Dear Editor,

please find below our replies to the comments by both reviewers and the revised manuscript where deleted text is marked in red colour and new text in blue.


Best regards,

Michael Höpfner and co-authors

# *Interactive comment on* "First detection of ammonia (NH$_3$) in the Asian monsoon upper troposphere" *by* M. Höpfner et al.

M. Höpfner et al.

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We would like to thank Michelle Santee (referee 1) for her valuable comments and corrections all of them leading to an improvement of our manuscript. Comments and questions of the referee are marked in bold face and manuscript changes in italics.

**Just to avoid any potential for ambiguity (since there is also an Asian winter monsoon), I suggest that the word "summer" be inserted before "monsoon" in a few more places in the manuscript, for example: the title of the article, the Abstract (L3), the Discussion section (L193), and the Conclusions (L243).**

We agree and have inserted *"summer"* at the suggested locations.

**L142-143: Shouldn't the total error be the RSS of the individual sources of un-**

**certainty? That is, shouldn't the error components being summed be squared?**

Right, this is an error in the text (not in the Figure). We have corrected the text accordingly by inserting *"squared"* before *"error components"*.

**Figure 4 shows the seasonal distributions of NH$_3$ during MIPAS period 1. But I am not sure that it is necessary to show all 7 seasons in that interval, especially given that the first panel covers only July and August 2002 and is thus not completely comparable to the 3-month averages depicted in the other panels. Perhaps the information could be conveyed with just one row of 4 maps, starting with MAM 2003, then JJA 2003, SON 2003, and ending with DJF 2003/2004. Then the fact that the other seasons from period 1 show similar results could simply be stated in words. For completeness, such a statement about the other seasons in period 2 should be made in any case, as should a statement about other altitudes in period 1.**

The text has been changed according to the reviewer's suggestions:

From: *"During all other seasons and outside the region influenced by the Asian monsoon, no similarly high concentrations of NH$_3$ can be found."*

To: *"During all other seasons of the two MIPAS periods and outside the region influenced by the Asian monsoon, no similarly high concentrations of NH$_3$ can be found within the entire altitude region covered by our measurements."*

Regarding the proposed update of Figure 4, we tend not to change it in order, (a) to demonstrate that also in Jul/Aug 2002 there have been enhancements of NH$_3$ in the Asian monsoon region, and, (b) to cover one period of the MIPAS observations entirely.

**When I first read through Section 4, I thought that although there may not be any correlative measurements of UTLS NH$_3$ to validate the MIPAS retrievals against, there surely must be some model simulations that could provide a zeroth-order "sanity check" on the morphology if not the magnitude of the retrieved distribu-**

**tion. It turns out that model results (or the lack thereof) are discussed at length in Section 5, but it might be useful to add a sentence in this section that points forward to that discussion, so that readers do not assume at this point that opportunities for validation have been overlooked.**

We agree and have added some text at the end of Section 4:

*"Due to the lack of ammonia observations in the upper troposphere, we cannot validate our dataset with correlative measurements. However, in the next section we discuss its plausibility by comparing with the few previous observations and atmospheric model results."*

**It is stated (L177–178) that: "the maximum concentrations of $NH_3$ are always larger within the eastern part of the Asian monsoon". However, this statement is only true at certain altitudes; it is not the case above 13 km in 2008 or above 15 km in 2010.**

This wording might be misleading. What we meant here relates to the maximum values over the whole altitude range of the profile. We have tried to make it clearer by changing the sentence to:

*"The profiles in the region of the Asian monsoon reveal that the maximum concentrations over the whole altitude range within one year are always larger within the eastern part of the Asian monsoon compared to the western part. Maximum concentrations of $NH_3$ in the eastern part reach about 10–22 pptv at 11–13 km altitude."*

**It is noted (L181) that in the western portion of the monsoon region enhanced $NH_3$ "can only be observed during the years 2003, 2008, and 2010". As written, this makes such enhancements sound like a rare occurrence. But that sample includes half of the years observed.**

Agreed: we have skipped the word *"only"*.

**L196–197: Nor could random errors account for the enhancements appearing**

C3

**only in one season.**

Thanks for pointing to this argument. We have added it by changing the sentence to: *"However, random errors cannot explain why the enhancements should appear in a contiguous geographical pattern nor could they account for the enhancements appearing only in one season."*

**L250–254: The point about the differences in the altitudes of the peaks in the $NH_3$ profiles in the eastern and western parts of the monsoon region being consistent with the "general view" has not been made previously in the manuscript, and it seems to me that it would be more appropriate to make such a point for the first time in the Discussion section (or in Section 4 where the differences in the two regions are initially discussed) and not the Conclusions. Moreover, a reference or two should be provided for the description of the "general view" of the monsoon system.**

In the revised version we have (1) moved this part to Section 4, as suggested by the referee, and, (2) weakened the statement on the "general view", since we could not support it clearly on basis of published material.

Text added after line 184 of the original manuscript:

*"The position of the $NH_3$ maximum at higher altitudes in the western compared to the eastern part of the monsoon system might be due to convective uplift of boundary layer air in the east followed by upper tropospheric transport and further uplift towards the west. Such an uplift of air from east to west is indicated in Vogel et al. (2014, Fig. 10) by trajectory calculations, however mainly located at the border of the anticyclone."*

**Fig 1: The orange lines are helpful but somewhat hard to see. It might be better to use solid or dashed rather than dotted lines.**

OK, we have changed them to dashed style and used a thicker line width.

**Typos and other minor wording and grammar corrections / suggestions:**

C4

Thanks for the list of technical corrections! We have implemented all of them as suggested.

**New references**

Vogel, B., Günther, G., Müller, R., Grooß, J.-U., Hoor, P., Krämer, M., Müller, S., Zahn, A., and Riese, M.: Fast transport from Southeast Asia boundary layer sources to northern Europe: rapid uplift in typhoons and eastward eddy shedding of the Asian monsoon anticyclone, Atmos. Chem. Phys., 14, 12 745–12 762, 600 doi:10.5194/acp-14-12745-2014, http://www.atmos-chem-phys.net/14/12745/2014/, 2014.

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Discussions

# *Interactive comment on* "First detection of ammonia (NH$_3$) in the Asian monsoon upper troposphere" *by* M. Höpfner et al.

M. Höpfner et al.

michael.hoepfner@kit.edu

Received and published: 18 October 2016

We thank referee 2 for carefully evaluating our manuscript. For the revised version we have tried to take all suggestions into account. Comments and questions of the referee are marked in bold face and manuscript changes in italics.

**In the introduction, I found that the discussion of previous measurements needs to be clarified and enhanced. The description of what has been done via in-situ and remote sensing techniques should be made much more distinct. These were somewhat mixed together in the text. Specifically, the platforms used (e.g. ground, balloon, satellite) and the altitude range for measurement sensitivity needs to be described more thoroughly. In particular, the authors should establish how far into the UT the nadir and balloon measurements reach to support**

**their "first" measurement claim within the Asian monsoon.**

We agree with the referee that this part of the introduction was difficult to read and a bit too compressed. Thus, we have restructured the description of NH$_3$ observations to clearly separate in-situ from remote sensing observations. Further we have added more information about the platforms and the altitude regions of sensitivity to support our claim of "first evidence for NH$_3$". Lines 37–68 of the paper will be replaced by the following text in the revised version:

*"With regard to the predicted increase in NH$_3$ emissions and the possible compensating effect on aerosol radiative forcing, Paulot et al. (2016) emphasize the need to better constrain also the vertical distribution of ammonia. However, there is a lack of observations of NH$_3$ at mid- and upper tropospheric levels. Before 2008, measurements of ammonia were almost exclusively based on in-situ technologies (von Bobrutzki et al., 2010). Compared to the wealth of observations on ground, vertical profiles of NH$_3$ from in-situ observations above the boundary layer are relatively sparse. Recently, aircraft-borne campaign measurements over the US obtained concentration profiles in the free troposphere reaching altitudes of about 6 km (Nowak et al., 2007; Nowak et al., 2010, 2012; Leen et al., 2013; Schiferl et al., 2016). At these altitudes maximum observed NH$_3$ mixing ratios reached about 800 pptv (Schiferl et al., 2016) with detection limits of 70 pptv (Nowak et al., 2010). In- situ air-borne observations over Germany by Ziereis and Arnold (1986) restricted concentrations to the sub-pptv range at altitudes between 8 and 10 km . To our knowledge, these are the only upper tropospheric in-situ-measurements of NH$_3$ published so far.*

*A first step in the direction of observations with global coverage was achieved by Beer et al. (2008), who reported the detection of NH$_3$ in the lower troposphere from space-borne nadir sounding measurements by the Tropospheric Emission Spectrometer (TES) on the EOS Aura satellite. Subsequently, various papers have been published describing retrieval, validation and interpretation of NH$_3$ derived from the nadir sounders TES (Clarisse et al., 2010; Shephard et al., 2011), IASI (Infrared Atmospheric*

*Sounding Interferometer) (Coheur et al., 2009; Clarisse et al., 2009, 2010; Van Damme et al., 2014), CrIS (Cross-track Infrared Sounder) (Shephard and Cady-Pereira, 2015), and AIRS (Atmospheric Infrared Sounder) (Warner et al., 2016). The vertical sensitivity of these satellite retrievals is mainly limited to the lower troposphere up to about 3–4 km and no altitude resolution is achieved (e.g., Clarisse et al., 2010; Shephard and Cady-Pereira, 2015). Recently, retrievals of $NH_3$ vertical column amounts from ground-based FTIR solar observations located at various sites have been presented by Dammers et al. (2015) and are being used for the quantitative validation of space-borne nadir-viewing datasets (Dammers et al., 2016). As shown by Dammers et al. (2015) in case of high amounts of $NH_3$ near the surface, the retrieval sensitivity peaks within the boundary layer where also the altitude-gradient can be derived. For low concentrations, the retrieval is only sensitive to the total vertical column amount.*

