

7. Summary and Outlook

In this chapter I will first give an overall summary of the results supported by answering the research questions listed in the introduction. This will be followed by a section on my observations working with NH_3 measurements and research in general and I will couple that to a future outlook.

7.1 Summary

7.1.1 Aim and approach

Large uncertainties exist in the total atmospheric budget and distribution of NH_3 in both space and time (Erisman et al., 2007; Sutton et al., 2013). Since the first reported satellite observations of NH_3 with the Tropospheric Emission Spectrometer (TES, Beer et al., 2008), remote sensing of NH_3 with satellite instruments has rapidly developed. Recently, several NH_3 retrievals were developed for satellite infrared instruments such as the Infrared Atmospheric Sounding Interferometer (IASI, Clarisse et al., 2009; Van Damme et al., 2014a) and Cross-track Infrared Sounder (CrIS, Shephard and Cady-Pereira, 2015). The NH_3 products have the potential to be (and are) used for various applications such as concentration monitoring, emission and deposition estimates (Zhu et al., 2013; Van Damme et al., 2015b; Whitburn et al., 2015; Luo et al., 2015), and model validation (Heald et al., 2012; Zhu et al., 2013; Schiferl et al., 2014, 2016; Van Damme et al., 2014b), but without validation the overall performance of the products and quantitative conclusions made in studies using the satellite-products can be questioned. NH_3 measurements are scarce with most measurement networks and measurement campaigns based in the Northern Hemisphere and especially in the United States and North-western Europe. Earlier research showed that validating the IASI product with only surface concentrations measurements was unfeasible, mostly related to the large variability of NH_3 concentrations and the lack of knowledge on its vertical distribution (Whitburn et al., 2016, for an overview of all observations).

The goal of this PhD research was the validation of remote sensed NH_3 distributions with specific attention to the vertical distribution of NH_3 . A crucial aspect was the assessment of the vertical distribution of NH_3 in the atmosphere using FTIR instruments and tower measurements with open-path instruments. Furthermore, special attention was given to the uncertainties in the individual products.

At the start of this PhD research a cooperation with the Insitut für Umweltphysik at the Universität of Bremen was started, to explore the feasibility of retrieving NH_3 from FTIR solar spectra. The value of the measurements from these instruments has been recognized by the NDACC and TCCON networks, which operate FTIR sites around the world. The development of the FTIR- NH_3 retrieval (Chapter 2, Dammers et al., 2015) was key to this thesis. The possibility to measure vertical profiles of NH_3 for a range of concentration regimes, from high intensity farming regions (Bremen) to sites with almost no NH_3 burden (Jungfraujoeh), enabled the creation of a valuable FTIR- NH_3 dataset. The FTIR observations have never been interpreted for NH_3 on this scale and here we standardised the method to obtain NH_3 profiles and quantified its uncertainty.

The FTIR- NH_3 dataset was extended with more sites becoming available for use during the course of time. The dataset was first used for the evaluation of the IASI-LUT dataset (Chapter 3, Dammers et al., 2016a) resulting in an improved estimate of the uncertainty in the IASI-LUT observations, showing the consistency of the observations as well as the limitations for sites with low NH_3 concentrations to be represented by the satellite data. After this initial product evaluation the datasets were used for the validation of the CrIS-FRP (Chapter 4,

Dammers et al., 2017a) and the IASI-NN products (Dammers et al., 2016b, Dammers et al., 2017a).

This PhD was part of the ALW-GO/12-36 grant and one of the goals was to organize and perform a field campaign to validate atmospheric NH₃ products obtained through remote sensing and improve the understanding of the vertical distribution of NH₃. The *Measuring atmospheric Ammonia with Remote Sensing* (MARS) field campaign at Cabauw took place between April and October 2014, combining the FTIR-NH₃ instrument with the MARGA instrument and a set-up of mini-DOAS instruments at various levels in the meteorological tower. The campaign was unique through the combination of instruments capable of measuring NH₃ with high temporal resolution in the tower and a FTIR instrument capable of measuring NH₃ at higher altitudes. The data from the field campaign were used to characterize the atmospheric behaviour of NH₃ at Cabauw (Chapter 5, Dammers et al., 2017b) and to explore the use of various vertical profiles needed to scale surface measurements, so that these can be used for comparison with FTIR and satellite observations (Chapter 6, Dammers et al., 2017c).

In the following paragraphs, my main findings are described and the research questions posed at the start of this thesis (Chapter 1) are answered.

7.1.2 Research Questions and outcome

How can one retrieve vertical profiles of ammonia from FTIR spectra and what are the uncertainties of ammonia concentrations derived from the FTIR measurements?

