Aircraft- and space-borne infrared remote sensing observations of ammonia (NH_3) and solid ammonium nitrate aerosols in the upper troposphere during Asian monsoons

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Institute of Meteorology and Climate Research

Two nobel prices 100 years ago

Chemistry

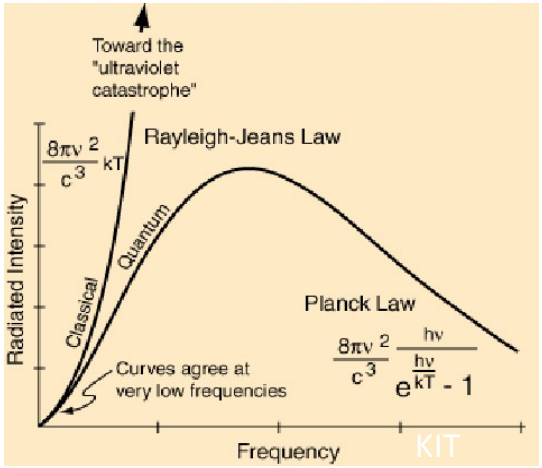
Physics

Fritz Haber

Nobel foundation archive

The Nobel Prize in Chemistry 1918 was received by Fritz Haber in 1919: "for the synthesis of ammonia from its elements."

The Nobel Prize in Physics 1918 was received by Max Planck in 1919: "in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta."



Max Planck

Nobel foundation archive

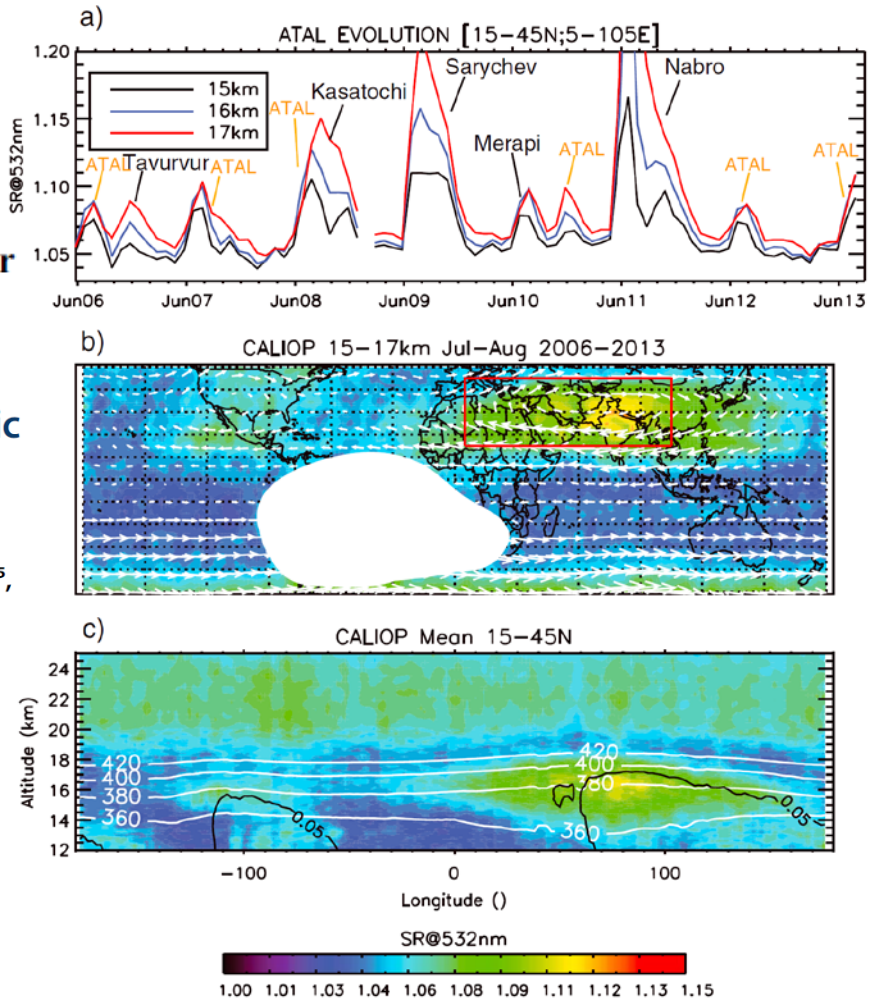
The Asian Tropopause Aerosol Layer

CALIPSO detection of an Asian tropopause aerosol layer

J.-P. Vernier,[1] L. W. Thomason,[1] and J. Kar[2] GRL, 2011

Increase in upper tropospheric and lower stratospheric aerosol levels and its potential connection with Asian pollution

J.-P. Vernier[1,2], T. D. Fairlie[2], M. Natarajan[2], F. G. Wienhold[3], J. Bian[4], B. G. Martinsson[5], S. Crumeyrolle[6], L. W. Thomason[2], and K. M. Bedka[2] JGR, 2014

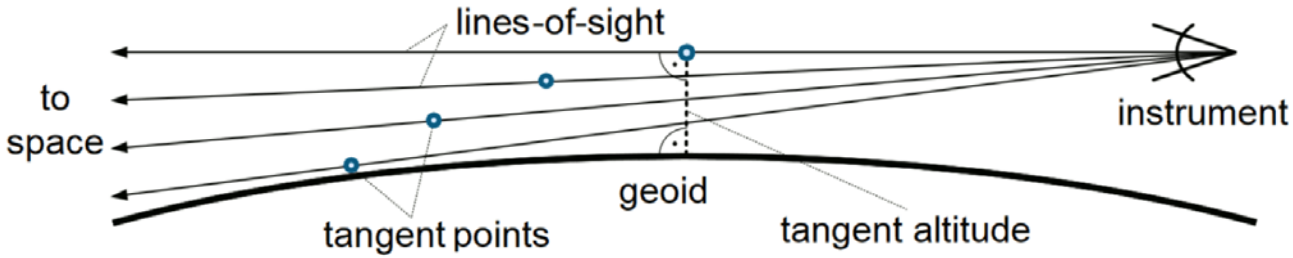


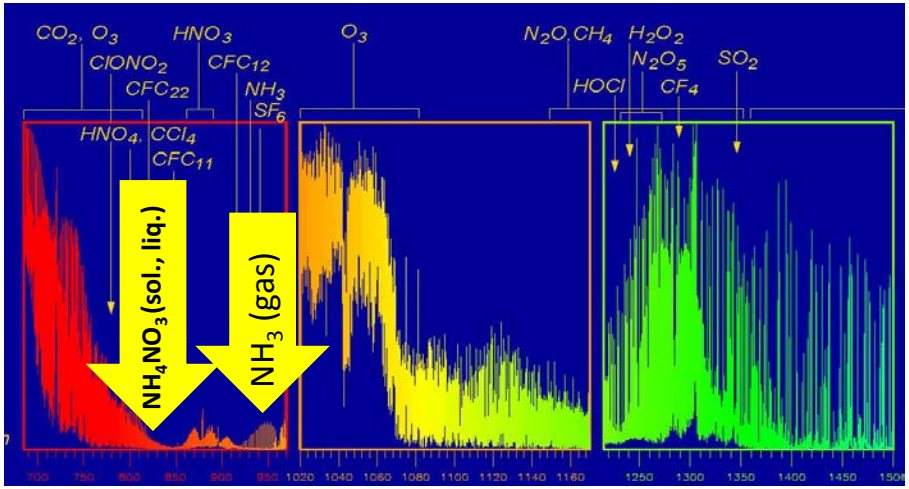
Small direct aerosol radiative effect - but: influence on ice particle nucleation?