*To achieve vertically resolved profiles of trace gases in the upper troposphere and above, limb-sounding techniques have been applied frequently. Regarding ammonia, Oelhaf et al. (1983) reported upper limits of 100 pptv above 10 km by analysis of balloon-borne limb solar absorption spectra measured over the US. Space-borne solar occultation measurements obtained with the ACE-FTS instrument within a plume of biomass burning over Tanzania have been studied by Coheur et al. (2007). In that publication, the authors mention only a "tentative identification" of $NH_3$ in the spec- tra, while the spectral signals of various other trace species, such as $C_2H_4$ , $C_3H_6O$, $H_2CO$ and PAN were detected unequivocally. Nonetheless, Coheur et al. (2007) derived a vertical profile of $NH_3$ between 6.5 and 17 km with typical values of less than 20 pptv and a maximum of about 50 pptv at 8 km. Burgess et al. (2006) report on first attempts to retrieve global distributions of ammonia using limb infrared emission spectra measured by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on Envisat. They obtained one climatological vertical profile with $NH_3$ volume mixing ratios below 5 pptv at altitudes above 9 km. However, no evidence for the presence of $NH_3$ in the limb spectra nor any indication for enhanced values within the area of the Asian summer monsoon is shown.*

C3

*In summary, considering the reported observations, neither the in-situ measurements by Ziereis and Arnold (1986) nor the limb-sounding remote sensing data (Oelhaf et al., 1983; Coheur et al., 2007; Burgess et al., 2006) prove the presence of ammonia at altitudes above about 8 km."*

**Because different coordinate systems are used by the different measurements, when discussing altitude or pressure ranges for current or previous results, both z and p should be given to help the reader to make these connections clearly.**

According to the reviewers suggestion we have indicated the approximate altitudes everywhere in the manuscript where only pressure was given.

Text changes:

Line 260: *"between 300 hPa ($\approx$9.5 km) and 200 hPa ($\approx$12.5 km)"*

Line 268: *"above 500 hPa ($\approx$6 km) also in tropical regions"*

Line 271: *"at the 200 hPa pressure level ($\approx$12.5/11 km in tropical/polar regions)"*

**In the discussion of the definition of the detection limit, it would be useful to give further description of the impact of choosing 2-sigma versus 1-sigma as the limit. How frequently are the enhancements above 15 pptv (3-sigma)? Would this choice of limit impact detection in certain years or all years?**

We have added this information in the updated version of the manuscript.

Lines 196–198 have been extended as follows:

*"For example within the data shown in Fig. 5 at 12 km, there are 176 values larger than 5 pptv outside the region 20–50° N × 30–120° E compared to 55 inside. However, at the 15 km level, only 5 data points exceed 5 pptv outside but 37 inside. Using 2-$\sigma$, there are no data points outside compared to 23 and 15 exceeding 10 pptv inside the region at 12 km and 15 km, respectively. Further, the detected enhancements inside the monsoon region are in many cases (13 times at 12 km and 8 times at 15 km) even*

C4

*above 15 pptv and, thus, larger than a 3-$\sigma$ limit. Temporally resolved, values above 10 pptv in the monsoon region exist during all years at both altitude levels with the exception of 2011 at 15 km. 15 pptv are exceeded at 10 km in 2003–2010 and at 15 km in all years but 2007 and 2011."*

**When discussing the model results, I missed a bit more detail on the type of model results used. This could be added to the introduction or put into the discussion section. Are there any dependences of results on the met. fields driving the models or any emissions included? In the conclusion, the term "locally resolved model" was used. This stated lack of model results needs to be supported better in the discussion.**

As suggested by the referee, we have added more information on the models used. The four quoted publications use e.g. different dynamic kernels and emission inventories. However, it is outside the scope of this paper to explain the reasons for different model results regarding the global distribution of ammonia. Further, in the discussion, we state a lack of published model data resolving $NH_3$ within the Asian monsoon period. Thus, we do not exclude the existence of model runs from which this information could be drawn - we just have not found those in literature.

Text changes:

Line 209: *"These calculations were based on the tropospheric transport model Moguntia with a horizontal resolution of $10° \times 10°$ with 10 layers up to 100 hPa in combination with, at that time, the first global emission inventory of $NH_3$ with the same resolution as the transport model."*

Line 219: *"Their aerosol chemistry transport model (Umich/IMPACT) had a horizontal resolution of $2°$ latitude $\times 2.5°$ longitude with 26 layers up to 0.1 hPa using the $1° \times 1°$ global $NH_3$ emission inventory of Bouwman et al., 1997."*

Line 221: *"These data were based on runs with the general circulation model GISS*

*GCM II-prime with $4°$ latitude $\times 5°$ longitude horizontal resolution, nine vertical layers up to 10 hPa and $NH_3$ emissions according to Bouwman et al., 1997."*

Line 228: *"They used the global chemistry-transport model TM3 with $7.5°$ latitude $\times 10°$ longitude horizontal resolution, 19 vertical levels and the EDGAR database for the emissions of $NH_3$."*

**Specific comments:**

**L24-27 Could the authors clarify a bit further how this would impact clouds? Increase their presence?**

Thanks for this comment. In response, we have included, the paper by Abbatt et al. (2006) who investigated the effect of ammonium sulfate on heterogeneous cirrus nucleation resulting in fewer and larger ice particles compared to the case of homogeneous nucleation.

Text changes line 27ff:

*"Such a heterogeneous nucleation pathway might influence size and number of cirrus particles and, consequently their radiative impact (Abbatt et al., 2006)."*

**L65-68 While the quote "tentative identification" was taken from Coheur et al., a profile was retrieved from the ACE measurements. This should be clarified in the introduction.**

Even if there was no clear visible "evidence" for ammonia in the spectra, a retrieval can be performed. We have added this information in the revised manuscript.

Added text: *"Nonetheless, Coheur et al., 2007 derived a vertical profile of $NH_3$ between 6.5 and 17 km with typical values of less than 20 pptv and a maximum of about 50 pptv at 8 km."*

**L89-91 Please provide the average number of spectra used in the monthly averages. Does this vary significantly by year (maybe based on cloud presence?)**

**Also, what is the typical signal to noise ratio of the averaged spectra? Is it much better than the minimum stated? Are the spectra evenly distributed throughout each month?**

According the referee's suggestion, we have added two figures in the supplement showing the number of co-added spectra per data bin for each sub-plot of Figures 4 and 5 of the paper. The mean number of co-added spectra is by a factor of 2-3 higher than the minimum value of 25, and, thus the noise is reduced by factors of about 0.5-0.6 compared to the noise reduction obtained by the minimum allowed number of co-added spectra. The temporal variation of this number between years (see supplement, Fig. 2) is mainly determined (a) by the different sampling frequencies between phase 1 and phase 2 of the MIPAS operational period and the reduced sampling in 2007 compared to the later years. Its variation between different months is not very strong (see supplement, Fig. 1).

Added text at line 91:

*"The resulting mean number of co-added spectra per time/latitude/longitude bin varies from 53–56 for the years 2003 and 2007 to 65–70 for 2008–2011 reaching maximum numbers of around 140 (see supplemental material for the detailed geographical and temporal distribution). This leads to a typical reduction of the spectral noise by 0.1 ranging from 0.2 to 0.08 and signal-to-noise values resulting in retrieval errors near and below 1 pptv of $NH_3$ (see detailed error estimation below)."*

**L112-116 It seems that the spectral windows between the two periods differ by one spectral "grid point". Could the authors comment on why this seemly small change was necessary?**

These changes have been necessary for technical reasons due to the change in the spectral grid from MIPAS phase 1 (0.025 $cm^{-1}$) to phase 2 (0.0625 $cm^{-1}$).

**L130-132 If MWs 2 and 3 show the "best fit", why is MW 1 included? Can it be**

**omitted?**

In case of the high spectral resolution, a clear improvement is visible also in MW 1. This spectral signal is also fitted in MW 1 in case of the lower resolution, reducing e.g. the peak in the residual around 951.8 $cm^{-1}$ and contributing information. However, due to the lower strength of the $NH_3$ line in MW1, this is much less obvious. We agree that it should be possible to skip MW 1 entirely from the retrieval. However, we have not taken this option in order to keep the differences between the retrievals between MIPAS phase 1 and phase 2 as small as possible.

**L154-155 It would be useful to state the vertical resolution also for the altitude levels used later on in the discussion. Is it closer to the higher or lower value?**

We have specified the vertical resolutions more clearly in the revised manuscript.

Changed text at lines 154-155:

*"The globally average vertical resolution at the altitude levels 12, 15, and 18 km, which are discussed in more detail below, is 6.6 km, 7.9 km and 8.8 km during period 1 and 3.5 km, 4.3 km, and 5.6 km during period 2."*

**L172-179 Are the same months used for the background as the Asian Monsoon average? To identify the grid boxes within the Asian monsoon, is the ERA Interim contour used or a fixed latitude-longitude box? If a box, does this change by year or month?**

Yes, the same months are used for the background values. We have specified this better in the revised version. Regarding the grid boxes: a temporally fixed box area has been applied as stated in the text (lines 172-174) and in the legend within Figure 6.