At the start of this PhD, a new retrieval strategy was designed to retrieve NH₃ vertical profiles from solar spectra measured with ground-based FTIR instruments. Various combinations of micro-windows were selected focusing on strong absorption lines of NH₃ while reducing the influence of interfering species such as water vapour (H₂O), Carbon Dioxide (CO₂) and Ozone (O₃) to a minimum. The combination of the two spectral micro-windows MW1 [930.32 – 931.32 cm⁻¹] and MW2 [966.97–967.68 cm⁻¹] showed the best performance, optimizing the information gained while reducing the residual to a minimum. The retrieval was applied to observations from Bremen (53.10° N, 8.85° E), Lauder (45.04° S, 169.68° E), La Réunion (20.9° S, 55.50° E) and Jungfraujoch (46.55° N, 7.98° E) to illustrate the capability of retrieving concentrations for a range of the NH₃ total columns spanning several orders of magnitude. The measurements at Bremen showed the highest total columns with a mean of 13.47×10^{15} [molecules cm⁻²] while the smallest values with a mean of 0.18×10^{15} [molecules cm⁻²] were retrieved for Jungfraujoch. The retrieved total columns showed station-specific seasonal cycles which are consistent with known seasonal cycles of the dominant NH₃ sources in the station surroundings. As for the vertical profiles this thesis shows that for conditions with high surface concentrations of NH₃, in the order of 20 ppb and greater, it was possible to retrieve enough information on the vertical profile with up to 2 and in cases with extremely high concentrations up to 3 independent layers. Most of the retrievals sensitivity comes from the NH₃ in the boundary layer, where the concentration is highest. For conditions with small concentrations, in the order of 3 ppb and smaller, only the total column could be retrieved. The systematic and random errors are dependent on the location and atmospheric NH₃ concentrations, with total errors in the range of 26 % of the total column for retrievals

performed on spectra from Bremen to 34 % for spectra measured at Jungfraujoch. The systematic uncertainty is dominated by the spectroscopic parameters, while the random uncertainty is mostly related to the measurement error. The results are published in Dammers et al. (2015).

What is the overall quality of the recently developed IASI-LUT and CrIS-FRP products?

To create a more representative dataset the FTIR-NH₃ dataset was extended to twelve sites, using most of the sites operating FTIR instruments in the NDACC network. Nine sites with observations between 2008 and 2015 were eventually used for the first evaluation of the IASI-LUT product. The remaining three sites either didn't have measurements coinciding with IASI overpasses or are characterized by total columns far lower than the expected sensitivity of the IASI-LUT product. This thesis demonstrated the importance of strict spatial and temporal collocation criteria, ensuring the comparison of similar air masses and reducing effects from orography, and the short lifetime of atmospheric NH₃. The results of the study (Chapter 3, published in Dammers et al., 2016a) revealed that both the FTIR and IASI-LUT retrieved columns show comparable seasonal cycles for most measurements sites. Medium to high correlations were found for locations with high NH₃ concentrations while correlations are lower for sites with small concentrations. The relation of performance with total column level gives an indication of the detection limit of the IASI instrument.

While the retrieved total columns of the two instruments compared well, IASI-LUT showed an overall mean relative difference (MRD) of -32.4 ± 56.3 % compared to the FTIR total columns. Because of the lack of an averaging kernel the influence of the sensitivity of the IASI instrument could not be explored further. There are several possible factors that might explain the difference. The first difference is the retrieval techniques, with IASI retrieval using the HRI-based approach using fixed profiles instead of retrieving the full shape, possibly restricting more optimal solutions. The lack of an averaging kernel limits the evaluation of the sensitivity of the instrument. Earlier products (Clarisse et al., 2009) showed potentially large variations in the averaging kernels as well as the retrieved profiles. Arguably it would be better to use a larger selection of profiles with the shape of the profiles depending on the vertical distribution of NH₃. Finally, note that although we compare the IASI with the FTIR data, the FTIR retrieved profiles are not perfect. The FTIR instrument does not fully resolve the vertical distribution and uncertainties remains for each retrieved level. Furthermore, the IASI instrument is possibly be more sensitive to NH₃ at higher levels as we shown in the CrIS validation.

The study on the performance of IASI-LUT was followed by the validation of the CrIS Fast Physical Retrieval (CrIS-FPR, Dammers et al., 2017a). Instead of an HRI based approach the CrIS-FRP product uses an optimal estimation approach. Data from seven FTIR sites were used for the validation, due to restrictions in computation time designated for NH₃ retrievals from the CrIS spectra. At the end of this PhD the CrIS retrieval speed has been drastically improved enabling the retrieval of NH₃ from more spectra, but we chose to keep focus on the original seven sites. Similar spatio-temporal restrictions were applied to the CrIS measurements as for the IASI-LUT comparison.

