

# Validation of ammonia satellite retrievals with ground-based FTIR

Enrico Dammers<sup>1</sup>, M. Palm<sup>2</sup>, Martin Van Damme<sup>3</sup>, Mark W. Shephard<sup>4</sup>, Lieven Clarisse<sup>3</sup>, Karen E. Cady-Pereira<sup>5</sup>, Simon Whitburn<sup>3</sup>, Pierre Francois Coheur<sup>3</sup>, M.Schaap<sup>6</sup> and Jan Willem Erisman<sup>1,7</sup>

<sup>1</sup> Cluster Earth and Climate, Department of Earth Sciences, Vrije Universiteit Amsterdam, Amsterdam, the Netherlands.  
[E.Dammers@vu.nl](mailto:E.Dammers@vu.nl)

<sup>2</sup> Institut für Umweltphysik, University of Bremen, Bremen, Germany

<sup>3</sup> Spectroscopie de l'Atmosphère, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles (ULB), Brussels, Belgium

<sup>4</sup> Environment Canada, Toronto, Ontario, Canada

<sup>5</sup> Atmospheric and Environmental Research (AER), Lexington, Massachusetts, USA

<sup>6</sup> TNO, Climate Air Sustainability, Utrecht, the Netherlands

<sup>7</sup> Louis Bolk Institute, Driebergen, the Netherlands

## Abstract

Global emissions of reactive nitrogen have increased due to human activities and are estimated to be a factor four larger than pre-industrial levels. Concentration levels of NO<sub>x</sub> are declining, but ammonia (NH<sub>3</sub>) levels are increasing globally. At its current concentrations NH<sub>3</sub> poses a large threat to both the environment and human health. Still relatively little is known about the total budget as well as the global distribution. Surface observations are sparsely available, mostly for north-western Europe, the United States and China, and are limited by the high costs and poor spatial and temporal resolution. The lifetime of atmospheric NH<sub>3</sub> is short, in the range of several hours to a few days and the existing surface measurements are not sufficient to estimate global concentrations. Space-based InfraRed-sounders such as the Infrared Atmospheric Sounding Interferometer (IASI) and the Cross-track Infrared Sounder (CrIS) enable global observations of atmospheric NH<sub>3</sub> which can overcome the limitations of existing surface observations. One challenge with satellite NH<sub>3</sub> retrievals is that they are complex and require extensive validation. Presently only a limited number of satellite NH<sub>3</sub> validation campaigns have been performed with limited spatial, vertical and temporal coverage. In this study we demonstrate the use of a recently developed retrieval methodology for ground-based Fourier Transform Infrared Spectroscopy (FTIR) instruments to obtain vertical concentration profiles of NH<sub>3</sub>. We will use the retrieved profiles from eight stations with a range of NH<sub>3</sub> pollution levels to validate satellite NH<sub>3</sub> products.

## Key Words

Ammonia, atmosphere, retrieval validation, FTIR, retrieval strategy

## Introduction

Global emissions of reactive nitrogen (Nr) have increased substantially these past decades with current emission estimates around a factor of four times larger than pre-industrial totals. The increase of Nr causes a cascade of problems from damage to ecosystems and reduction in biodiversity (Erisman et al., 2008) to poor air quality and hazards to health (Pope et al., 2009). Ammonia (NH<sub>3</sub>) is an important component of Nr with global emissions totalling up to 50% of the total reactive nitrogen (Reis et al., 2009). Although it is known that NH<sub>3</sub> is a major threat to human health and the environment there is still a large uncertainty in its total budget and global distribution (Sutton et al., 2013). Only a sparse number of surface observations are available mainly in Europe, the United States and China (Van Damme et al., 2015a). Furthermore, in situ measurements are mostly performed with low temporal resolutions due to high cost of reliable high resolution measurements. Measurements are further hampered by sampling artefacts such as the evaporation of ammonium nitrates (for example on inlets), and the ready reaction of NH<sub>3</sub> with other species (von Bobruzki et al., 2010). Open path instruments are increasingly used (Sintermann et al., 2016) but are expensive and currently only operated in one country scale measurement network. The lifetime of NH<sub>3</sub> is short, on the order of hours to days; this combined with the poor resolution of most available measurements leads to large errors in the quantification of the Nr budgets. Finally there is a lack of knowledge on the vertical distribution of NH<sub>3</sub> which further increases the uncertainty in the budget estimates.