Changed text 174–176:

*"In the same Figure, the dotted curves show the $NH_3$ mean Jun/Jul/Aug profiles for*

*all years outside the Asian monsoon area, for the same longitude and latitude range (30–110° E, 30–40° S) of the southern hemisphere."*

**L241-242 This sentence seems to be overstating the results as the authors report that UT NH$_3$ measurements over Germany were made by Ziereis and Arnold. This should be clarified by the authors and supported by the text.**

At their highest levels, 9 and 10 km, Ziereis and Arnold present upper limits for NH$_3$, i.e. not a detection. We have clarified this in the revised version:

Changed text lines 241–242:

*"We have presented first evidence of ammonia being present in the Earth's upper troposphere above 10 km by analysis of MIPAS infrared limb emission spectra."*

**Data availability should be discussed in the paper at end of conclusions or in a separate data section.**

Added text at the end of the conclusions:

*"The NH$_3$ dataset is available upon request from the author or at http://www.imk-asf.kit.edu/english/308.php."*

**Technical comments:**

**L8 aersol should be aerosol.**

Corrected.

**L60 Are these transmission or emission spectra?**

This has been specified more clearly in the revised version:

*"balloon-borne limb solar absorption spectra"*

**L75 Has UTLS been defined prior to this in the text? Also, the altitude range used for the UTLS should be specified in the text.**

C9

We have deleted "UTLS" in the new version since it appeared only three times where it could be replaced by more quantitative expressions:

Line 75: *"in the UTLS"* replaced by *"up to about 42 km"*

Line 78: *"27 tangent levels with 1.5 km steps in the UTLS"* replaced by *"27 tangent levels up to about 70 km altitude with 1.5 km steps up to ≈23 km"*

Line 99: *"within the region of the UTLS"* has been deleted, since the entire altitude grid has a spacing of 1 km.

**L78 Should be "in the horizontal" direction.**

Corrected.

**L102 "oder" should be "order".**

Corrected.

**L108 simultaneously with NH$_3$.**

Corrected.

**New references**

Abbatt, J. P. D., Benz, S., Cziczo, D. J., Kanji, Z., Lohmann, U., and Möhler, O.: Solid Ammonium Sulfate Aerosols as Ice Nuclei: A Pathway for Cirrus Cloud Formation, Science, doi:10.1126/science.1129726, 2006.

Schiferl, L. D., Heald, C. L., Van Damme, M., Clarisse, L., Clerbaux, C., Coheur, P.-F., Nowak, J. B., Neuman, J. A., Herndon, S. C., Roscioli, J. R., and Eilerman, S. J.: Interannual variability of ammonia concentrations over the United States: sources and implications, Atmos. Chem. Phys., 16, 12 305–12 328, doi:10.5194/acp-16-12305-2016, 2016.

Please also note the supplement to this comment:

C10

C11

# First detection of ammonia ($NH_3$) in the Asian summer monsoon upper troposphere

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*Correspondence to:* M. Höpfner (michael.hoepfner@kit.edu)

**Abstract.** Ammonia ($NH_3$) has been detected in the upper troposphere by analysis of averaged MIPAS (Michelson Interferomter for Passive Atmospheric Sounding) infrared limb-emission spectra. We have found enhanced amounts of $NH_3$ within the region of the Asian summer monsoon at 12–15 km altitude. Three-monthly, $10°$ longitude $\times$ $10°$ latitude average profiles reaching maximum mixing ratios of around 30 pptv in this altitude range have been retrieved with a vertical resolution of 3–8 km and estimated errors of about 5 pptv. These observations show that loss processes during transport from the boundary layer to the upper troposphere within the Asian monsoon do not deplete the air entirely of $NH_3$. Thus, ammonia might contribute to the so-called Asian tropopause aerosol aerosol layer by formation of ammonium aerosol particles. On a global scale, outside the monsoon area and during different seasons, we could not detect enhanced values of $NH_3$ above the actual detection limit of about 3-5 pptv. This upper bound helps to constrain global model simulations.

## 1 Introduction

In the Earth's atmosphere the trace gas ammonia ($NH_3$) represents the major form of reduced nitrogen. With a share of around 70–80%, the wealth bulk of ammonia emissions is due to anthropogenic activity, namely by the use of synthetic fertilizers and livestock manure management (Bouwman et al., 1997; Paulot et al., 2015). Major source regions of $NH_3$ are located in south-east China and , northern India (Paulot et al., 2014; Van Damme et al., 2015).

Neutralization of acids by the alkaline gas $NH_3$ leads to the formation of ammonium salts in the atmosphere. For example, reaction of $NH_3$ with sulfuric acid ($H_2SO_4$) or nitric acid ($HNO_3$) forms aerosol particles composed of ammonium sulfate, $(NH_4)_2SO_4$ , or ammonium nitrate, $NH_4NO_3$ (e.g. Behera et al., 2013, and references therein). These inorganic aerosols are important not only

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with regard to air quality considerations (Hamaoui-Laguel et al., 2014) but they also affect climate through various direct and indirect radiative impacts (Adams et al., 2001; Martin et al., 2004; Liao and Seinfeld, 2005; Forster et al., 2007; Xu and Penner, 2012; Boucher et al., 2013). Further, also cirrus clouds might also be affected by the presence of $NH_3$ and ammonium (Tabazadeh and Toon, 1998; Wang et al., 2008). E.g. ammonium sulfate aerosols that are partially coated and have exposed surface sites are active with respect of to ice nucleation (Prenni et al., 2001; Wise et al., 2004). Such a heterogeneous nucleation pathway might influence size and number of cirrus particles and, consequently their radiative impact (Abbatt et al., 2006). Moreover, through stabilization of sulfuric acid clusters, ammonia itself may play an important role regarding the initial nucleation of sulfuric acid aerosols (Ortega et al., 2008; Kirkby et al., 2011; Schobesberger et al., 2013; Kürten et al., 2015).

Global emissions of $NH_3$ are expected to rise strongly due to the need to sustain a growing population and due to enhanced emissions under increasing temperatures (Erisman et al., 2008; Vuuren et al., 2011; Sutton et al., 2013). As a result, in future prospects for a positive radiative forcing by a decrease of the shortwave albedo caused by reductions of industrial $SO_2$ emissions may partly be compensated by increasing amounts of ammonium containing aerosols (Bellouin et al., 2011; Xu and Penner, 2012; Shindell et al., 2013; Hauglustaine et al., 2014).

With regard to the predicted increase in $NH_3$ emissions and the possible compensating effect on aerosol radiative forcing, Paulot et al. (2016) emphasize the need to better constrain also the vertical distribution of ammonia. However, there is a vast lack of observations of $NH_3$ at mid- and upper tropospheric levels.

Before 2008, measurements of ammonia were almost exclusively based on in-situ technologies (von Bobrutzki et al., 2010). Compared to the wealth of observations on ground, vertical profiles of $NH_3$ from in-situ observations above the boundary layer are relatively sparse. Recently, aircraft-borne campaign measurements over the US obtained concentration profiles in the free troposphere reaching altitudes of about 6 km (Nowak et al., 2007; Nowak et al., 2010, 2012; Leen et al., 2013; Schiferl et al., 2016). At these altitudes maximum observed $NH_3$ mixing ratios reached about 800 pptv (Schiferl et al., 2016) with detection limits of 70 pptv (Nowak et al., 2010). In-situ air-borne observations over Germany by Ziereis and Arnold (1986) restricted concentrations to the sub-pptv range at altitudes between 8 and 10 km . To our knowledge, these are the only upper tropospheric in-situ-measurements of $NH_3$ published so far.

A first step in the direction of observations with global coverage was achieved by Beer et al. (2008), who reported the detection of $NH_3$ in the lower troposphere from space-borne nadir sounding measurements by the Tropospheric Emission Spectrometer (TES) on the EOS Aura satellite. Subsequently, various papers have been published describing retrieval, validation and interpretation of $NH_3$ derived from the nadir sounders TES (Clarisse et al., 2010; Shephard et al., 2011), IASI (Infrared Atmospheric Sounding Interferometer) (Coheur et al., 2009; Clarisse et al., 2009, 2010;

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Van Damme et al., 2014), CrIS (Cross-track Infrared Sounder) (Shephard and Cady-Pereira, 2015),
and AIRS (Atmospheric Infrared Sounder) (Warner et al., 2016). The vertical sensitivity of these
satellite retrievals is mainly limited to the lower troposphere up to about 3–4 km and no altitude res-
olution is achieved (e.g., Clarisse et al., 2010; Shephard and Cady-Pereira, 2015). Recently, retrievals
of $NH_3$ vertical column amounts from ground-based FTIR solar observations located at various sites
have been presented by Dammers et al. (2015) and are being used for the quantitative validation of
space-borne nadir-viewing datasets (Dammers et al., 2016). As shown by Dammers et al. (2015) in
case of high amounts of $NH_3$ near the surface, the retrieval sensitivity peaks within the boundary
layer where also the altitude-gradient can be derived. For low concentrations, the retrieval is only
sensitive to the total vertical column amount.

All these observations sample atmospheric $NH_3$ either as in-situ concentrations on ground or from
ground or space as total column amounts, which are dominated by the large amounts in the lower
part of the atmosphere. With regard to the predicted increase in $NH_3$ emissions and the possible
compensating effect on aerosol radiative forcing, Paulot et al. (2016) emphasize the need to better
constrain also the vertical distribution of ammonia. However, there is a vast lack of observations of
$NH_3$ at mid- and upper tropospheric levels.