The StratoClim campaign 2017: the first high-altitude aircraft measurements in the Asian monsoon upper troposphere

- M55 Geophysica research aircraft
  - Altitude up to 21 km
  - Range up to 4000 km
- Basis: Kathmandu (Nepal)
- July and August 2017
- 8 local research flights

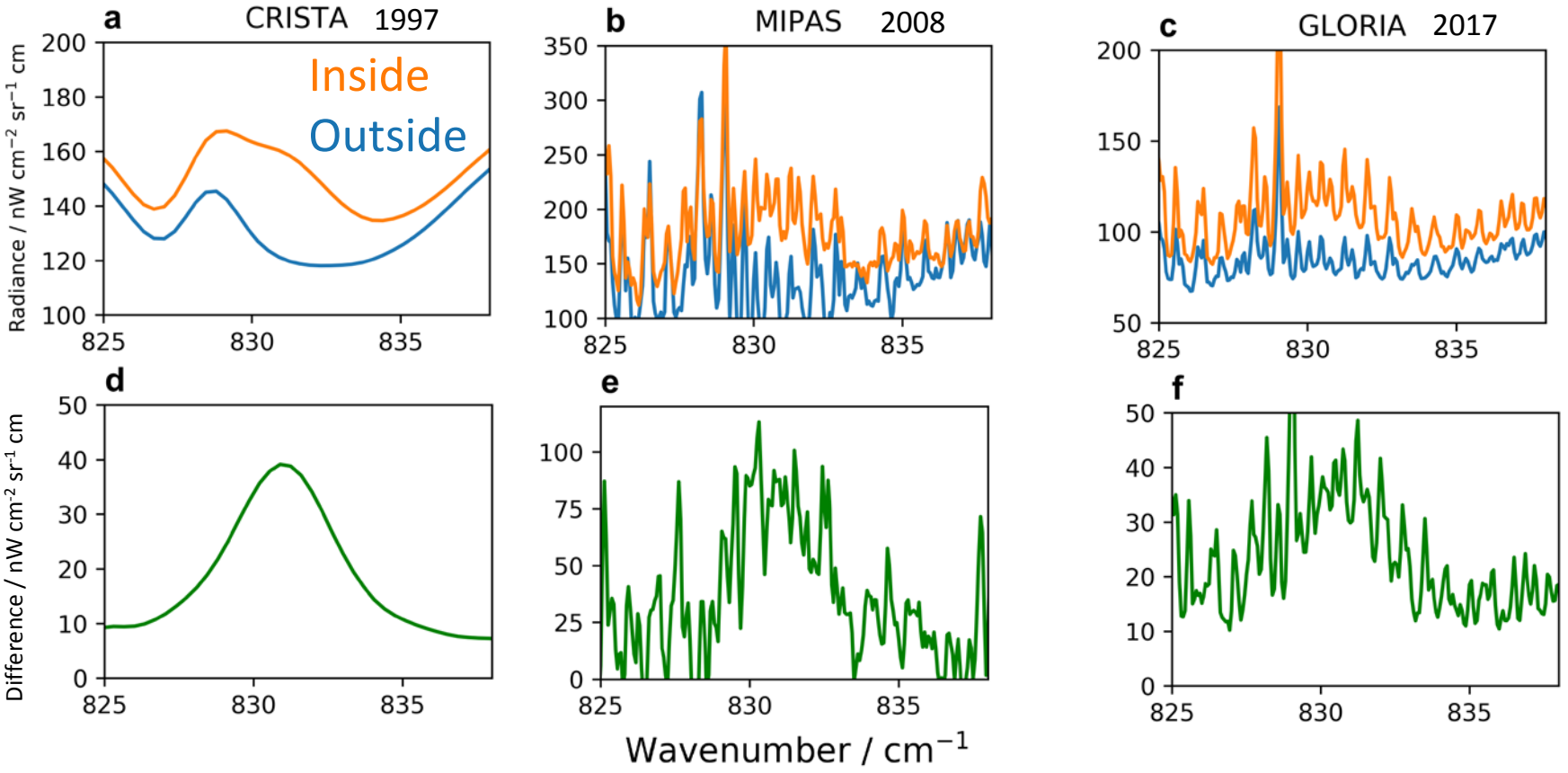
Infrared limb sounding



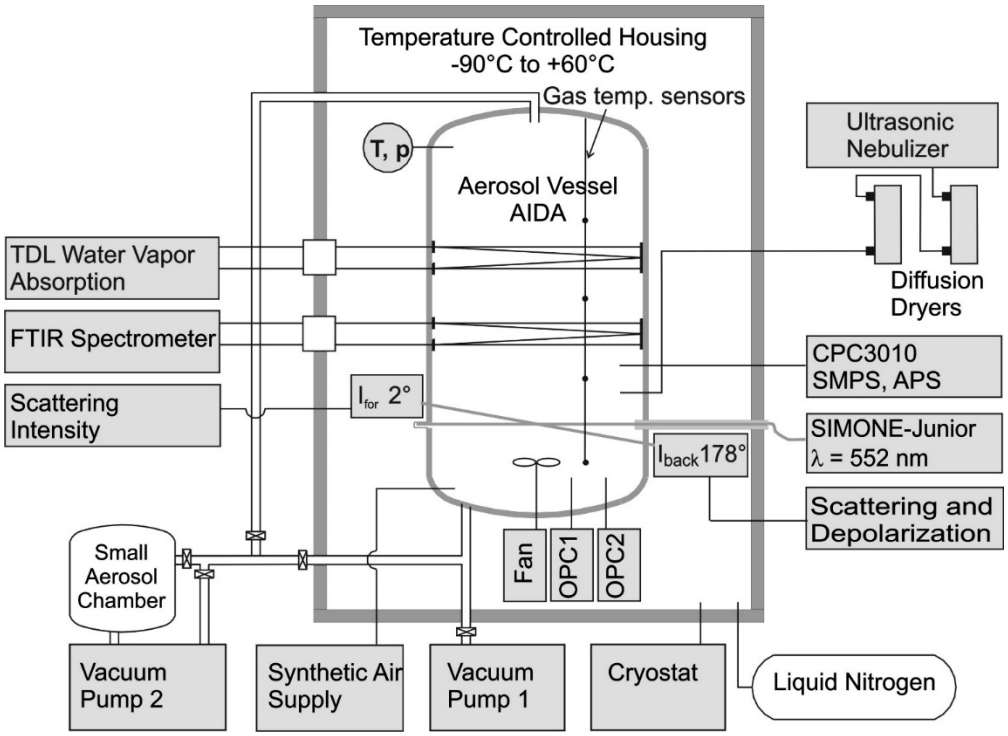


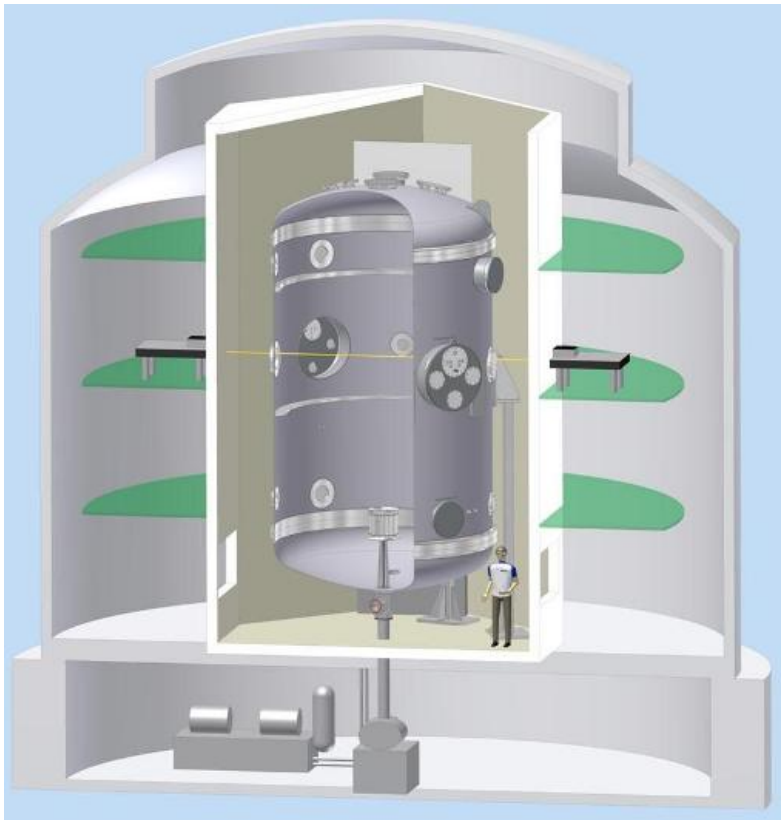
GLORIA@ Geophysica 2017

¿ A peak in infrared spectra inside the monsoon upper troposphere at 831 cm^{-1} ?