The FTIR and CrIS total columns compared well with a correlation of $r = 0.77$ and a small bias (a slope of 1.02). For concentrations larger than 10.0×10^{15} [molecules cm^{-2}] i.e. ranging from moderate to polluted conditions, the relative difference was found to average ~ 0 to 5% with a standard deviation in the range of 25 to 50%. This is comparable to retrieval uncertainties in both the CrIS and FTIR retrievals. For the smallest total column range, with FTIR total columns smaller than 10.0×10^{15} [molecules cm^{-2}] there are a large number of observations at or near the CrIS noise level (detection limit), and the absolute differences between CrIS and the FTIR total columns become larger. In such cases CrIS shows a positive column bias around $+2.4 \times 10^{15}$ [molecules cm^{-2}] with a standard deviation of 5.5×10^{15} [molecules cm^{-2}], which corresponds to a relative difference of $\sim +50\%$ and a standard deviation of almost 100%. The retrievals were also compared at a profile level. The CrIS retrievals had a good vertical sensitivity down to ~ 850 hPa. At that level the retrieved profiles compared well with a median absolute difference of $0.87 (\pm 0.08)$ ppb and a corresponding median relative difference of $39 (\pm 2) \%$. Similar to the column comparison, most of the absolute and relative differences are in the range of the retrieval uncertainties. The CrIS retrieval does however tend to overestimate the concentrations for levels near the surface for conditions with low surface concentrations. This is probably due to the detection limit of the instrument. At the same time the retrieval shows an underestimation at larger concentrations, possibly due to the a-priori restricting the final retrieval shape and the reduced sensitivity of CrIS in the lowest layers.

To conclude both the IASI and CrIS-NH₃ products show high consistency with the FTIR observations. Both systems are somewhat limited in the observation of NH₃ in less to non-polluted regions (roughly < 3 ppb ground-level concentrations) indicated by the overestimation by the CrIS product and increased underestimation by the IASI products (NN & LUT, Chapter 4). For concentrations in more polluted regions (> 3 ppb) the CrIS product gives high quality observations with most of the uncertainty ($\sim 25\%$) related to the line spectroscopy and measurement noise. Similarly the IASI products (both IASI-NN and -LUT) show consistent results with high correlations although underestimating the concentrations (-30 to -50%), with IASI-NN showing improvements over the LUT product. Compared to the outcome of the FTIR to IASI/CrIS product validation the comparison with the in-situ measurements shows a worse outcome. The performance drop is mostly related to the difference in the location of the in-situ instrument compared to the large footprint of the satellite instrument. One should be careful however in such situations in directly comparing satellite retrieved “surface concentrations” with in-situ observed concentrations, considering the limited amount of information is available from the satellite on the vertical profile. For sites with more homogeneous concentration distribution the effect is less observable and results are highly correlative. I will come back to this point in the answer of the next research questions.

Can tower measurements be used to provide enough information of the ammonia vertical profiles?

Measurements of the vertical distribution of NH_3 are scarce. Only a few airborne and tower measurements are available which usually only cover time periods of a few days or involve measurements with coarse temporal resolutions. The MARS field campaign at Cabauw, the Netherlands was organised to improve the general understanding of the vertical distribution of NH_3 . A selection of instruments installed in and around the meteorological tower at Cabauw (CESAR) were operated between May and October 2014. Four mini-DOAS instruments were installed at levels in the tower (20m and 160m) and cabin beside the tower (1m and 4m), as well as a MARGA instrument with the inlet at the base of the tower(4m). The instruments at and in the tower were supplemented by an FTIR instrument, operated ~ 500 m to the South of the tower. The measurements between May and October 2014 showed large variations in the concentrations, with maximum concentrations reaching ~330 ppb. The lower three mini-DOAS and MARGA measurements showed large differences on an hourly basis, which were shown to originate from multiple measurement artefacts of the MARGA and the lower two mini-DOAS instruments. While the artefacts have an influence on the concentrations measured by the MARGA and the lower two instruments, the concentrations measured with the top two instruments have a smaller uncertainty. The conclusions made in the next sentences are based on the measurements of the top two instruments (20m and 160m). The concentrations measured by the mini-DOAS instruments showed a lot of variability between the instruments. The lower three instruments measured maxima at night while the mini-DOAS at 160m in the tower observed daytime maxima. The analysis of the measurements showed the difference in sources driving the concentration levels. The instrument at 20m had higher concentrations for air masses transported from the north, which is also the direction of the largest local emission sources. The instrument at 160m however, showed the highest concentrations coming from the east pointing at a more regional influence. The measurements illustrated that the daytime boundary layer is well-mixed with only small gradients found between DOAS 20 and DOAS 160. During night time conditions the DOAS at 160 meter was often above the nocturnal boundary layer, with most of the background concentration coming from national or continental long range transport. The well-mixed boundary layer during daytime is an assumption made in several chemistry transport models, which seems to be valid in the case of NH_3 . Interestingly, most a-priori profiles used in FTIR and satellite remote sensing retrievals do not assume a vertical distribution with a mixed layer. A lesson from the campaign would be to preferably use a well-mixed boundary layer assumption for the satellite retrievals of NH_3 . The measured concentrations were comparable with an earlier study at Cabauw in 2007 (Schaap et al., 2011), the difference explained by the shorter measurement period. Comparison with measurements performed between 1984 and 1986 (Erisman et al., 1988) showed an increase of ~5.5 ppb for each of the levels. The difference in the concentrations can be explained by a possible increase in livestock and/or the difference in measurement period.