Satellite observations have a high potential of increasing our knowledge. NH<sub>3</sub> retrievals being applied to IR-sounders such as the Infrared Atmospheric Sounding Interferometer (IASI) and the Cross-track Infrared Sounder (CrIS) provide continuous global NH<sub>3</sub> distributions without the need for expensive large scale measurement networks (Shephard et al., 2015, Van Damme et al., 2014). Global satellite observations have

the potential to increase our knowledge on distributions and seasonal cycles due to their global coverage and daily observations (Van Damme et al., 2015b). However, the state of validation of these products needs more attention with only a handful of studies available with limited spatial, vertical and temporal resolution (Van Damme et al., 2015a; Sun et al., 2015). A recently developed retrieval strategy for Fourier Transform InfraRed spectroscopy (FTIR) instruments (Dammers et al., 2015) to obtain NH<sub>3</sub> profiles from solar spectra provides vertical NH<sub>3</sub> for FTIR sites around the world. In a follow-up paper the IASI- NH<sub>3</sub> product by Van Damme et al. (2014a) was compared to NH<sub>3</sub> total columns derived from FTIR observations from nine sites around the world. In this study we follow a similar approach and apply it to two other NH<sub>3</sub> satellite retrievals, respectively the IASI-NN retrieval by Whitburn et al. (2016) and the CrIS- NH<sub>3</sub> retrieval by Shephard et al. (2015).

## Methods

### *Satellite ammonia products*

In this study we use three satellite NH<sub>3</sub> products. Two of the products are based on the IASI observations, the IASI-LUT retrieval (Van Damme et al., 2014a) and the more recently development IASI-NN retrieval (Whitburn et al., 2016). The third product is the CrIS Fast Physical Retrieval for NH<sub>3</sub> by Shephard et al., (2015). made available for a preliminary study. Both IASI products are based on the calculation of a dimensionless spectral index (Hyperspectral Range Index; HRI), which is representative of the amount of NH<sub>3</sub> in the measured column. In the IASI-LUT retrieval the HRI is converted to a total column value using a look-up-table (LUT). The LUT is built using a large number of forward simulations for various atmospheric conditions, linking the thermal contrast (i.e. the difference in air temperature at 1.5 km altitude and the Earth's skin temperature) and HRI to a total column density. The IASI-NN retrieval also relies on the calculation of a HRI, but uses a neural network for the radiance conversion to an NH<sub>3</sub> total column. Instead of a single thermal contrast the neural network uses complete temperature, pressure and humidity vertical profiles. It also allows the use of third party NH<sub>3</sub> profile information to improve the representation of the vertical distribution. The CrIS retrieval is a physically-based optimal estimation algorithm described by Rodgers (2000), which reduces the difference between the measured spectrum and a radiative transfer model. The CrIS retrieval provides a profile, similar to the FTIR, and uses a specific a priori selection based on the initially observed NH<sub>3</sub> infrared spectral signature and thermal contrast. Earlier validation attempts show a ~ -30% bias for the IASI-LUT total columns (Dammers et al., 2016). Estimates for CrIS show a positive retrieval bias of ~6% (+20%) when comparing the retrieved profiles with simulated "true" profiles, which can be considered as a lower bound as no systematic errors were included.

### *FTIR ammonia product*

The FTIR ammonia product is a set of NH<sub>3</sub> profiles which are retrieved from ground-based solar FTIR absorption spectra. The FTIR retrieval methodology is based on Dammers et al. (2015). The methodology uses two micro-windows in a relatively clean infrared spectral region. A-priori profiles are adapted to local NH<sub>3</sub> concentrations (e.g. estimates in some cases based on model results). In this study we use observations from eight sites which are described in Dammers et al. (2015) excepting the Mexico City site. Overall the FTIR observations have an error of ~30% or less depending on the site, mostly caused by uncertainties in the spectroscopic parameters (Dammers et al., 2015).

### *Data criteria and analysis*

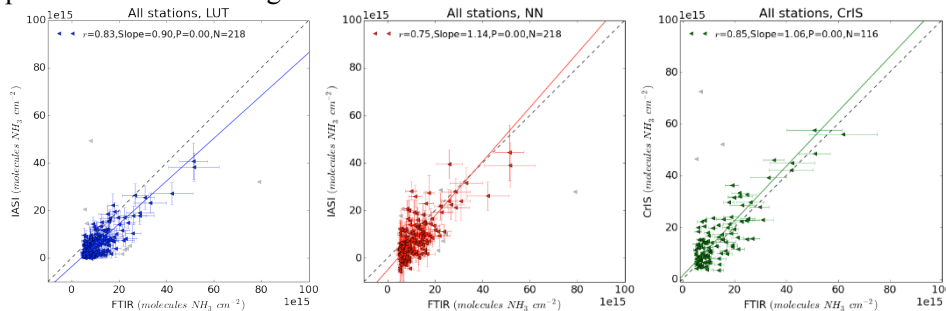
Due to the high variability of NH<sub>3</sub> in space and time we apply a strict spatial and temporal collocation criterion of 90 minutes between observation sampling time and a maximum difference of 25 km in space. Observations are further excluded if there is a height difference of above 300m between the FTIR site and satellite observations, this includes any terrain between the two. For the IASI observations a surface temperature filter is applied to ensure the exclusion of frozen soils. Furthermore we only use observations with a cloud cover below 10%. In the interest of time for this initial analysis we only performed the CrIS retrievals where the FTIR observed values are above  $5 \times 10^{15}$  molecules cm<sup>-2</sup>. This criterion will be removed for future CrIS retrievals used in the FTIR comparisons, but it is expected to have minimal impact on the comparisons as most of these cases will have limited satellite information content. For consistency a similar filter was applied to the IASI values. The FTIR averaging kernels are applied to the satellite observations to account for the effects of the a-priori information and vertical sensitivity of the FTIR retrieval. Satellite observed profiles are interpolated to the FTIR altitude grid to which the averaging kernel is applied following eq. 1,