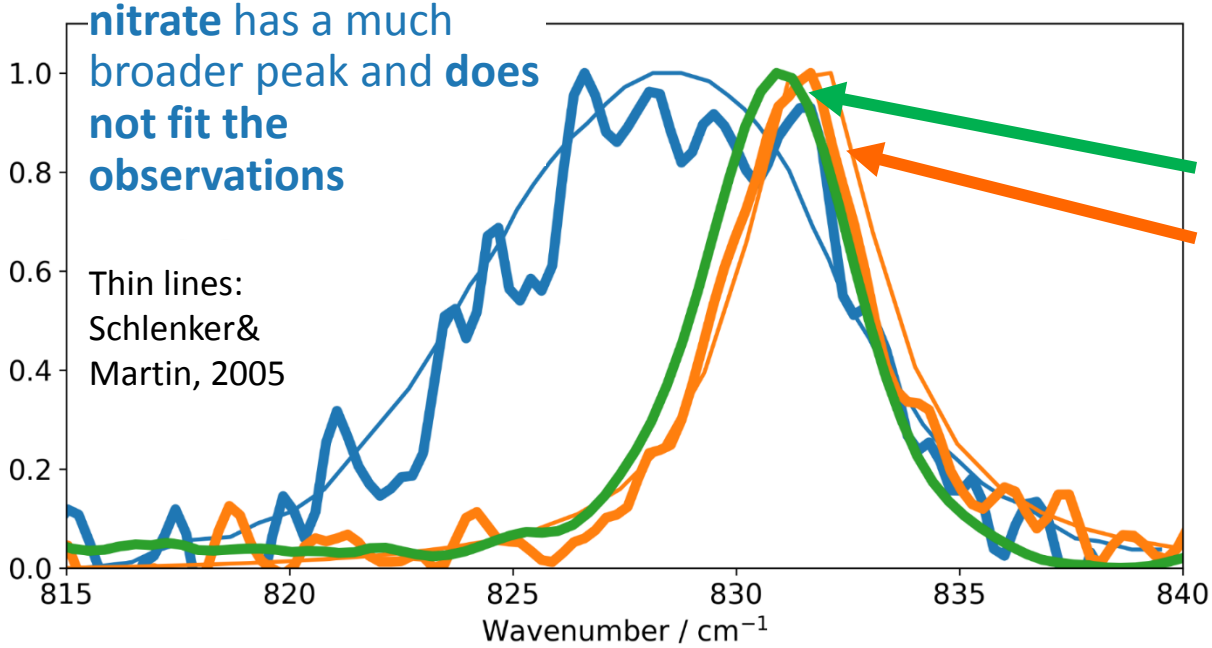


The AIDA aerosol and cloud chamber





Laboratory infrared spectra of the $\nu_2(NO_3^-)$ band of NH_4NO_3 particles compared to the observations



Observed atmospheric peak fits to the signature of **solid ammonium nitrate**

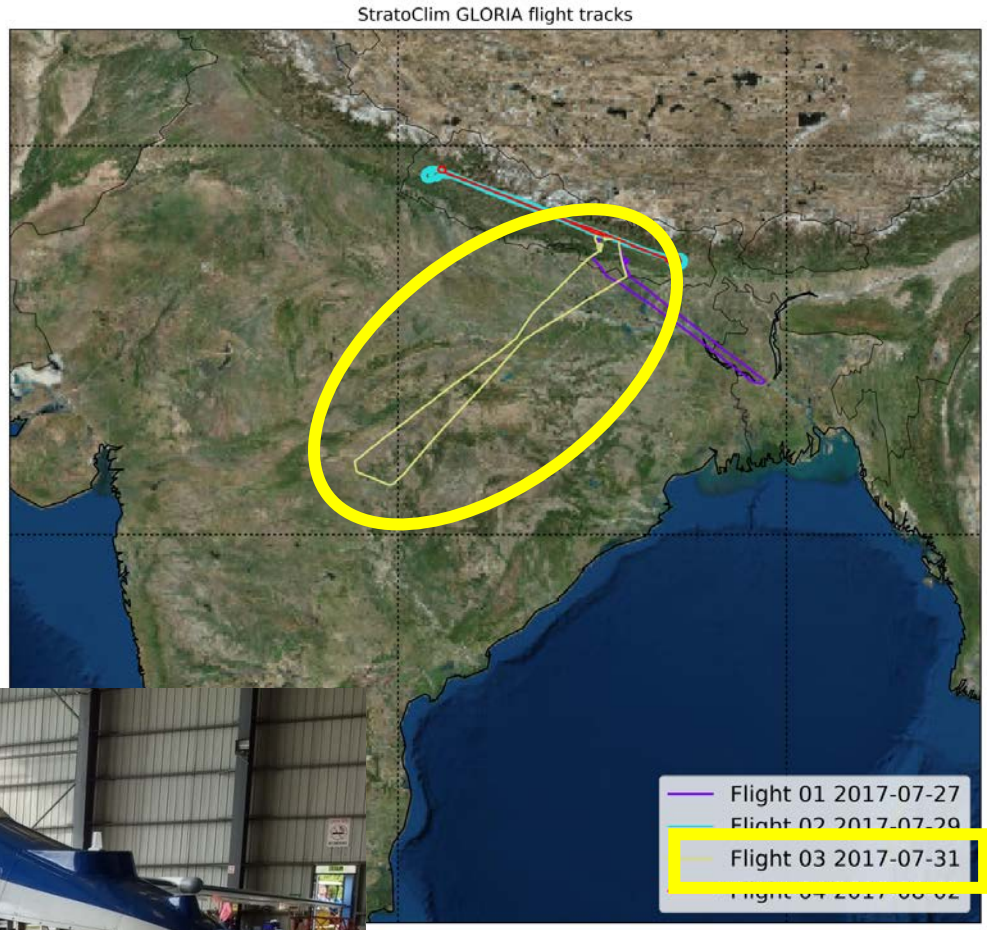
- **Laboratory observations show that the infrared signature is due to solid ammonium nitrate particles**
- **Solid AN particles only form when impurities of ammonium sulfate are present**
- **This allows to derive ammonium nitrate mass concentration profiles from the infrared limb observations**

Formation and possible impact of solid ammonium nitrate in the UT

- Cziczo & Abbatt, 2000: **NH_4NO_3 shows strong inhibition to efflorescence down to 2% RH (298 – 238 K)** "*These findings strongly suggest that, in the absence of heterogeneous nuclei, a* ***wide variety of inorganic aerosols will exist as liquid solutions*** *in the atmosphere regardless of relative humidity and temperature conditions*"
- Abbatt et al., Science, 2006: ***Solid Ammonium Sulfate Aerosols as Ice Nuclei****: A Pathway for Cirrus Cloud Formation*" (Laboratory and model study)
- Our AIDA experiments: **solid Ammonium Nitrate particles form in presence of small impurities (3 mol%) of ammonium sulfate at upper tropospheric temperatures**