The results of the campaign were restricted by the artefacts and problems of individual instruments. The lower two instruments in the tower had an uncertainty of up to four times the normal level, which makes it impossible to derive a gradient between the levels. However, their results contributed to the confidence on the data for the instruments at 20m and 160m.

The issues with the MARGA instrument illustrated the importance of taking into account all the possible artefacts. The delay in the measured NH_3 concentrations compared to the mini-DOAS concentrations, following the inlet problems and fluid transport inside the MARGA, further illustrated the value of open-path measurements.

How do tower measurements of ammonia compare to FTIR and satellite observed ammonia profiles and total columns and to what extent does this improve the interpretation on satellite-derived ammonia?

The analysis in Chapter 5 focused on the choice of a vertical profile distribution for NH_3 to compare in-situ measurements with FTIR and satellite observations. The final profile choice was based on the results found in Chapter 4, being that the boundary layer is well mixed. The profile shape is approximated by the shape of a three parameter Gaussian with the mixing layer height one of the main parameters. Essential to this profile is the mixing layer height information, for which we tested two types of data. The first dataset was derived from LD-40 measurements, whereas the second was produced through modelling with the METPRO model. The set was extended with the fixed profiles used in the IASI-LUT and IASI-NN retrievals. The IASI-NN allows using an alternative profile shape, which was used to also retrieve NH_3 using the LD40 and METPRO profiles. The profiles were scaled to match the tower measurements for the height at which the instruments are positioned and compared to FTIR, IASI, and CrIS observations.

Using vertical profiles that take into account a well-mixed boundary layer, scaled with tower measurements from the MARS campaign, shows a better performance in comparison with FTIR, IASI and CrIS observations than using fixed profiles. Comparison of FTIR to mini-DOAS total columns showed correlations of up to $r \sim 0.5$, and MRD between -20 to $+36\%$ (std ~ 0.6 to 0.7). The comparison is analysed as a function of the local concentrations with a larger ratio between the FTIR and the mini-DOAS total columns for atmospheric transport from the north-east compared to the other wind directions. Comparison to CrIS total columns gave similar results with $r \sim 0.5$ and slopes between 1.04 and 1.67 depending on the choice of profile. Similarly comparison to IASI columns showed correlations $r \sim 0.45$ to 0.55 and slopes between ~ 0.7 for the METPRO retrieval to ~ 2.6 for the LUT retrieval. Next the evaluation exercise was expanded to the Dutch LML (Landelijk Meetnet Luchtkwaliteit) monitoring network sites. The comparison of the IASI and CrIS products with the LML sites revealed a large influence on the regression results depending on the mean and variability of the NH_3 concentrations. The effect was larger than seen for the mini-DOAS results which was explained by the height of measurement, stressing the importance of vertical gradients. The results indicate a stronger effect of these surface variations on the comparison with IASI than with the CrIS observations, possibly due to a lower sensitivity of the former instrument for surface concentrations due to general less favourable thermal contrast conditions.

The tower measurements were most helpful for the interpretation of the satellite observations, showing the influence of mixing in the boundary layer and the potential large influence of the concentration gradients in the surface layer. Although there were several problems with the individual instruments, the dataset is unique. To our knowledge this is the first dataset of high

temporal resolution measurements of NH_3 at several levels in a meteorological tower. The data is freely available for use in future model and satellite validation.