$$\hat{x}_{sat} = x_{ftir}^{apriori} + A(x_{sat}^{mapped} - x_{ftir}^{apriori}) \quad (1)$$

The  $\hat{x}_{sat}$  profiles are then converted to total columns which are used in the analysis. Since IASI does not provide averaging kernels in this study we simply applied the FTIR observational operator to the satellite observations. However, since CrIS does provide averaging kernels they will also be taken into account for future CrIS/FTIR comparisons. A 3-sigma outlier rejection method is applied before calculating the statistics to reduce the effect of the few outliers. IASI outliers from both datasets are calculated using the IASI-LUT values.

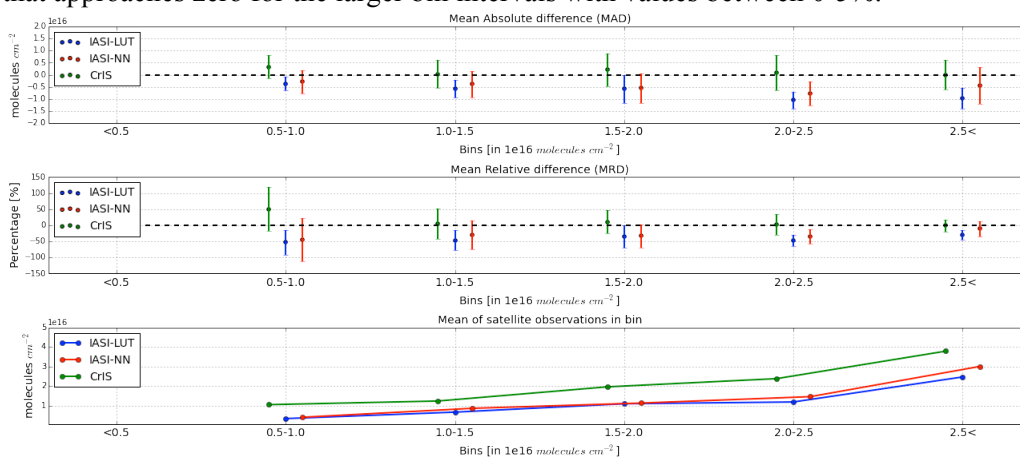
## Results

Figure 1 shows a direct comparison of the IASI and FTIR columns. All three satellite products show good correlations between 0.75 and 0.85 with slopes around the 1:1 line (0.9-1.15). The CrIS retrieval shows a larger number of increased NH<sub>3</sub> levels which can be explained by the overpass time 13.30 P.M. compared to the IASI overpass at 9.30 AM. During the day NH<sub>3</sub> emissions typically increase which makes it more probable to observe high column values.



**Figure 1. Scatterplot of FTIR vs satellite total columns for a combination of all sites. Left panel shows IASI-LUT(blue), middle panel shows IASI-NN(red), right panel shows CrIS(green). Inserted in the top left of each panel are the statistics for each of the comparisons (r the correlation, the slope, P value and the number of observations). The line shows the regression result. Removed outliers shown in grey.**

The criterion to only use FTIR values influences the results as the LUT retrieval shows improved results compared to the study by Dammers et al. (2016). Observations with low total columns will have a greater uncertainty due to the increased ratio of measurement noise to footprint of the NH<sub>3</sub> molecules in the spectrum. To account for this effect the satellite observations are split into a number of bins using the total columns measured with the FTIR. Each of the bins covers a range of FTIR values with an increment size of  $5 \times 10^{15}$  molecules  $\text{cm}^{-2}$ . For each of the bins we calculate the mean absolute difference (MAD) and the mean relative difference (MRD). The mean of the satellite observations in each bin are also shown to make it easier to interpret the relative and absolute differences. Figure 2 shows the results of this approach. The CrIS retrieval shows a small overestimation for the smallest magnitude bin, as indicated by the MAD and MRD, that approaches zero for the larger bin intervals with values between 0-5%.