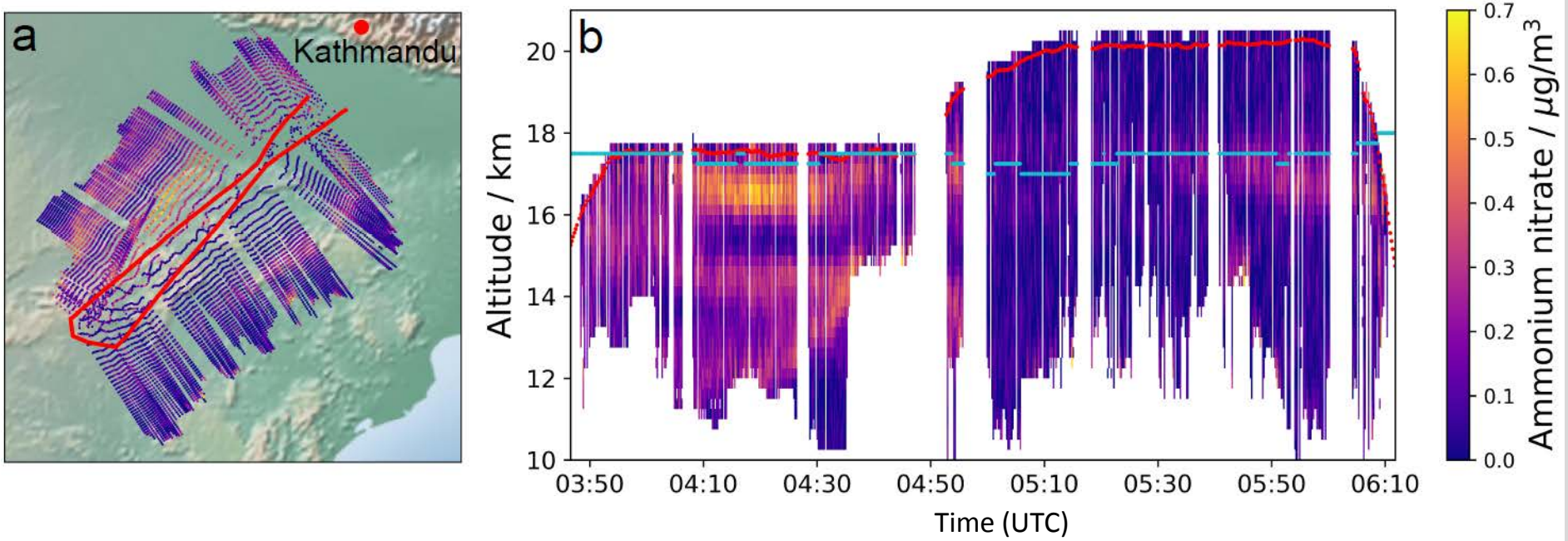
Simultaneous measurements:

- **GLORIA IR-limb sounder**
- **In-situ particle instruments (size distribution, composition)**



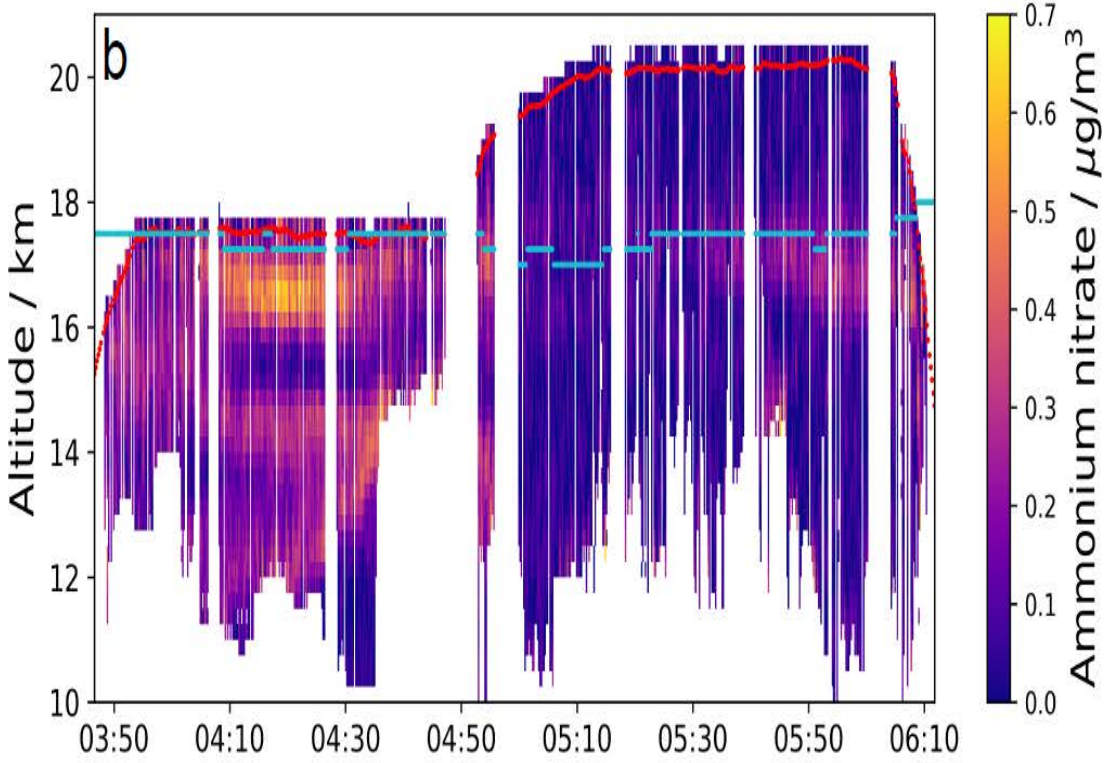
StratoClim flight 31 Jul 2017

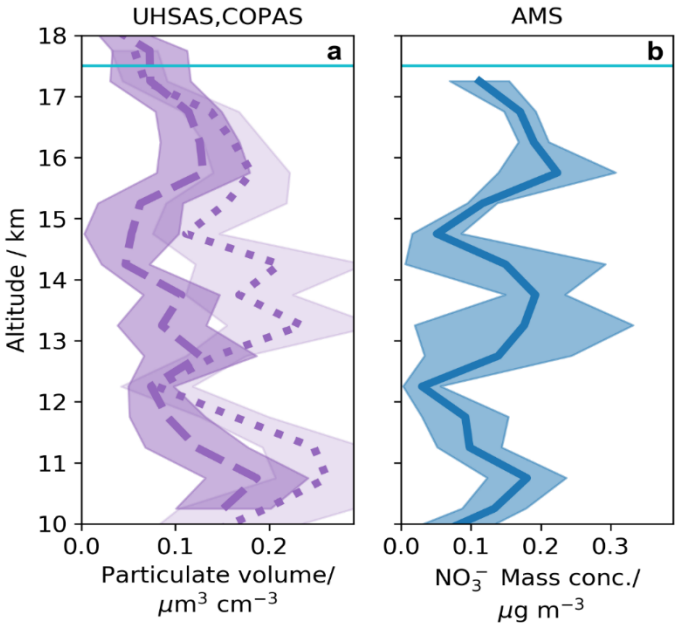
Ammonium nitrate aerosol mass density



- **Ammonium nitrate layers at the tropopause and at 12-14 km**
- **Higher concentrations in NW-direction**