Are we able to validate ammonia satellite observations, what is the uncertainty in the IASI-LUT and CrIS-FPR products?

To synthesise I will answer the first two parts of the central question of this thesis. The FTIR- NH_3 dataset developed during this project enables us to validate the satellite NH_3 observations as it measures a similar vertical column as the satellite instruments. However there are still difference in the observed vertical distribution. The FTIR instrument is more sensitive for NH_3 located near the surface while the satellite is (usually) more sensitive to NH_3 at higher altitudes. Furthermore while the FTIR instrument is more sensitive to the surface layer it does not fully resolve the vertical distribution thus uncertainty remains for each retrieved level. Also the FTIR observations are not without error and a third set of observations covering the same vertical axis will be needed to further constrain the uncertainties in both the FTIR and satellite retrievals. As shown in this thesis both products correlate well, with CrIS-FPR product overall having less uncertainty than IASI. The increased sensitivity of the CrIS instrument over IASI, due to the overpass time and lower spectral noise, is noticeable and might be the major difference. The overpass at 13:30 instead of 9:30 greatly enhances the thermal contrast of the atmosphere, which combined with the instruments $\sim 4\times$ lower spectral noise improves the capability to observe smaller NH_3 concentrations. As a trade-off the CrIS instrument does have a lower spectral resolution (0.625 cm^{-1} vs 0.5 cm^{-1}). This can potentially lead to a bias as was visible in the FTIR resolution tests, which showed difference of a few percent when reducing the resolution from 0.005 cm^{-1} to 0.11 cm^{-1} . It also has a slightly lower spatial resolution (14 km^2 vs 12 km^2 at nadir) meaning it is slightly harder to resolve gradients in the concentration field. The IASI retrieval, although quick, limits the possible solutions which might be the reason for its underestimation. The mini-DOAS observations made during the MARS campaign were an excellent example of the well-mixed boundary layer and gave the basis to use the Gaussian shaped profiles for the IASI-LD40 and IASI-METPRO retrievals. The new profile shapes used in IASI-NN, IASI-LD40 and IASI-METPRO seems to work quite well. Obtaining a high quality mixing layer height estimate will be vital for future retrievals on a global scale.

7.2 Impact and outlook for future research

Most of the work in this thesis is related to uncertainties in measurements and retrievals. Understanding the strengths and weaknesses of instruments and retrievals is paramount to correctly using and applying the obtained information. Throughout this PhD research I have gained insight in many aspects of the “ NH_3 field” and would like to make some observations and recommendations for future research.

FTIR and satellite retrievals, improvements and future validation

This thesis illustrated the most important causes of uncertainty in FTIR and satellite NH_3 retrievals. Based on the analysis and conclusions in this thesis the following recommendations can be made. An excellent point to continue the research on NH_3 includes future improvements

to- and validation of the FTIR and satellite retrievals. The first concerns the line spectroscopy. A large percentage of the uncertainty, especially for the FTIR retrieval, comes from the uncertainty in the line parameters. Both the pressure and temperature broadening parameters as well as the overall line strength are quite uncertain for NH_3 with an estimated uncertainty of up to 20% in all three parameters (HITRAN, Rothman et al., 2013). The line spectroscopy is an essential input parameter in all remote sensing retrievals for NH_3 . Any future retrieval and application will be greatly helped by an improvement of the NH_3 lines in the existing line spectroscopy database. The IASI- NH_3 product has steadily improved over the course of the last years but if the use of fixed profiles continues in the future, better estimates of for example the mixing layer height will be needed as shown in this thesis. Another point of uncertainty is the unknown sensitivity of the IASI instrument. Applying for example the FPR optimal estimation retrieval to the IASI spectra would gain some further insight and a direct comparison of the current retrievals used by IASI and CrIS respectively. Another option would be to perform one iteration of optimal estimation retrieval on the IASI spectra using the current IASI-NN retrieval as an input. This would gain the valuable insight of where the information content is located per observation and make the product more usable in for example modelling applications. As for the CrIS-FPR retrieval there is a hint that the two smallest a-priori profiles might be too restrictive. Often the profile peak far above the surface due to a lack of instrument sensitivity for the surface layer. A way to solve this would be to use a more restricted profile shape for the lowest parts of the atmosphere. In the case of analysis of plumes from biomass burning one could fall back to the old approach. In this research an effort was made to validate all recently developed satellite NH_3 products. The AIRS- NH_3 product however has not yet been validated and I recommend to validate the product with the FTIR- NH_3 dataset. My recommendation is to validate the FTIR and satellite products with a third information source, for example observations with a plane flying in an upward or downward helix around FTIR sites during satellite overpasses.