Vertical profiles of $NH_3$ concentrations through airborne in-situ observations are very sparse,
reaching maximum altitudes of about 5.5 km (Nowak et al., 2010; Leen et al., 2013) with detection
limits for $NH_3$ of 70 pptv and maximum observed values at 4–5.5 km of 300–500 pptv (Nowak
et al., 2010).

To achieve vertically resolved profiles of trace gases in the upper troposphere and above, limb-
sounding techniques have been applied frequently. Regarding ammonia, Oelhaf et al. (1983) reported
upper limits of 100 pptv above 10 km by analysis of balloon-borne limb solar absorption spectra
measured over the US. Space-borne solar occultation measurements obtained with the ACE-FTS
instrument within a plume of biomass burning over Tanzania have been studied by Coheur et al.
(2007). In that publication, the authors mention only a "tentative identification" of $NH_3$ in the spec-
tra, while the spectral signals of various other trace species, like such as $C_2H_4$, $C_3H_6O$, $H_2CO$ and
PAN were detected unequivocally. Nonetheless, Coheur et al. (2007) derived a vertical profile of
$NH_3$ between 6.5 and 17 km with typical values of less than 20 pptv and a maximum of about
50 pptv at 8 km. Burgess et al. (2006) report on first attempts to retrieve global distributions of am-
monia using limb infrared emission spectra measured by the Michelson Interferometer for Passive
Atmospheric Sounding (MIPAS) on Envisat. They obtained one climatological vertical profile with
$NH_3$ volume mixing ratios below 5 pptv at altitudes above 9 km. However, no evidence for the
presence of $NH_3$ in the limb spectra nor any indication for enhanced values within the area of the
Asian summer monsoon is shown.

At higher altitudes, Oelhaf et al. (1983) reported upper limits of 100 pptv above 10 km by anal-
ysis of balloon-borne limb-transmission spectra. In-situ observations by Ziereis and Arnold (1986)

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restricted the concentrations to below the pptv-range between 8 and 10 km NH$_3$ concentrations to the sub-pptv range at altitudes between 8 and 10 km .

In the case of space-borne limb sounding instruments, no unequivocal detection of NH$_3$ has been published so far. Burgess et al. (2006) report on first attempts to retrieve ammonia distributions from the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on Envisat but no spectral evidence for its presence is presented. Further, within a plume of biomass burning observed with the ACE-FTS instrument, Coheur et al. (2007) mention only a "tentative identification" of NH$_3$, while the spectral signals of various other trace species, like C$_2$H$_4$, C$_3$H$_6$O, H$_2$CO and PAN were detected unequivocally.

In summary, considering the reported observations, neither the in-situ measurements by Ziereis and Arnold (1986) nor the limb-sounding remote sensing data (Oelhaf et al., 1983; Coheur et al., 2007; Burgess et al., 2006) prove the presence of ammonia at altitudes above about 8 km. In the work presented below we show, to our knowledge, the first evidence for the presence of NH$_3$ together with quantitative retrievals at upper tropospheric levels by use of MIPAS averaged limb spectra.

## 2 MIPAS/Envisat

On board the Envisat satellite the MIPAS limb sounder recorded infrared spectra of the radiation emitted by atmospheric constituents from June 2002 until April 2012 (Fischer et al., 2008). Between June 2002 and March 2004 (period 1), the spectral resolution was 0.025 cm$^{-1}$ with one limb-scan consisting of 17 spectra from about 6–60 km altitude with steps of 3 km in the UTLS up to about 42 km in the case of nominal mode observations. From January 2005 until April 2012 (period 2), the spectral resolution was degraded to 0.0625 cm$^{-1}$. This was accompanied by a better vertical sampling (27 tangent levels up to about 70 km altitude with 1.5 km steps in the UTLS up to ≈23 km). Also in the horizontal direction along the satellite track the sampling improved from a distance between subsequent limb-scans of 550 km during period 1 to 420 km during period 2.

## 3 Retrieval and spectral detection

Here we report on the detection and retrieval of NH$_3$ from MIPAS observations in the upper troposphere on the basis of averaged limb-spectra. This method has already been applied successfully for the detection of bromine nitrate (BrONO$_2$) (Höpfner et al., 2009) and for the compilation of a global climatology of stratospheric sulfur dioxide (SO$_2$) from MIPAS measurements (Höpfner et al., 2013). In these those investigations the mean spectra consisted of monthly zonal averages within 10° latitude intervals, whereas for the present work we have chosen seasonal (3-monthly) averages within bins of 10° latitude by 10° longitude. Thus, we have refrained from zonal averaging in order to obtain resolution in the meridional direction, albeit slightly sacrificing temporal resolution. To obtain at least a reduction of the spectral noise of at least To reduce the spectral noise by at least a factor

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of five, we have chosen a lower limit of 25 single spectra (MIPAS level-1b version 5) for averaging. The resulting mean number of co-added spectra per time/latitude/longitude bin varies from 53–56 for the years 2003 and 2007 to 65–70 for 2008–2011 reaching maximum numbers of around 140 (see supplemental material for the detailed geographical and temporal distribution). This leads to a typical reduction of the spectral noise by 0.1 ranging from 0.2 to 0.08 and signal-to-noise values resulting in retrieval errors near and below 1 pptv of $NH_3$ (see detailed error estimation below). In the troposphere the number of available spectra is limited as a result of cloud contamination along the limb line-of-sight. We have applied a cloud filter to deselect cloud-contaminated spectra before averaging. As For the cloud detection scheme the established cloud-index method (Spang et al., 2004) with a cloud index limit of 2.0 has been used.

To derive altitude profiles of $NH_3$ from each averaged limb-scan we have applied a constrained non-linear multi-parameter least-squares fitting procedure where whereby measurements from all spectra of one limb scan are analysed in one step (e.g., von Clarmann et al., 2003; Höpfner et al., 2009). The unknown atmospheric state is described in terms of trace gas volume mixing ratios at discrete altitude levels with a grid distance of 1 km within the region of the UTLS. This grid is finer compared to the instrumental vertical field-of-view width of about 3 km at the tangent points and also finer than the vertical sampling distance of 1.5–3 km. To dampen vertical oscillations arising from the ill-posedness of the inverse problem a first oder order smoothing constraint has been chosen (Tikhonov, 1963; Steck, 2002). The regularization strengths have been adjusted independently for each species being retrieved simultaneously.

For fitting of the $NH_3$ signatures we have chosen spectral windows within the interval 950–970 $cm^{-1}$, which have the advantage that they are situated in the region of one of the optically thinnest mid-infrared atmospheric windows. Furthermore, there are relatively few spectrally interfering species which have to be retrieved simultaneously to with $NH_3$. Spectroscopic line parameters of the HITRAN 2012 database (Rothman et al., 2013) have been used.

A scheme consisting of two subsequent steps has been identified as adequate for the retrieval of $NH_3$. First, the broader wavenumber range 962–968 $cm^{-1}$ has been chosen to fit the strong $CO_2$ lines of the laser band together with the interfering species $O_3, H_2O, NH_3, COF_2$. In the second step, narrow analysis windows have been placed around the strongest signatures of $NH_3$: 951.6–952.0 $cm^{-1}$, 965.1–965.6 $cm^{-1}$, and 966.6–967.5 $cm^{-1}$ (MIPAS period 1) and 951.625–952.0 $cm^{-1}$, 965.125–965.625 $cm^{-1}$, and 966.625–967.5 $cm^{-1}$ (MIPAS period 2), thereby avoiding the peaks of the strong $CO_2$ lines. At this stage $CO_2$ is kept fixed to the results from the initial retrieval, while $O_3, H_2O$ and $COF_2$ are retrieved jointly with $NH_3$.

Figure 1 presents the spectral fit and the detection of $NH_3$ for two examples from both MIPAS periods at tangent heights around 12.5 km within the region of the Asian monsoon in June-August 2003 (top panel) and 2009 (bottom panel). Within each panel the top row shows the observations in black, the fit without taking $NH_3$ into account in blue and the retrieval including $NH_3$ in red. In

the second row of each panel the residual spectra are shown for the retrieval without (blue) and with (red) consideration of $NH_3$. Here the green line is the difference between both the two simulations (with minus without $NH_3$) in order to show the spectral signature of $NH_3$ without any instrumental effect, like such as spectral noise.

The top panel of Fig. 1 reveals clearly the presence of $NH_3$ in MIPAS limb spectra. Radiative transfer simulations without consideration of $NH_3$ lead to largest residuals (bold blue curves) at the position of the ammonia lines (dotted orange curves). Only when ammonia is taken into account are, the observed spectra within all three microwindows are fitted sufficiently well. Comparing the first row of the bottom panel in Fig. 1 with that of the top panel, the worse spectral resolution of MIPAS period 2 becomes obvious. Still the residuals of the $NH_3$ spectral lines and the better fit upon their consideration are visible, especially in microwindows 2 and 3.

Results of the altitude dependent error estimation are presented in Fig. 2 for the two examples of the limb scans for which the spectral fits have been shown in Fig. 1. A summary of the assumptions on the various sources of uncertainty is provided in Table 1. For spectral noise, the actual error numbers referring to the two limb-scans discussed are given together with their range over all observations in brackets. While noise is directly mapped into the state space for each individual retrieval, the error estimation for all other uncertainties has been performed by sensitivity calculations for atmospheric conditions representative for observations within the influence of the Asian monsoon (Höpfner et al., 2009; Höpfner et al., 2013).

