

Interactive comment on “First detection of ammonia (NH₃) in the Asian monsoon upper troposphere” by M. Höpfner et al.

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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

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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 Bobruzki 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 spectra, while the spectral signals of various other trace species, such as C_2H_4 , $\text{C}_3\text{H}_6\text{O}$, 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.

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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 (≈ 9.5 km) and 200 hPa (≈ 12.5 km)”*

Line 268: *“above 500 hPa (≈ 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 $20\text{--}50^\circ\text{N} \times 30\text{--}120^\circ\text{E}$ compared to 55 inside. However, at the 15 km level, only 5 data points exceed 5 pptv outside but 37 inside. Using $2\text{-}\sigma$, 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

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above 15 pptv and, thus, larger than a $3\text{-}\sigma$ 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 $10^\circ \times 10^\circ$ 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 $1^\circ \times 1^\circ$ global NH_3 emission inventory of Bouwman et al., 1997.”*

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

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GCM II-prime with 4° latitude × 5° longitude horizontal resolution, nine vertical layers up to 10 hPa and NH₃ emissions according to Bouwman et al., 1997.”

Line 228: *“They used the global chemistry-transport model TM3 with 7.5° latitude × 10° longitude horizontal resolution, 19 vertical levels and the EDGAR database for the emissions of NH₃.”*

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 NH₃ 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?)

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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 to 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 NH₃ (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 seemingly 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

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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

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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 NH₃ 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 NH₃, 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 NH₃ dataset is available upon request from the author or at <http://www.imk-asf.kit.edu/english/308.php>.”

Technical comments:

L8 aerosol 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.

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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 NH₃.

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:

<http://www.atmos-chem-phys-discuss.net/acp-2016-392/acp-2016-392-AC2-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-392, 2016.

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