The mini-DOAS and MARGA instruments

A respectable amount of time was spent on the development and improvement of the mini-DOAS retrieval strategy, but this has not been published in this thesis. Analysis of measured concentration data showed discrepancies between the measured concentrations of two instruments measuring alongside each other. Further analysis showed that there were several issues with the mini-DOAS concentration retrievals and that uncertainties that were not well incorporated in the final error budget. Most of the issues have by now been resolved with the updated instruments measuring concentrations at high precision. While some adjustments can be made in hindsight, as done for the MARS dataset, this is not possible for all issues. My recommendation for the mini-DOAS instrument is to write a publication focussed on the recent changes and describing the uncertainties in detail. Furthermore, the mini-DOAS instruments have to be compared with their Swiss counterparts and other commonly used instruments. The Met NH_3 campaign organized near Edinburgh in September 2016 and the Dronten campaign organized in June 2016 were an excellent start, with a large number of instruments measuring the NH_3 concentrations before, during and after manure application to the surrounding fields. These kind of inter-comparison studies are rather unique as it is a lot of effort to bring together all commonly used instruments. This thesis illustrated the problems encountered when

measuring NH_3 with the MARGA instrument. Several studies report NH_3 diurnal profiles measured with the MARGA, showing similar morning peaks, while never questioning the uncertainty that comes with it. The set-up of the MARGA however changes from instrument to instrument thus it is not certain that the same artefacts are involved. For example the first results of the Met NH_3 campaign did not show any of the morning peaks. A re-assessment of the outcome of studies using the MARGA instrument might be needed.

Monitoring, distributions & atmospheric chemistry

Globally, high quality monitoring of atmospheric NH_3 is performed at relatively few sites, which by far is not representative of the global variety in NH_3 concentrations. In the Netherlands we have one of the most extended and in depth networks but even here one can say that the Dutch LML network is not representative of the mean “Netherlands” concentrations, due to the small number of sites. The Dutch MAN (Meetnet Ammoniak in Natuurgebieden) network does approach this level but is equipped with instruments that measure with a temporal resolution of one month, missing much of the variability. Satellite observations will play a key role in future monitoring as the observations are representative over large areas, measure globally and daily, and can complement the existing networks in many ways. The best would be to continue using all three sources of information complementing one another as none of the individual instruments gives all the information required to give a good estimate of the global budget and distribution of NH_3 . Hourly and better time scale measurements, such as those performed in the LML network, can be used to give more detail at process level, although in its current state these observations are limited as nothing is known about the flux, to which I will come back later. A more widespread measurement network such as the Dutch MAN network, can complement the first system by spatially adding depth for relatively low cost. While in the Netherlands such system is possible, in larger countries with more remote regions it is unfeasible. The satellite observations will complement the first two networks, being more representative at a region or country wide level for temporal analysis, and depending on the footprint size of future instruments, will give longer time-averaged information of concentrations at field level. Satellite products can especially play a role in more remote regions, for example monitoring atmospheric concentrations near biomass burning in the boreal forests.

Satellite and FTIR instruments also add information on a vertical scale, something which is missed by in-situ measurements. For example it is possible to monitor biomass burning plumes, measuring the chemical composition of the plume, while it is transported to for example vulnerable ecosystems in the northern Arctic. For the FTIR instruments this was demonstrated by using measurements of the FTIR instruments in Toronto and Eureka, Canada, to simultaneously observe CO , NH_3 , HCN (Hydrogen Cyanide) and C_2H_6 (Ethane), linking it to a plume originating from the Great Slave Lake fires (Lutsch et al., 2016). Using the ratios it is possible to estimate the emissions of the constituents.

The tower measurements performed during the MARS campaign showed the influence of mixing in the boundary layer and the potential large influence of the concentration gradients in the surface layer on comparisons with satellite instruments. The five month dataset of the

MARS campaign gave an idea on the overall importance of knowing the vertical distribution but in the end it is a time limited dataset, with only a few coinciding observations with the IASI and CrIS satellite instruments. Hence, it is recommended to build a longer time series with the set-up used here. In addition, it could be beneficial to start tower measurements around the world to cover a wide range of NH_3 concentrations, to develop models and proxy's linking the satellite observed NH_3 with in-situ surface concentrations.