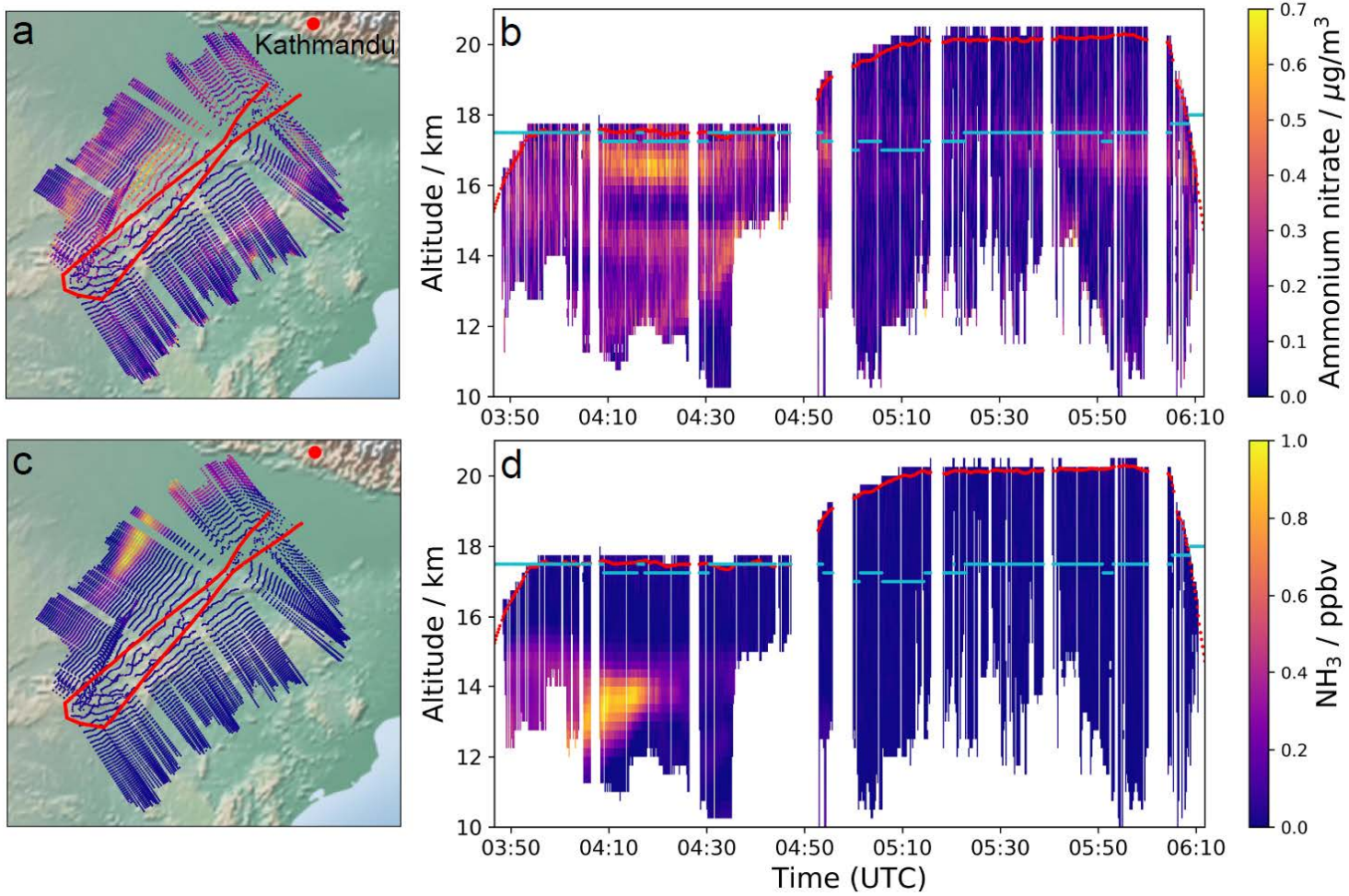
StratoClim flight 31 Jul 2017:
comparison with in-situ aerosol measurements of Univ./MPI Mainz





- **Ammonium nitrate concentrations from IR-limb and in-situ compare well**
- **Most of the particle mass measured in-situ are nitrate aerosols (with traces of sulfate)**

StratoClim flight 31 Jul 2017: ammonium nitrate aerosols and ammonia gas



NH_4NO_3 aerosol mass density

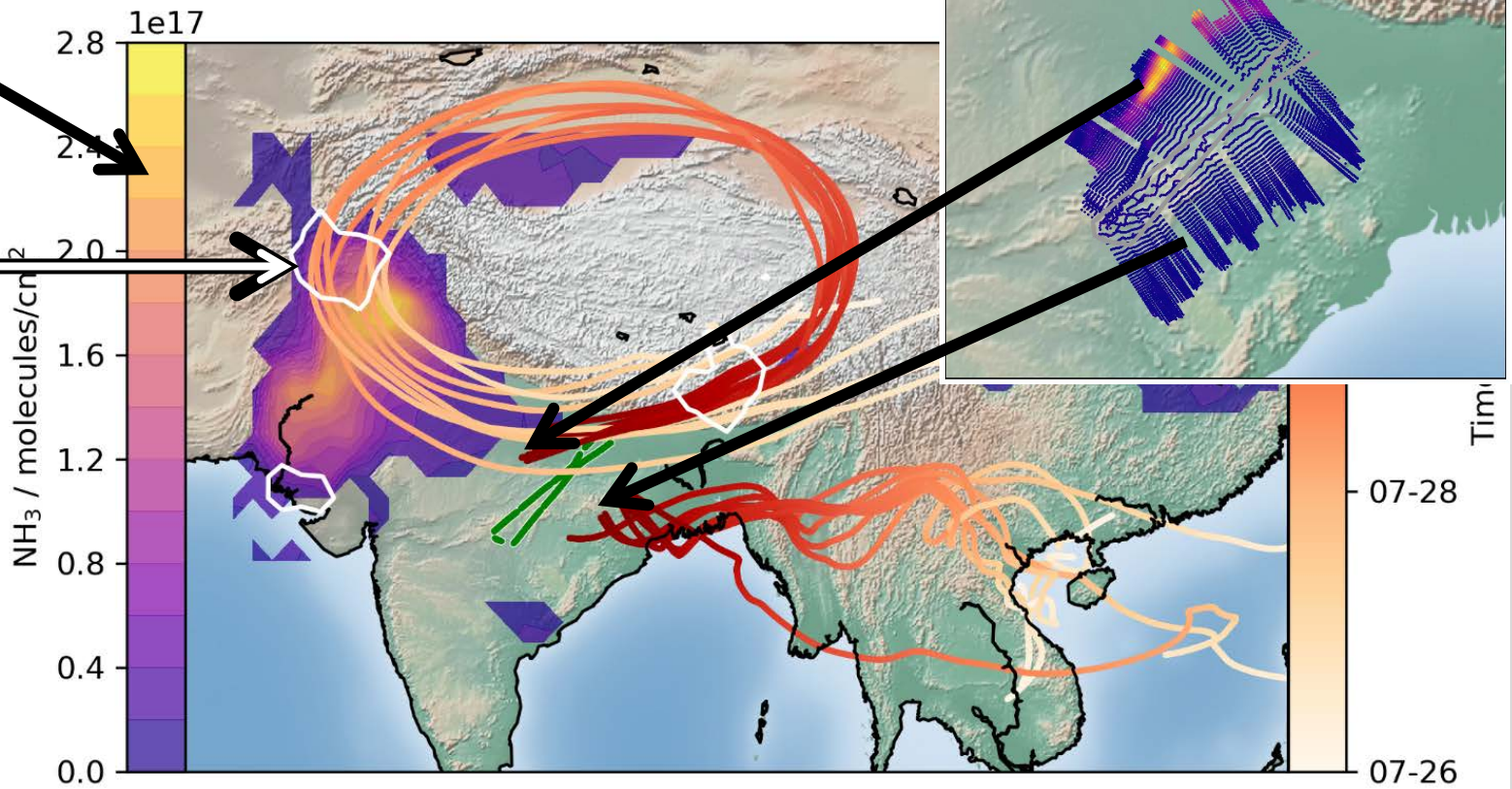
NH_3 trace gas mixing ratio

- Large concentrations of NH_3 observed at 14 km
- Ammonium nitrate at layers in the vicinity of regions with enhanced NH_3