In the left panels of Fig. 2 the bold dotted curves indicate the reconstructed vertical profiles of $NH_3$. The concentrations reach maximum values of around 24–29 pptv. The bold solid lines represent the total error calculated as the square root of the sum of all squared error components. The total errors amount to around 2–6 pptv (17–80%, right panels) in the altitude region up to about 20 km. Above, the estimated errors are larger than the mixing ratios of $NH_3$. The leading error components are tangent altitude uncertainties, uncertainties in the HITRAN line intensity data of $NH_3$ and nonlinearity effects in the averaging procedure as discussed in Höpfner et al. (2009). On the other hand, the use of averaged spectra reduces the noise term to less than 1 pptv within the altitude range of interest.

The vertical resolution of the resulting altitude profiles of $NH_3$ mixing ratios is directly connected to the noise error values through the applied setting of the regularization strength. The altitude resolution of the retrieval is described by the retrieval averaging kernel matrix (Rodgers, 2000). Examples for both MIPAS periods are provided in Fig. 3. From these, typical vertical resolutions are derived as the retrieval grid width divided by the inverse of the diagonal matrix elements (Rodgers, 2000). Within the altitude region up to 20 km the resulting vertical resolutions vary between 4–8 km during period 1 and 3–6 km during period 2. The globally average vertical resolution at the altitude levels 12, 15, and 18 km, which are discussed in more detail below, is 6.6 km, 7.9 km and 8.8 km during period 1 and 3.5 km, 4.3 km, and 5.6 km during period 2.

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## 4 The global dataset

205 Retrievals of NH$_3$ have been performed for the entire period of MIPAS observations, i.e. from July 2002 until April 2012. Figure 4 presents the global volume mixing ratio distributions at 15 km altitude during seven seasons from July 2002 until February 2004. There are enhanced values of up to 33 pptv within a region between 30°–110°E and 20°–50°N during boreal summer, coinciding with the occurrence of the Asian monsoons. During all other seasons of the two MIPAS periods and 210 outside the region influenced by the Asian monsoon, no similarly high concentrations of NH$_3$ can be found within the entire altitude region covered by our measurements.

An overview for all years with sufficient data coverage in the Asian summer monsoon season during the MIPAS mission lifetime is provided in Fig. 5 for altitude levels of 12, 15, and 18 km. Due to the less frequent presence of clouds, the number of pixels with valid measurements increases with 215 altitude. Similar to the results from MIPAS period 1, also during period 2 the enhancement of NH$_3$ within the Asian monsoon region is present for all years of observation. Further, on a global scale there are no other areas visible in the dataset with similarly enhanced values of NH$_3$. While at 12 and 15 km altitude NH$_3$ enhancements compared to the global background state are visible during all years, at 18 km altitude increased values of NH$_3$ are present only during the years 2003, 2008, 220 and 2010.

A comparison between vertical profiles of NH$_3$ averaged within the western (30–70°E, solid lines) and eastern (70–110°E, dashed lines) parts of the monsoon region for the latitude band 30–40°N is presented in Fig. 6 for the years 2003 and 2007–2011. In the same Figure, the dotted curve shows the NH$_3$ mean profile of all curves show the NH$_3$ mean Jun/Jul/Aug profiles for all years outside 225 the Asian monsoon area, for the same longitude and latitude range (30–110°E, 30–40°S) of the southern hemisphere. The profiles in the region of the Asian monsoon reveal that the maximum concentrations of NH$_3$ are always larger within the eastern part of the Asian monsoon, reaching values of 10–22 pptv at 11-13 km altitude. The profiles in the region of the Asian monsoon reveal that the maximum concentrations over the whole altitude range within one year are always larger in 230 the eastern part of the Asian monsoon compared to the western part. Maximum concentrations of NH$_3$ in the eastern part reach about 10–22 pptv at 11-13 km altitude. Largest vmr values are found in 2003 and 2009 and lowest ones in 2007 and 2011.

In the western part of the area influenced by the Asian monsoon, enhanced averaged volume mixing ratios of NH$_3$ can only be observed during the years 2003, 2008, and 2010 with values 235 ranging from 6 to 15 pptv. Situated at around 13–15 km, the maximum concentrations in the western part are always located always at higher altitudes compared to those from the eastern part of the monsoon region. The position of the NH$_3$ maximum at higher altitudes in the western compared to the eastern part of the monsoon system might be due to convective uplift of boundary layer air in the east followed by upper tropospheric transport and further uplift towards the west. Such an uplift of

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240 air from east to west is indicated in Vogel et al. (2014, Fig. 10) by trajectory calculations, however mainly located at the border of the anticyclone.

The mean $NH_3$ profiles of the western part show no clear enhancements during the years 2007, 2009 and 2011. These profiles exhibit maximum values below 5 pptv, which are in the range of concentrations retrieved in the case of the 'background' state of the southern hemisphere (indicated

245 as by dotted lines in Fig. 6). These values are below our estimated detection limit (see below).

Due to the lack of ammonia observations in the upper troposphere, we cannot validate our dataset with correlative measurements. However, in the next section we discuss its plausibility by comparing with the few previous observations and atmospheric model results.


## 5 Discussion

250 As mentioned in the introduction, observations of $NH_3$ reaching upper tropospheric levels have been published by Ziereis and Arnold (1986). They report upper limits of about 0.04 pptv between 8 and 10 km over Germany in May 1985. At the present state of our MIPAS data analysis we cannot contradict those upper values outside the influence of the Asian summer monsoon system. Given the total error of a few pptv we would estimate the 1-$\sigma$ detection limit of our retrieval to be about 3–

255 5 pptv. One might argue that the use of a 1-$\sigma$ detection limit does not provide sufficiently significant evidence of the $NH_3$ enhancement within the monsoon. However, random errors cannot explain why the enhancements should appear in a contiguous geographical pattern nor could they account for the enhancements appearing only in one season.

For example within the data shown in Fig. 5 at 12 km, there are 176 values larger than 5 pptv

260 outside the region 20–50°N × 30-120°E compared to 55 inside. However, at the 15 km level, only 5 data points exceed 5 pptv outside but 37 inside. Using 2-$\sigma$, there are no data points outside compared to 23 and 15 exceeding 10 pptv inside the region at 12 km and 15 km, respectively. Further, the detected enhancements inside the monsoon region are in many cases (13 times at 12 km and 8 times at 15 km) even above the 15 pptv and, thus, larger than a 3-$\sigma$ limit. Temporally resolved, values

265 above 10 pptv in the monsoon region exist during all years at both altitude levels with the exception of 2011 at 15 km. 15 pptv are exceeded at 10 km in 2003–2010 and at 15 km in all years but 2007 and 2011.

Regarding the retrievals outside the monsoon area, there is a difference between the two MIPAS measurement periods at 10–12 km altitude (see e.g. the difference in the dotted lines in Fig. 6 or the

270 higher background level at 12 km altitude visible in Fig. 5 between the year 2003 and 2007–2011) which amounts up to that reaches 4 pptv. We attribute this discrepancy to an unexplained systematic uncertainty caused by the different spectral resolutions between both the two instrumental states. This observation corroborates our error estimation and supports our conclusion that retrieved values up to 3–5 pptv are below the detection limit of the actual dataset.

275    Nonetheless, our measurements impose constraints on the global distribution of upper tropo-
spheric NH$_3$ concentrations which can be compared to results from model calculations. One of the
first globally modeled distributions of NH$_3$ has been was presented by Dentener and Crutzen (1994,
their Fig. 2b). These calculations were based on the tropospheric transport model Moguntia with a
horizontal resolution of $10° \times 10°$ with 10 layers up to 100 hPa in combination with, at that time, the
280    first global emission inventory of NH$_3$ with the same resolution as the transport model. Yearly mean
mixing ratios of below 2 pptv are modeled at upper tropospheric levels at mid- and high-latitudes.
These are in agreement consistent with the MIPAS background values. However, at equatorial and
sub-tropical latitudes, annual mean values of some tens of pptv were simulated between 300 hPa
($\approx$9.5 km) and 200 hPa ($\approx$12.5 km) which are clearly larger than the MIPAS results. Dentener and
285    Crutzen (1994) attributed these values to natural emissions in the tropics. The comparison with our
results indicates that either these emissions might have been over- overestimated or the tropical sink
processes of NH$_3$ underestimated. In their conclusions Dentener and Crutzen (1994) also mention
high modeled concentrations of NH$_3$ in the free troposphere over India and China. However, since
these enhancements were not quantified, they cannot be compared to our observations.

290    In contrast to the results of Dentener and Crutzen (1994), the zonal and yearly averages of modeled
NH$_3$ shown in Feng and Penner (2007, Fig. 9) decrease to well below 10 pptv above 500 hPa
($\approx$6 km) also in tropical regions. Their aerosol chemistry transport model (Umich/IMPACT) had a
horizontal resolution of 2° latitude $\times$ 2.5° longitude with 26 layers up to 0.1 hPa using the $1° \times$
1° global NH$_3$ emission inventory of Bouwman et al. (1997). Thus, these global model results are
295    more compatible with the MIPAS dataset.

Globally resolved annual mean model results of NH$_3$ are given in Adams et al. (1999, Plate
3a). These data were based on runs with the general circulation model GISS GCM II-prime with
4° latitude $\times$ 5° longitude horizontal resolution, nine vertical layers up to 10 hPa and NH$_3$ emissions
according to Bouwman et al. (1997). Mean mixing ratios of about 3.2 pptv at the 200 hPa pressure
300    level ($\approx$12.5/11 km in tropical/polar regions) are reported. At that pressure level, a slight gradient
between both the two hemispheres is visible, with values of 0–1 pptv in the south and 3–10 pptv
in the north. We do not recognize such a gradient in the background NH$_3$ concentrations from the
MIPAS measurements, albeit although, compared to given our estimated error, we cannot clearly
conclusively refute such a gradient.

