, right axis) show the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

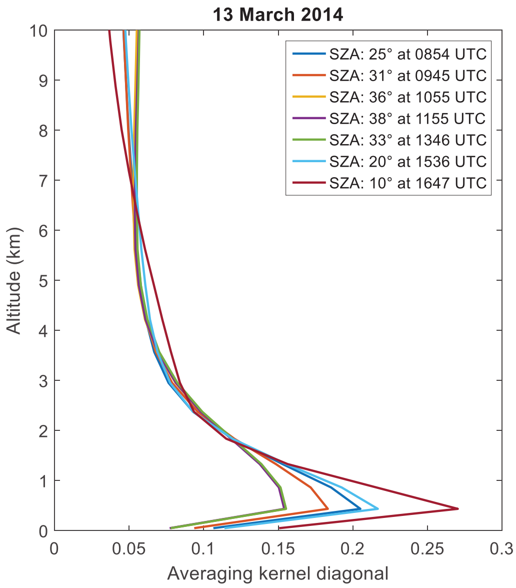
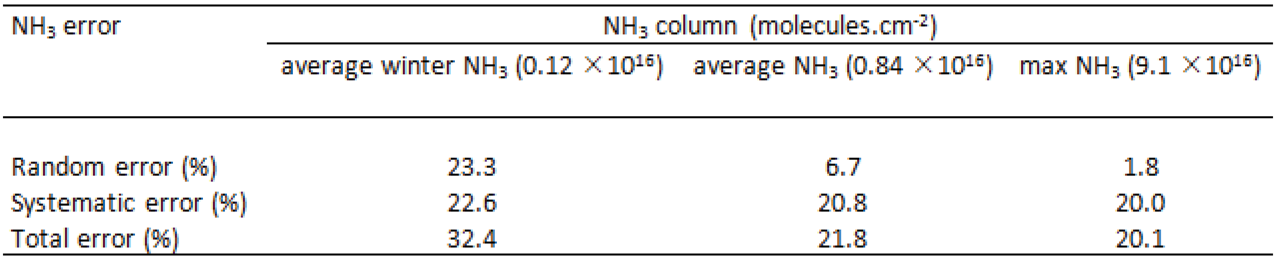


Figure 10: Typical NH_3-OASIS averaging kernel diagonal elements, illustrated on the 13 March 2014 at different times of the day and Solar Zenith Angles (SZA in degree) and using spectroscopic data from the HITRAN 2008 (HIT08) database (except for CO_2 lines).



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 (×10^{16} molecules.cm^{-2})	Median (×10^{16} molecules.cm^{-2})	Standard deviation (×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 ×10^{16} molecules cm^{-2}.