Origin of the NH_3 – plume observed by GLORIA

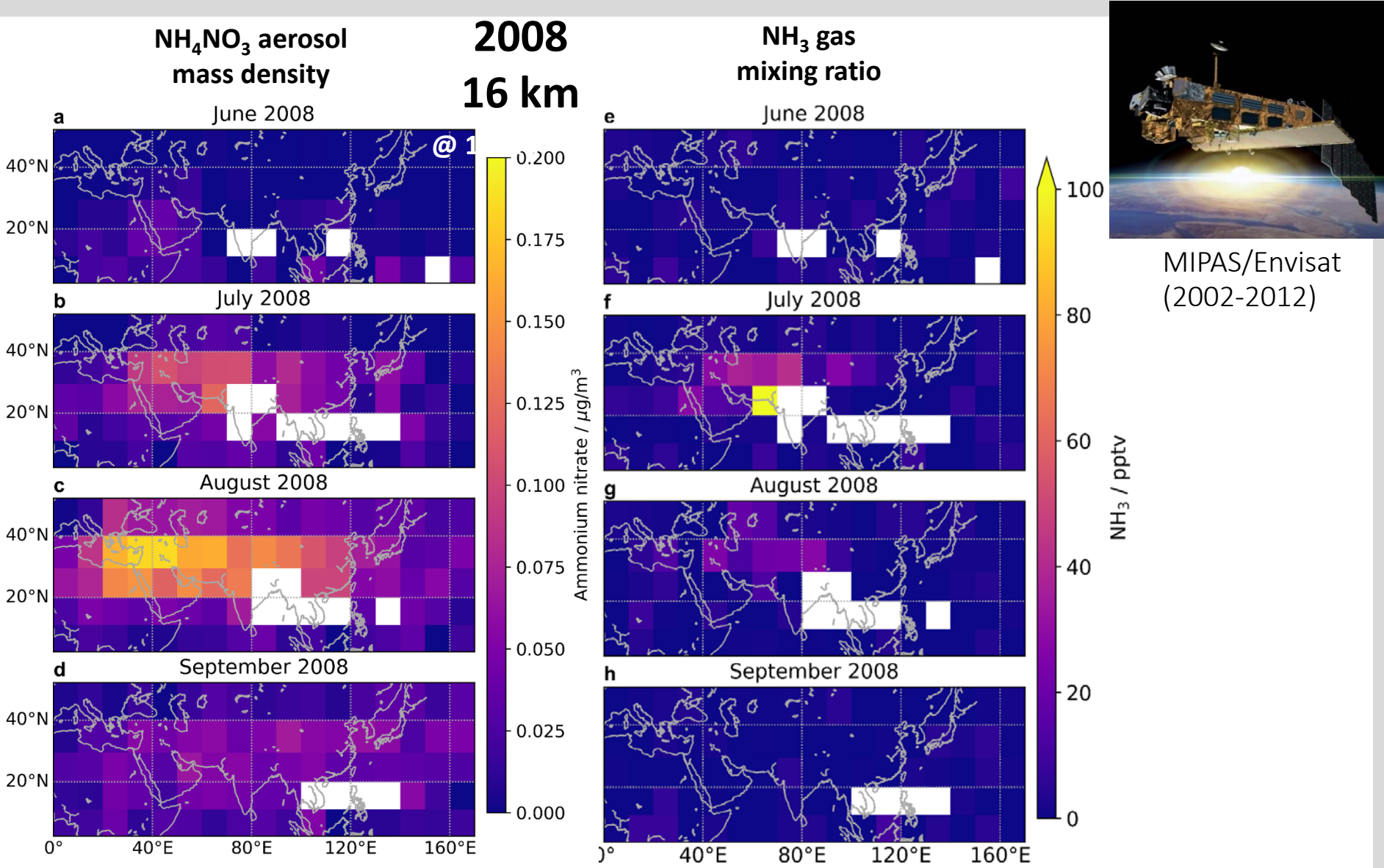
IASI NH_3 (low-mid troposphere)

Density of convective events along backward trajectories



http://iasi.aeris-data.fr/NH3
The data produced at Université Libre de Bruxelles (ULB) by Simon Whitburn and Martin Van Damme
Van Damme et al., AMT, 2017

- **High NH_3 at 14 km altitude traced back to regions with strong convection and with enhanced concentrations of NH_3 in the lower troposphere as detected by the IASI infrared nadir sounder**

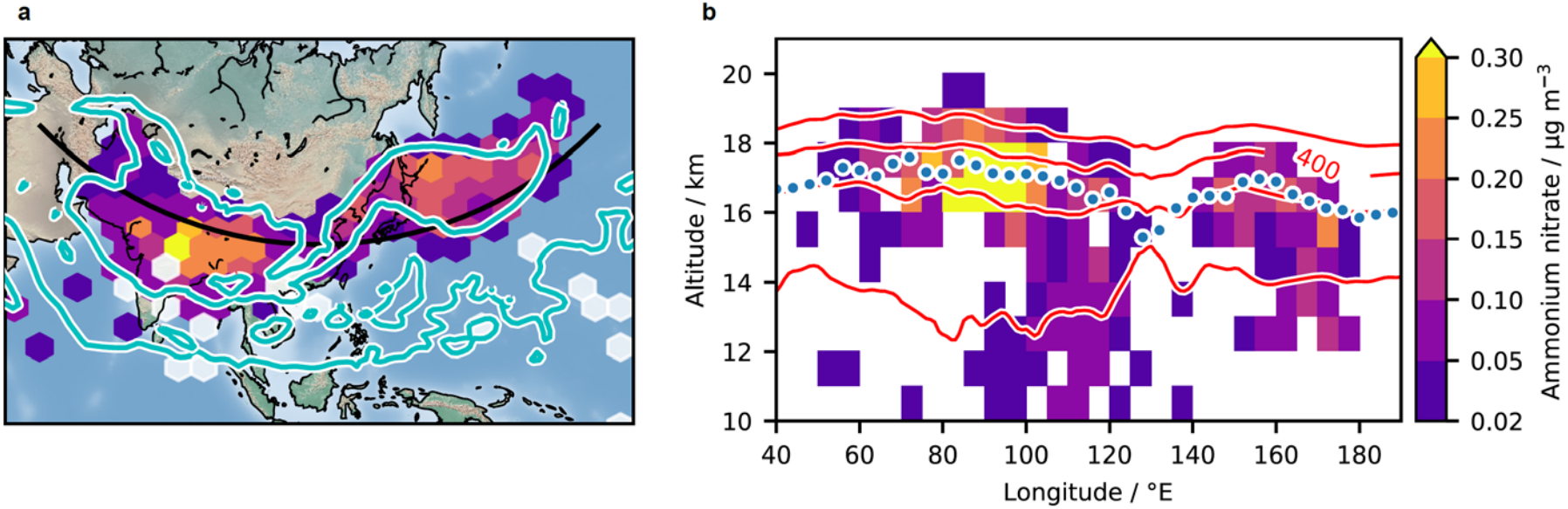


MIPAS/Envisat (2002-2012)

- **IR limb satellite observations allowed to derive the vertical and horizontal distribution and temporal evolution of ammonium nitrate and ammonia in the monsoon upper troposphere: 2002-2012**

CRISTA IR limb measurements in 1997

CRISTA
(Aug 1997)



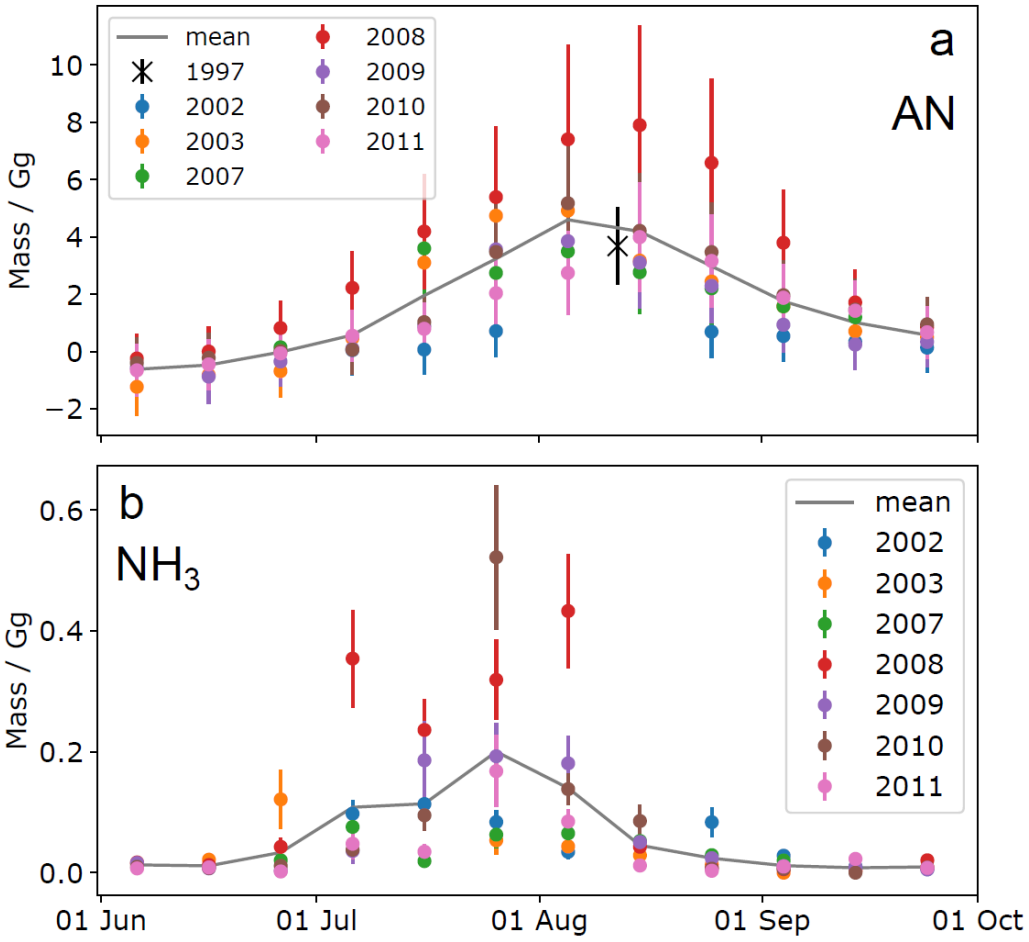
➢ **A layer of ammonium nitrate aerosols existed already during the monsoon in 1997**