305    Regarding ammonium nitrate aerosol during the Asian monsoon season, Metzger et al. (2002)
discuss their model results of enhanced values at upper tropospheric levels over Asia. They used the
global chemistry-transport model TM3 with 7.5° latitude $\times$ 10° longitude horizontal resolution, 19
vertical levels and the EDGAR database for the emissions of NH$_3$. These high amounts of ammo-
nium nitrate over Asia are attributed to in-situ production from NH$_3$ (and HNO$_3$) being convectively
310    transported to upper tropospheric levels. The fact that NH$_3$ is not removed by dissolution in droplets
and subsequent rainout is explained by the low acidity of convective clouds by which , such that

only part of the $NH_3$ would be dissolved. Our observations support these results with respect to the enhanced amounts of $NH_3$ which obviously survive the uplift within the Asian monsoon circulation. This indicates that a part of the Asian tropopause aerosol layer (ATAL) (Vernier et al., 2011) might be composed of ammonium nitrate, ammonium sulfate or other ammonium containing particles.

Further, through a possible influence of the Asian monsoon on the composition of the tropical tropopause layer (TTL), by transport of ammonia or ammonium, our measurements may help to explain why in-situ measurements of aerosols in the TTL indicate that the sulfate appears to be mostly or fully neutralized (Froyd et al., 2009, 2010). Measurements of particle acidity hold potential to inform low $NH_3$ concentrations further in the background UT outside the Asian summer monsoon system.

## 6    Conclusions

We have presented first evidence for of ammonia being present in the Earth's upper troposphere above 10 km by analysis of MIPAS infrared limb emission spectra. The region and period of detection is confined to the Asian summer monsoon system. Maximum average values of around 30 pptv over a three-monthly three-month period have been retrieved, thus, demonstrating that part of the $NH_3$ released on at the ground survives the loss processes on its way to the upper troposphere. As suggested by Metzger et al. (2002), ammonia may form ammonium nitrate aerosols under those circumstances. Thus, our observations indicate a possible contribution of ammonium aerosols to the composition of the ATAL.

The detection of enhanced amounts of $NH_3$ in the Western western part of the Asian monsoon anticyclone during several years suggests that its lifetime is long enough to survive transport to areas far from the source region. The position of the $NH_3$ maximum at higher altitudes in the Western compared to the Eastern part of the monsoon system is compatible with the general view: mainly convective uplift of boundary layer air in the East followed by upper tropospheric transport and further uplift in the anticyclone towards the West. The generally lower mixing ratios of $NH_3$ in the Western western compared to the Eastern eastern part indicate on-going ongoing loss processes at high altitudes.

Unfortunately, in the literature there seem to exist no locally resolved model results of $NH_3$ during the monsoon period to which we could compare our observations. We anticipate that such simulations would be of value to improve our understanding of $NH_3$ loss processes and aerosol production in the Asian monsoon. Also, airborne remote sensing observations, like the one planned within the EU project StratoClim with the GLORIA instrument on the Geophysica high flying aircraft, will would strongly increase our knowledge about ammonia distributions in the Asian monsoon on a much finer time, horizontal and vertical resolution scale than the MIPAS dataset presented here.

Regarding the global distribution of upper tropospheric $NH_3$ outside the Asian monsoon, within this study we could provide upper limits in the range of a few $pptv$. This will help to constrain global models and to improve their results.

The $NH_3$ dataset is available upon request from the author or at http://www.imk-asf.kit.edu/english/308.php.

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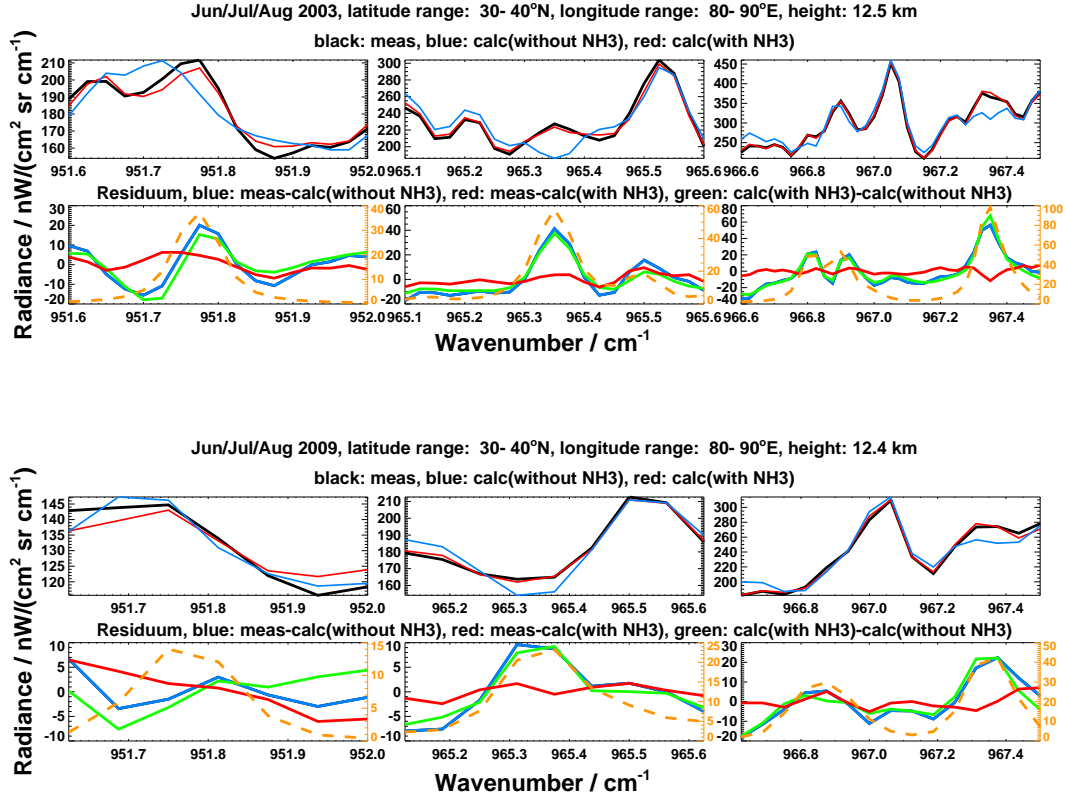       505, doi:10.1038/321503a0, 1986.