Trends analysis

The recent discussions about trends in the Dutch NH_3 concentrations compared to the trends in the emissions (Wichink Kruit et al., 2017; Van Zanten et al., 2017) to me shows that there should be a tool to validate and back up the in-situ measurements used for long term NH_3 concentrations trend-analysis. While at the start of this PhD there were eight measurement sites with long measurement records in operation in the Netherlands, this has been reduced to six in the past 4 years. With budgets for monitoring being cut and expensive stations being closed the trend analysis from the remaining stations becomes less representative of the Netherlands as a whole. Satellite instruments can be used to complement the trend analysis of concentrations. A potential problem in using satellite observations is the limited lifetime of individual satellite instruments. While satellite instruments used for Earth observation commonly have a long lifetime (5-15 years, depending on degradation, mission length, etc.), this is still limited compared to the ground based networks with records going back several decades. Successive satellite instruments will be needed for observing long term trends, which brings with it problems such as consistency in the performance of the retrievals and instruments. Another potential issue is the consistent input for the retrievals. For example, the quality of the IASI retrieved temperature and humidity profiles has slowly improved over the years, but no recalculation of the older observations has to date been performed. The new retrieval is more reliable, but one cannot say anything about long term trends when there are jumps in the retrieved NH_3 column totals just from an update on the input side of the retrieval [2010 & 2014]. Luckily such issues can be resolved. In the IASI case this would mean back processing the meteorological data, which has been scheduled for 2018. The recent switch from AMOR to mini-DOAS instruments in the Dutch LML network is also a good example of a switch in instruments and change in the measured concentrations levels. The researchers did a good job operating both types of instruments side-by-side for a year to notice differences in the observed concentrations, ensuring the quality of the measurement series, but the change will be noticeable and makes one question the validity in using the new and old measurements together in future trend analysis. Continuity is key in long-term monitoring, which cannot be stressed enough. Similarly, a satellite instrument lifetime is limited and follow up missions should overlap to make continuous monitoring possible. Ensuring quality should be the basis for future analysis. In the case of the AMOR to mini-DOAS switch continued measurements in unison and putting an increased effort in understanding all the uncertainties before deploying a new instrument in a measurement network.

Ammonia atmospheric budget (Emission and deposition estimates and measurements)

The current emission inventories, such as the national Dutch emission registry (ER, <http://www.emissieregistratie.nl/>), at best have an uncertainty estimated in the range of 50 to 100% (van Gijlswijk et al., 2004). Most of the uncertainty is related to a lack of emission measurements for example at field and per head of livestock scale. Furthermore, there is a lack of accuracy in the emission measurements itself, creating a large uncertainty in the emission factors of the various sources. The small number of emission measurements follows from the relatively high costs associated with operating a set of instruments capable of measuring NH₃ fluxes. Recent developments for the mini-DOAS instruments are focused on using the instruments in a setup capable of measuring deposition. In principle only one instrument is needed, which makes it a cost effective setup to measure dry deposition of NH₃. One way to improve the overall emission total is to use satellite observations to constrain emissions and deposition of NH₃. A direct conversion of retrieved surface concentration or total column to deposition using an inferential model might at this point in time not be viable due to the low sensitivity of the satellite instruments for the surface layer. Furthermore, satellite footprints are large and will miss a large part of the local variability. A proxy linking local variations with satellite observations will be needed. Such a proxy could be an extended deposition model or CTM, developed using satellite observations in conjunction with a large number of field sites measuring NH₃ fluxes, covering the typical emission sources and atmospheric conditions. Most of the deposition work is based upon a handful of experiments and an increase in available datasets will in no doubt be a help in improving current deposition models. In the case of the Netherlands some effort should be made to monitor fluxes besides monitoring NH₃ concentrations. For the LML network one could think about an upgrade of the six mini-DOAS systems currently in operation at the remaining six monitoring stations. The upgrade is relatively inexpensive compared to setting up new measurement sites and instruments. A possible extension is the addition of a small meteorological tower ~30m. This will make it possible to measure the NH₃ concentrations just outside the surface layer and away from the strong surface sources thus providing more representative measurements of the NH₃ observed by satellite observation and enabling to better validate such measurements. Another option is the combination of observing the concentrations (fluxes) several atmospheric species at the same time. This will make it possible to better constraint the source responsible for the measured concentrations and better constrain the emissions.