MIPAS 2002-2011
CRISTA 1997

Total mass within
10°- 110°E, 20°- 40°N, 13 -17 km

Ammonium nitrate aerosol

Ammonia gas



➢ **NH_3 preceeds ammonium nitrate by 1-2 weeks**

Summary

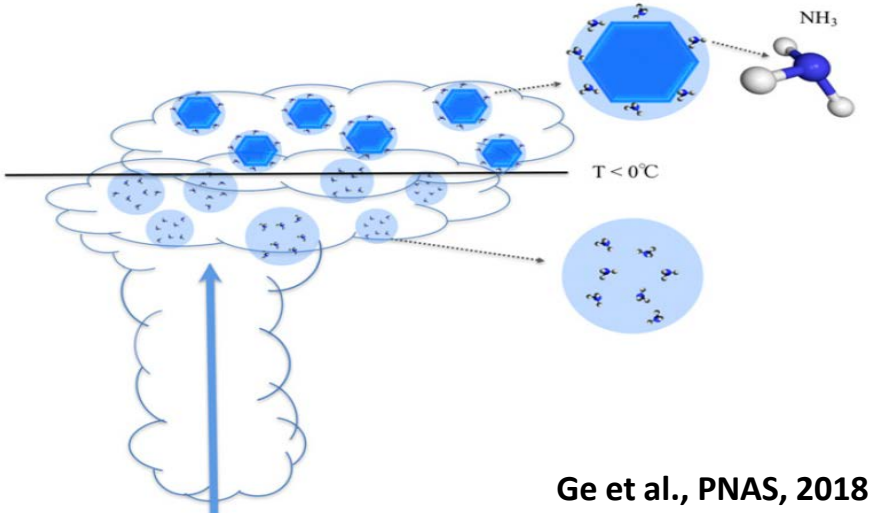
- Observations of **NH_3 concentrations > 1 ppbv in the upper troposphere** during StratoClim in Jul/Aug 2017
- NH_3 source region: Pakistan/NW India, **upward transport by convection**
- Detection of spectral signal of **solid ammonium nitrate aerosol** particles in limb infrared spectra of CRISTA, MIPAS and GLORIA and in IR absorption spectra in AIDA
- **NH_4NO_3 profiles** retrieved from limb-observations by use of **IR mass absorption coefficients as determined in AIDA fit with in-situ mass spectrometric observations**
- **NH_4NO_3 aerosols prevalent in the Asian monsoon anticyclone** following enhanced values of NH_3: evidence that the Asian tropopause aerosol layer (ATAL) consists (partly) of ammonium nitrate
- **Solid NH_4NO_3 particles may act as a good ice nuclei**
- **Publication**: Höpfner et al., NatGeosci., 2019; **Data:** doi: 10.5445/IR/1000095498

Why is NH_3 not washed out during convection?

A molecular perspective for global modeling of upper atmospheric NH_3 from freezing clouds

Cui Ge[a,1], Chongqin Zhu[b,1], Joseph S. Francisco[b,2], Xiao Cheng Zeng[b,2], and Jun Wang[a,2]

- Study trying to explain the MIPAS NH_3 observations
- "We show that the NH_3 dissolved in liquid cloud droplets is prone to being released into the UTLS upon freezing during deep convection."



Ge et al., PNAS, 2018

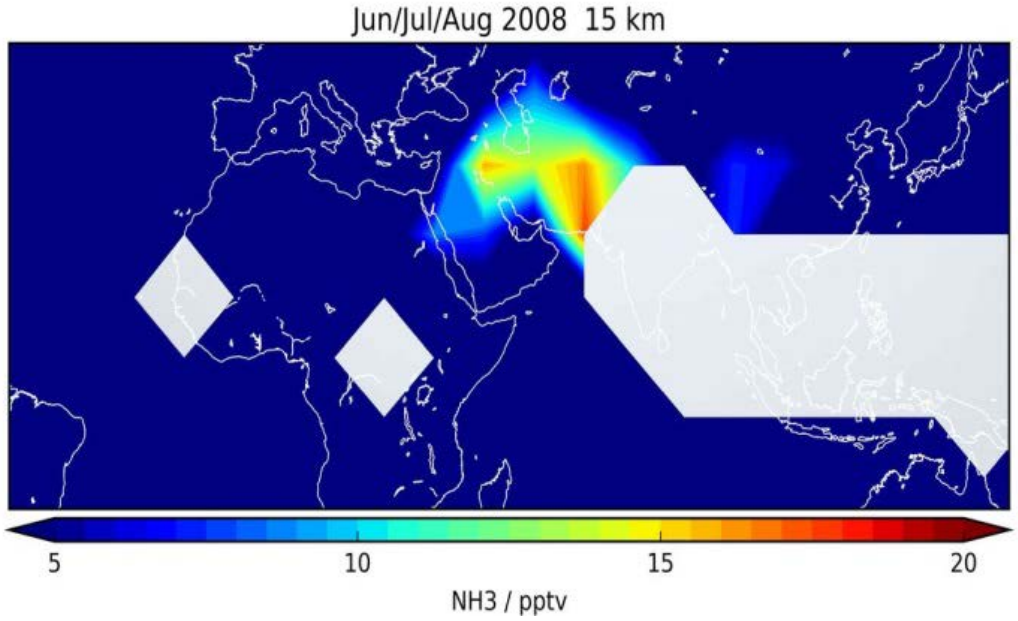
?