**Figure 1.** Spectral identification of $NH_3$ in MIPAS observations within the three spectral windows used for the retrieval (columns). The top two rows belong to the first observational period with higher spectral resolution. Rows 3 and 4 refer to the second period with lower spectral resolution. Rows 1 and 3 contain measured (black) and best fit spectra (blue: without, red: with $NH_3$). Row 2 and 4 show the spectral residuals without consideration of $NH_3$ (blue) and with $NH_3$ (red). Green curves in the second and fourth row represent the spectral features of $NH_3$ (calculation with $NH_3$ minus calculation without $NH_3$). To guide the eye, the orange dashed lines in rows 2 and 4 are simulated pure $NH_3$ spectra.
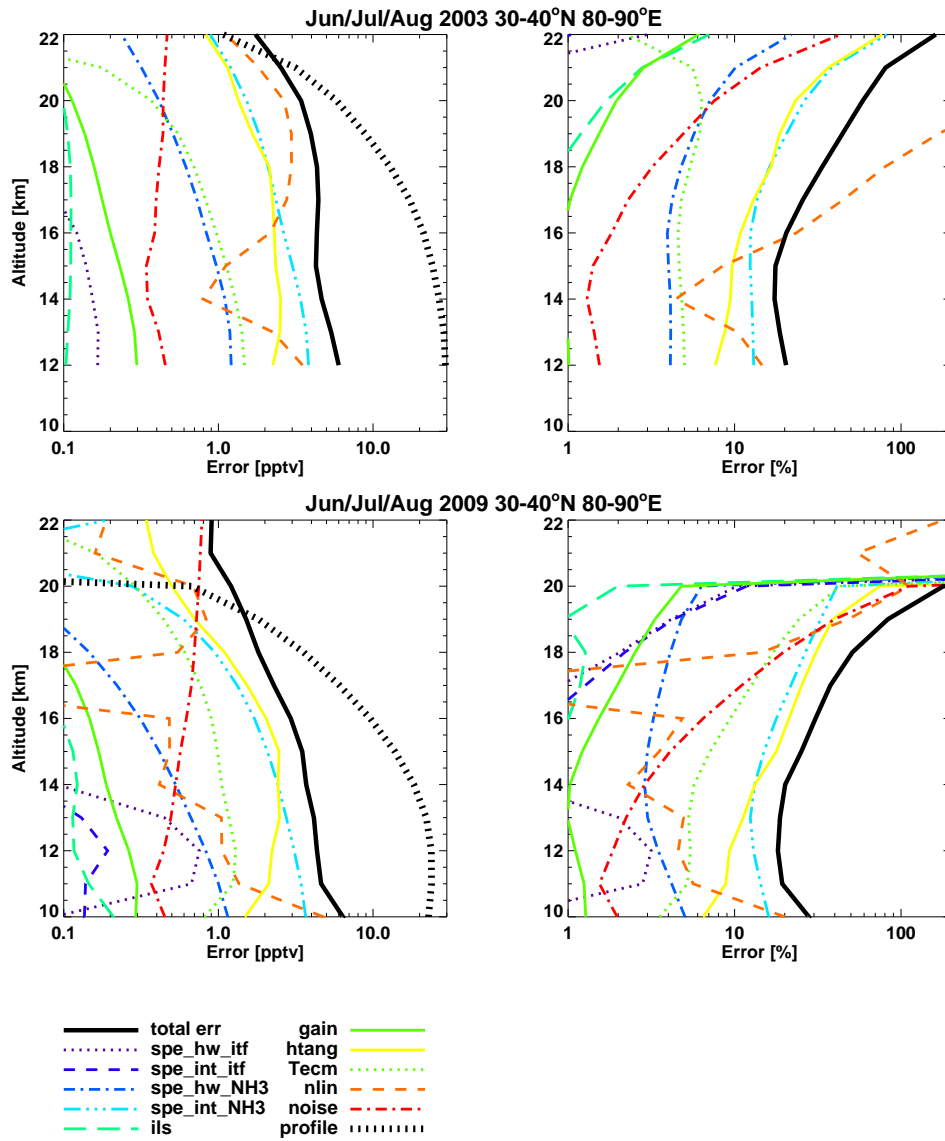
**Figure 2.** Estimated error profiles for two examples: one from measurement period 1 (June/July/August 2003, 30–40°N, 80–90°E) and one from period 2 (June/July/August 2009, 30–40°N, 80–90°E). The retrieved NH₃ vmr profiles are shown as bold black dotted lines ("profile"). Abbreviations of the error sources are resolved in Tab. 1.
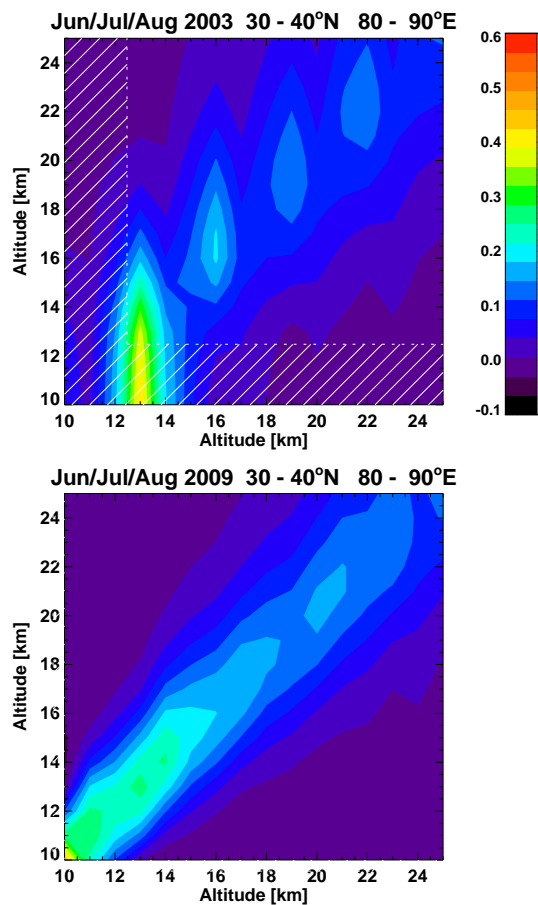
**Figure 3.** Averaging kernels of the MIPAS NH$_3$ retrieval during the first (top) and second (bottom) MIPAS measurement period. The number of degrees-of-freedom up to 25 km is 2.1 (top) and 3.5 (bottom). Hatched areas indicate altitudes below the lowest tangent height where no measurement information is available.
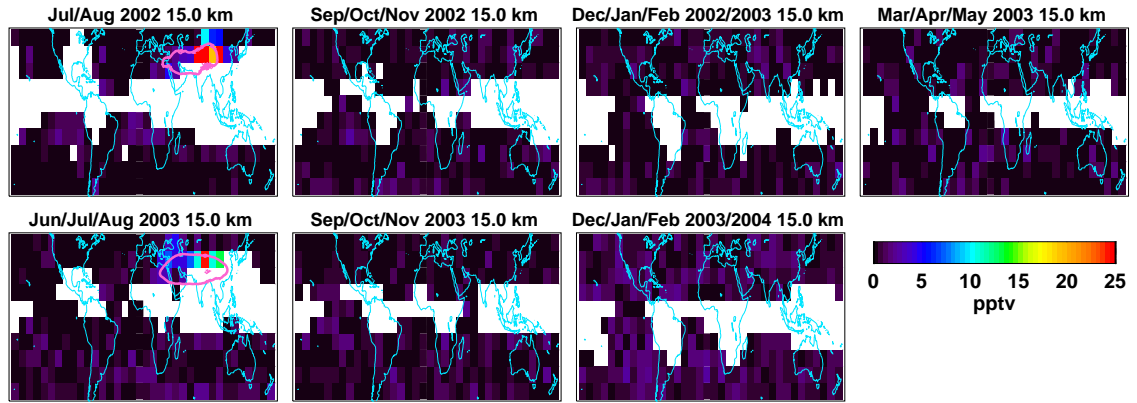
**Figure 4.** Distributions of $NH_3$ volume mixing ratios at 15 km altitude between 50°N and 50°S retrieved from MIPAS seasonal mean spectra during the first measurement period. Pixels where not enough spectra for averaging were available are left white. To guide the eye, the pink lines denote the approximate position of the Asian Monsoon Anticyclone. It is the $2 \times 10^{-6}$ $Km^2kg^{-1}s^{-1}$ contour of the mean potential vorticity for July/August in 2002 and June/July/August in 2003 at the potential temperature level of 370 K from the ECMWF ERA interim reanalysis (Dee et al., 2011) (e.g. Ploeger et al., 2015, and references therein).
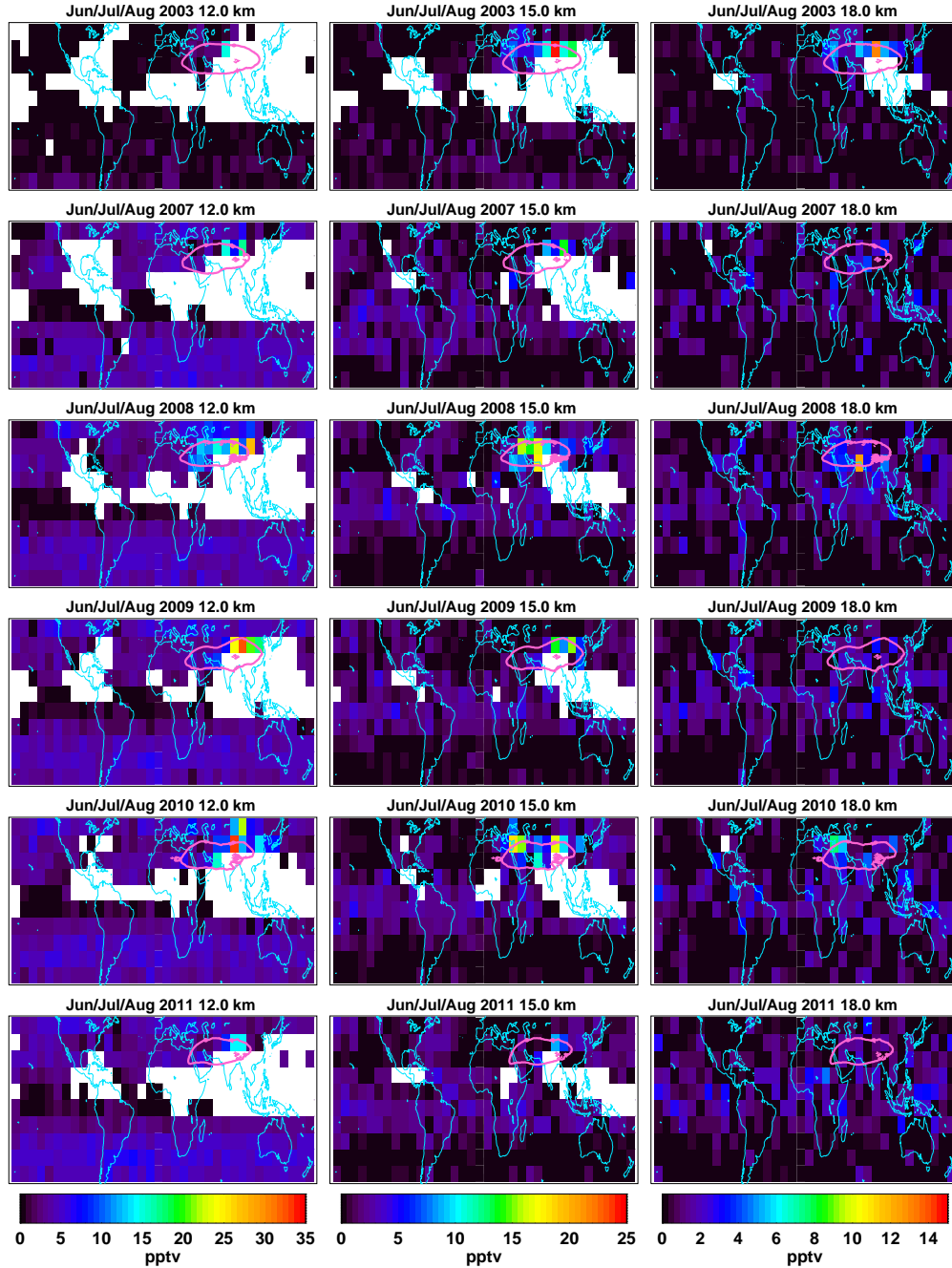
**Figure 5.** Distributions of NH$_3$ volume mixing ratios at 12 km, 15 km and 18 km altitude between 50°N and 50°S retrieved from MIPAS seasonal mean spectra for several years during the Asian monsoon period. during the Asian monsoon period for several years. Pixels where not enough spectra for averaging were available are left white. Pink contour lines denote the mean position of the Asian Monsoon Anticyclone for June/July/August as described in the caption of Fig. 4.
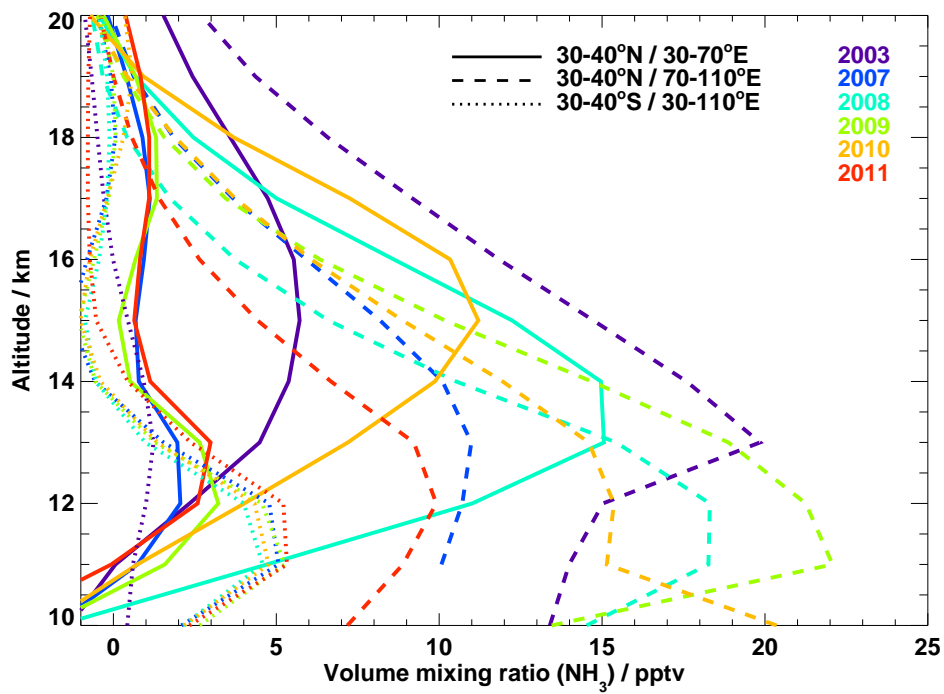
**Figure 6.** Mean profiles of $NH_3$ from MIPAS within the geographical range noted in the figure legend during June/July/August of each year. Solid: westerly western part, dashed: easterly eastern part of the Asian monsoon, dotted: reference profiles outside the monsoon in the southern hemisphere.