**Figure 2. Mean Absolute (MAD) and Relative (MRD) differences plotted as a function of the FTIR total column [molecules  $\text{cm}^{-2}$ ].**

The IASI-LUT retrieval shows similar results as in the study by Dammers et al. (2016). Each of the bins shows an underestimation, which increases in absolute size for the higher bins. At the same time the relative

differences become smaller following the decreased influence of any measurement noise. As described in Van Damme et al. (2015a) the retrieval uses fixed profiles for the NH<sub>3</sub> (scales with the HRI) and atmospheric parameters for all the retrieved columns. Deviations from the chosen atmospheric parameters can have a large effect on the retrieved columns, similarly any change in the vertical distribution of the NH<sub>3</sub> will induce a difference in the observed values. The IASI-NN retrieval improves on this by using the neural network to account for some of the atmospheric parameters. This has a positive effect as can be seen in Figure 2 with both smaller absolute and relative differences. An underestimation still remains which is probably due to the fixed profiles. Another cause could be the line parameters used in the retrieval with uncertainties up to 20% to be expected (Dammers et al., 2015).

## Conclusion

In this study we analysed the performance of three NH<sub>3</sub> satellite products. We showed that all three retrievals perform well with correlations to ground-based solar FTIR remote sensing measurements around the  $r \sim 0.8$ . We find an underestimation in the retrieved columns for both IASI retrievals and a small over estimation for the CrIS retrieval. Both are in the -50% - +50% range depending on the used total column interval. The IASI-NN shows an improvement over the former IASI-LUT retrieval as the MAD and MRD become smaller although the correlation coefficients do decrease a bit. Another improvement in IASI-NN will be tested in future work with the addition of specific boundary layer height for each site, as a restriction/improvement over the fixed profile approach. The CrIS retrieval shows excellent results, especially for value  $> 1e15$  molecules cm<sup>-2</sup>, although it should be noted that relative to IASI there is a reduced number of observations used in this initial comparison. Future work will include more CrIS retrievals in the low magnitude bin, as well as a full profile comparison and the application of the CrIS satellite averaging kernels.

## References

- von Bobruzki, K. et al., 2010. Field inter-comparison of eleven atmospheric ammonia measurement techniques. *Atmos. Meas. Tech*, 3(1), pp.91–112.
- Dammers, E. et al., 2015. Retrieval of ammonia from ground-based FTIR solar spectra. *Atmospheric Chemistry and Physics*, 15(22), pp.12789–12803.
- Dammers, E. et al., 2016. An evaluation of IASI-NH<sub>3</sub> with ground-based FTIR measurements 2. *Atmospheric Chemistry and Physics Discussions*, p.under–review.
- Erismann, J.W. et al., 2008. How a century of ammonia synthesis changed the world. *Nature Geoscience*, 1(10), pp.636–639.
- Pope III, C.A., Ezzati, M. and Dockery, D.W., 2009. Fine-particulate air pollution and life expectancy in the United States. *New England Journal of Medicine*, 360(4), pp.376–386.
- Reis, S. et al., 2009. Reactive nitrogen in atmospheric emission inventories. *Atmospheric Chemistry and Physics*, 9(19), pp.7657–7677.
- Sintermann, J. et al., 2016. A miniDOAS instrument optimised for ammonia field measurements. *Atmospheric Measurement Techniques*, 9(6), pp.2721–2734.
- Shephard, M.W. and Cady-Pereira, K.E., 2015. Cross-track Infrared Sounder (CrIS) satellite observations of tropospheric ammonia. *Atmospheric Measurement Techniques*, 8(3), pp.1323–1336.
- Sutton, M.A. et al., 2013. Towards a climate-dependent paradigm of ammonia emission and deposition. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, 368(1621), p.20130166.
- Van Damme, M. et al., 2014. Global distributions, time series and error characterization of atmospheric ammonia (NH<sub>3</sub>) from IASI satellite observations. *Atmospheric chemistry and physics*, 14(6), pp.2905–2922.
- Van Damme, M. et al., 2015. Towards validation of ammonia (NH<sub>3</sub>) measurements from the IASI satellite. *Atmospheric Measurement Techniques*, 8(3), pp.1575–1591.
- Van Damme, M. et al., 2015. Worldwide spatiotemporal atmospheric ammonia (NH<sub>3</sub>) columns variability revealed by satellite. *Geophysical Research Letters*, 42(20), pp.8660–8668. Available at: <http://doi.wiley.com/10.1002/2015GL065496> [Accessed November 16, 2015].
- Whitburn, S. et al., 2016. A flexible and robust neural network IASI-NH<sub>3</sub> retrieval algorithm. *Journal of Geophysical Research: Atmospheres*.