Model validation

Now the uncertainties of the satellite products are better constrained, the satellite observations can be readily used for model applications, such as validation and potentially data assimilation. Several studies have already shown the value of the IASI and TES observations for validation of chemistry transport models such as LOTOS-EUROS (Schaap et al., 2008, Van Damme et al., 2014b) and GEOS-Chem (Bey et al., 2001). The studies illustrated that the emission inventories underlying the model simulations showed large deficiencies, both spatially and temporally, and in most cases the models underestimated retrieved concentrations and columns. Taking into account that the IASI products themselves show an underestimation in comparison to in-situ and FTIR measurements, this would mean the emissions should be significantly higher than currently included in the inventories. Through assimilation, the retrieved satellite profiles and columns can play a role in constraining the emission inventories

and at the same time improve our knowledge on the temporal variability of the emissions. The latter is important to better constrain particulate matter formation and long range transport of eutrophying components. First assimilation work used the TES-NH₃ product but was hampered by the small number of available observations and spatial separation of each of the observations. Recent developments, include the use of the CrIS observations as it is more easily used with the availability of an averaging kernel indicating the sensitivity of the instrument. The current IASI-NH₃ products are harder to use due to the larger uncertainty in the individual observations and the lack of an averaging kernel. Further research will reveal how much information can be gained from the integration of satellite observations into state of the art chemistry transport models.

Future satellite missions

To conclude some recommendations for future earth observatory missions can be made. The next generation of Earth observation satellites is already being planned and developed and a number of instruments will focus on the infrared spectral region in which we can observe NH₃. While every new satellite instrument will be useful and improve our current understanding the properties of such instrument will determine how useful compared to the existing systems. The first point is the overpass time of the instrument. Currently the METOP satellites have an overpass at 9:30 and 21:30 local solar time and the Suomi-NPP and AQUA satellites at around 13:30 and 1:30. Optimally this gives 4 points of information with gaps of ~8 hours between the observations. Looking back at the NH₃ diurnal cycles presented in Chapter 5 it would be most useful to have several systems making twice daily overpasses together performing measurements at an (two) hourly time scale, such as to analyse a diurnal cycle of the emission sources. At a two hourly timescale it will also be viable to analyse biomass burning plumes and gain a better understanding of the chemistry involved under such conditions. It would thus be wise to consider one or two systems filling in the gaps, with morning overpasses for example at around 11:30 and 15:00. Another possibility would be to use a geostationary satellite capable of observing a large region at regular intervals, for example Europe or the US. A geostationary satellite however is located further away from the Earth, meaning that this might come at the cost of sensitivity of the instrument. Currently there is a European sounder planned to have a geostationary orbit, the MTG-S platform with the IRS instrument. The sounder is planned for ~2022 and will focus on Europe and Africa. The IRS instrument has a ground pixel size ~4 km diameter at nadir and will make observations with an hourly or even 30 minutes resolution. Another possibility is the use of a satellite capable of using a staring mode, pointing at a specific point during several overpasses, such as TES. One of the reasons that there aren't more satellite instruments in orbit is the high cost involved with such instruments. A potential idea for NH₃ is the use of multiple smaller platforms focussed on only observing the spectral region important to NH₃, which can reduce the overall cost of the systems itself. On a spatial scale there is the trade-off between high-resolution observations and coverage. High-resolution measurements are most interesting as they would enable the detection of specific NH₃ emission point sources and give estimates of the sources strength. One planned system that will focus on such high-spatial resolution is the Nitrosat satellite which will have a resolution of ~1 km² with a potential launch in 2024. As stressed before continuity of the measurement record is important for the detection of trends and luckily there is already an instrument planned that

will follow the IASI satellite instruments, the IASI-NG instrument. IASI-NG will have a similar overpass and orbit as the IASI instruments with an improved instrumental performance.

To conclude, most of this thesis was focused on the uncertainties in remote sensing measurements and retrievals. To me it is essential to first understand the uncertainties of a product before making claims on for example observed trends. At one point, however, one should decide that there is enough understanding about the pros and cons of an instrument and start using the data. Even though in its current state the uncertainties might seem large, I have no doubt that satellite observations of NH_3 in the future will be used for model validation, constraining emissions and observing trends. NH_3 satellite observations have already been used for several of such purposes and I hope that the results of this thesis will help future applications.

7.3 Data availability

FTIR- NH_3 data (Dammers et al., 2015) can be made available on request (M. Palm, Institut für Umweltphysik, University of Bremen, Bremen, Germany). The CrIS-FRP- NH_3 science grade (non-operational) data products used in this study can be made available on request (M.W. Shephard, Environment and Climate Change Canada, Toronto, Ontario, Canada). The IASI- NH_3 product is freely available at <http://www.pole-ether.fr> (Whitburn et al., 2016). The Mini-DOAS data are available on request (D. Swart, National Institute for Public Health and the Environment (RIVM), Bilthoven, the Netherlands). The MARGA NH_3 data are available on request (A. Hensen, Stichting Energieonderzoek Centrum Nederland (ECN), Petten, The Netherlands).