**Table 1.** Assumptions on uncertainties used for the error assessment in Fig. 2.

| Error source | Assumed uncertainty | Abbreviation |
|---|---|---|
| Spectral noise after apodization[1] | period 1: 2.2 (1.5–3.1) $\mathrm{nW/(cm^2\,sr\,cm^{-1})}$ | noise |
| | period 2: 1.3 (0.8–1.8) $\mathrm{nW/(cm^2\,sr\,cm^{-1})}$ | |
| Instrument line shape[2] | 3% | ils |
| Instrument gain calibration[3] | 1% | gain |
| Tangent altitude[4] | 300 m | htang |
| Temperature[5] | 2 K below/5 K above 35 km | Tecm |
| Retrieval from averaged spectra[6] | | nlin |
| Air-broadened half-width of $NH_3$ lines[7] | 10% | spe_hw_NH$_3$ |
| Intensity of $NH_3$ lines[7] | 15% | spe_int_NH$_3$ |
| Air-broadened half-width of interfering gas lines[7] | 15% | spe_hw_itf |
| Intensity of interfering gas lines[7] | 5% | spe_int_itf |

[1] ESA l1b dataset, depending on number of co-added spectra; [2] F. Hase, pers. comm., Höpfner et al. (2007); [3] Kleinert et al. (2007); [4] von Clarmann et al. (2003); von Clarmann et al. (2009); Kiefer et al. (2007); [5] ECMWF uncertainty Höpfner et al. (2013); [6] Höpfner et al. (2009); Höpfner et al. (2013); [7] HITRAN 2012 spectral line errors Rothman et al. (2013)
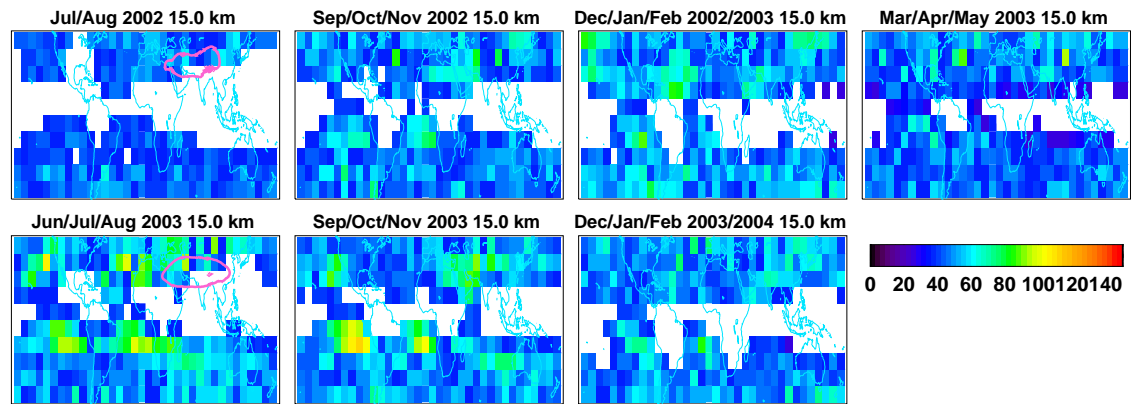
# Supplement

Figure 1: Same as Fig. 4 of the paper, but with a color scale indicating the number of observations used for calculating the averaged spectra.
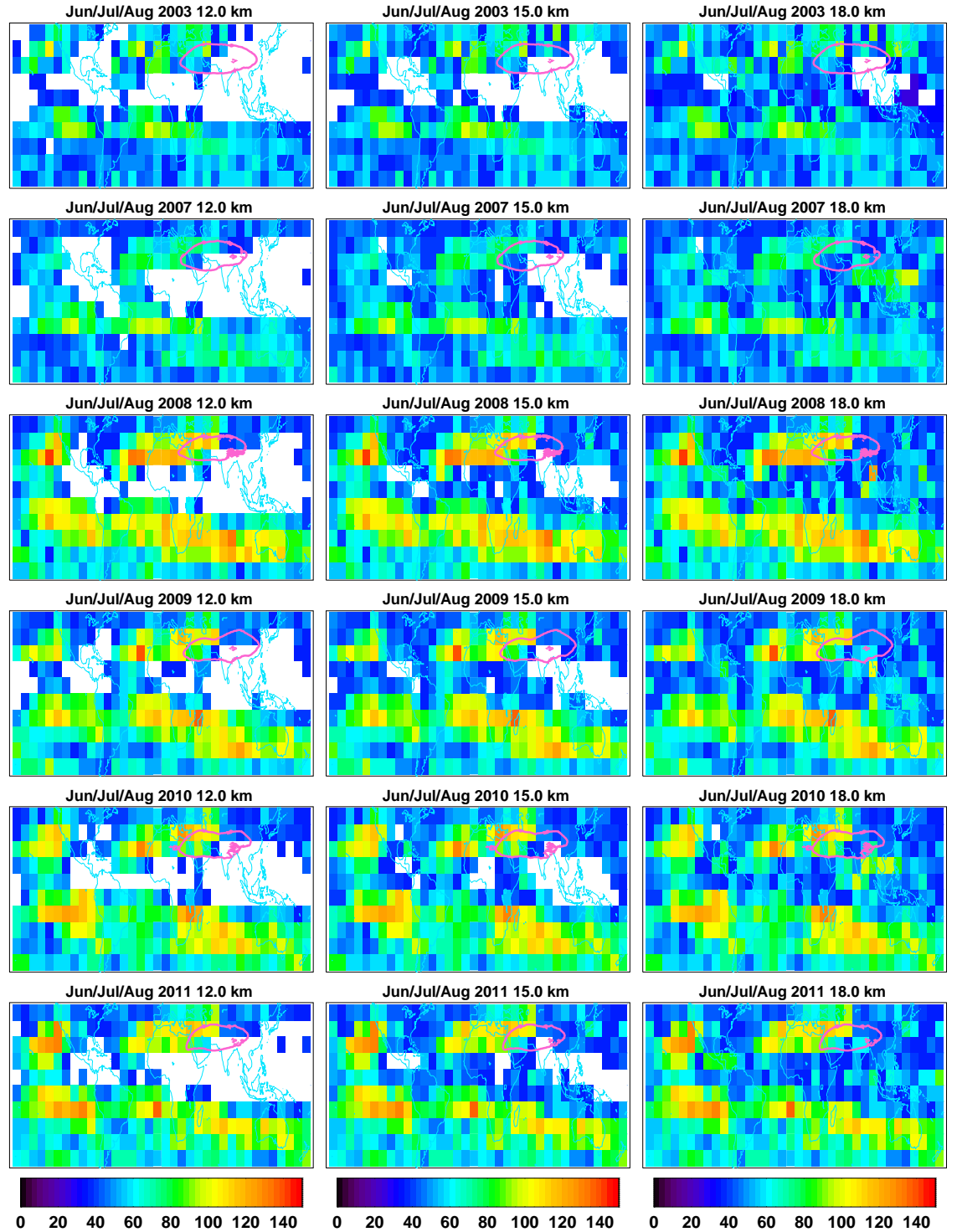
Figure 2: Same as Fig. 5 of the paper, but with a color scale indicating the number of observations used for calculating the averaged spectra..