- ph – dependence of NH_3 solubility in liquid water: „Convective clouds are hardly acidic so that NH_3 is only partly dissolved and removed by precipitation"

Metzger et al., JGR, 2002

MIPAS-Envisat: NH_3 in the Upper Troposphere

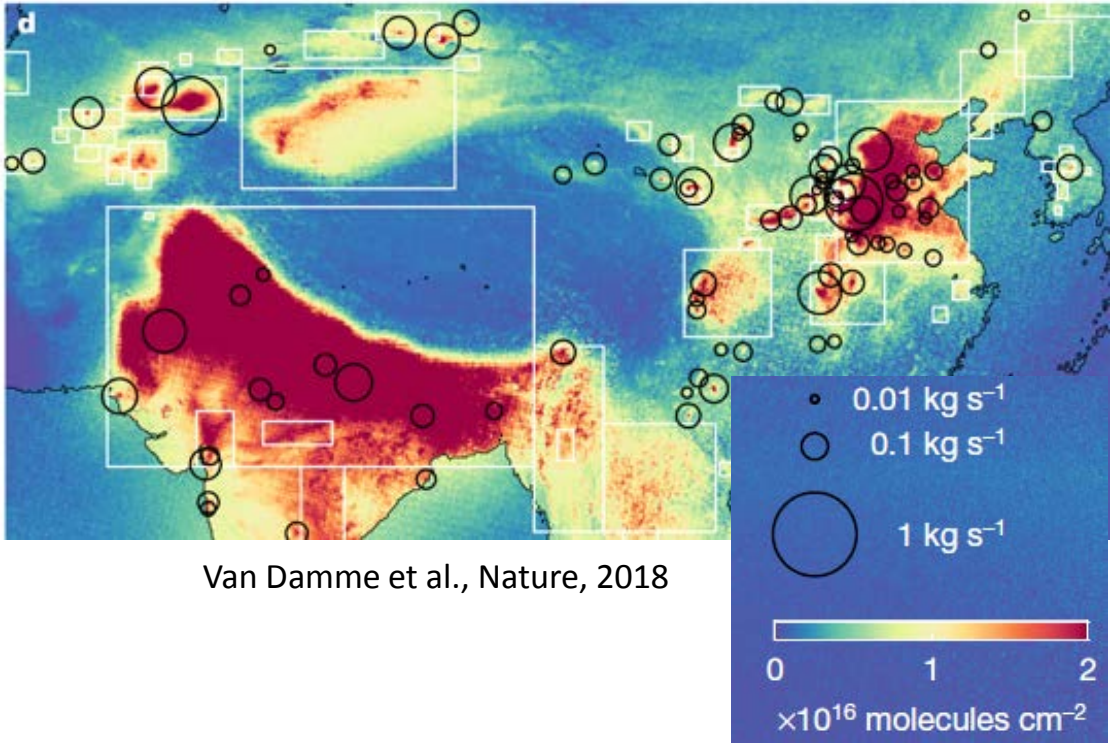
- Evidence for the presence of ammonia in the upper troposphere (Höpfner et al., ACP, 2016)
- Enhanced 3-monthly mean values of up to ~30 pptv within the Asian monsoon upper troposphere



Observing NH_3

- Ground-based in-situ
- Airborne in-situ up to ~5 km
- Balloon-borne in-situ (no detection above 8 km)
- Ground-based FTIR (columns)
- **Satellite: IR nadir sounding (e.g. IASI)**

- **For the first time detected in the upper troposphere by IR limb sounding (MIPAS)**

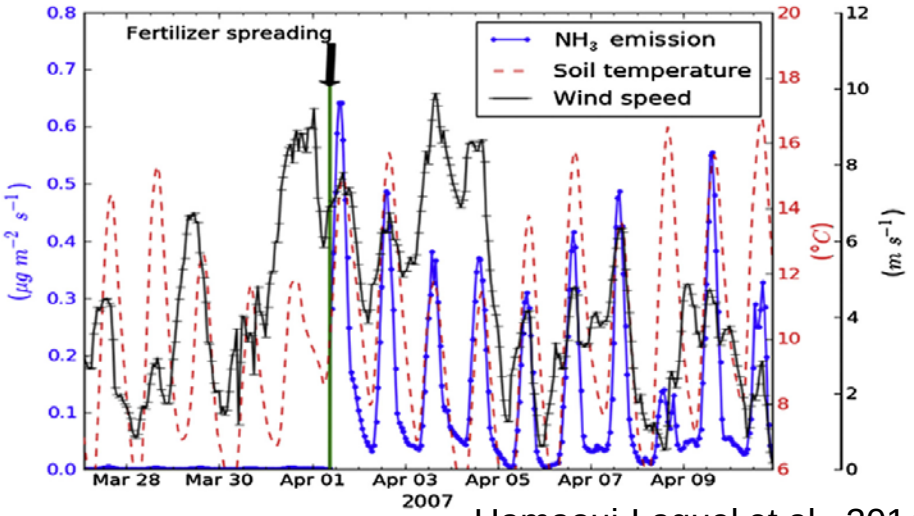


Van Damme et al., Nature, 2018

Significance of ammonia (NH_3)

- Main alkaline species in the atmosphere
- Major source: **agriculture**
- Formation of aerosols by neutralization of acids: **ammonium sulfate** and **ammonium nitrate** depending on the availability of H_2SO_4 and HNO_3
- Important fraction of fine particulate matter
- **Increase of NH_3 emissions in the future**: compensation of aerosol radiative forcing change by reduction of SO_2 emissions
- Important for the **initial nucleation of sulfate aerosols under cold temperatures**

But: Difficult to measure in-situ

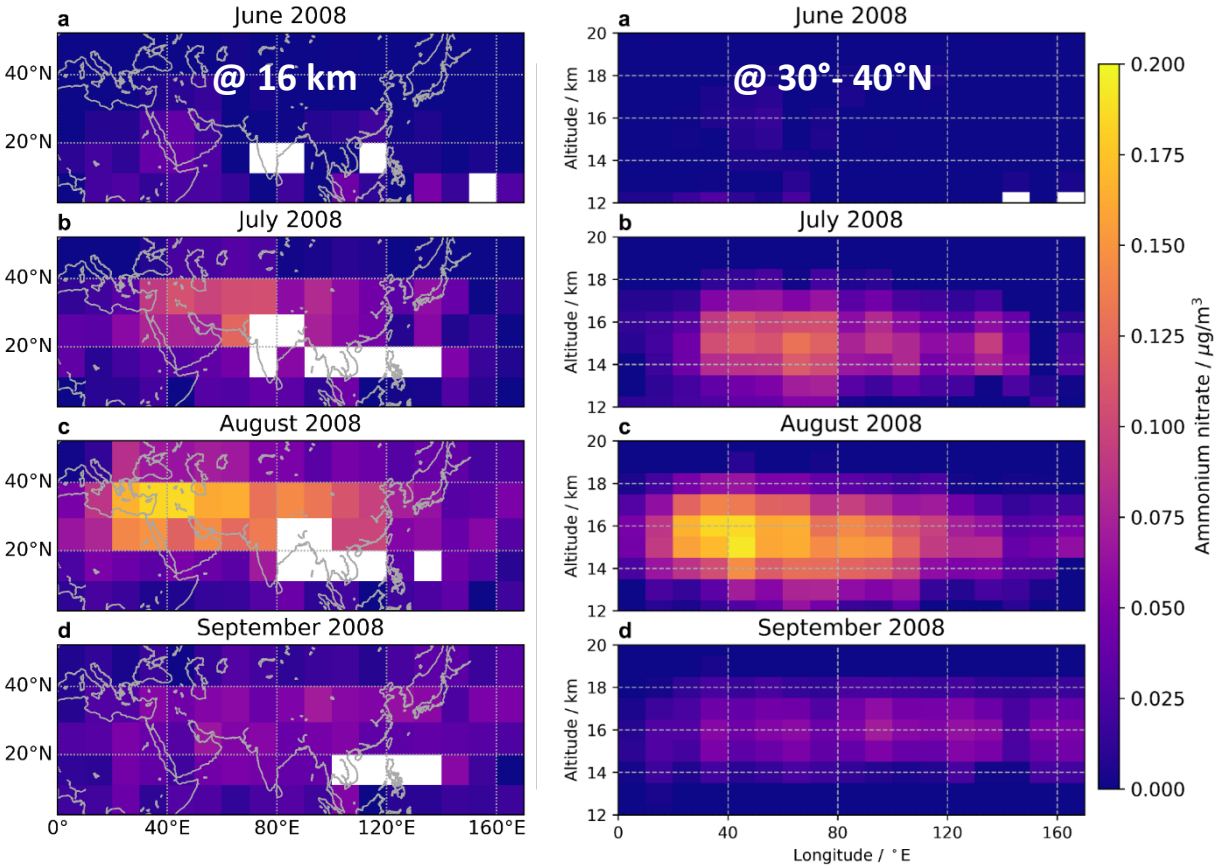


Hamaoui-Laguel et al., 2014

LETTER Kirkby et al., Nature, 2011 doi:10.1038/nature10343

Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation

MIPAS 2008: ammonium nitrate



Infrared spectroscopy of ammonium nitrate

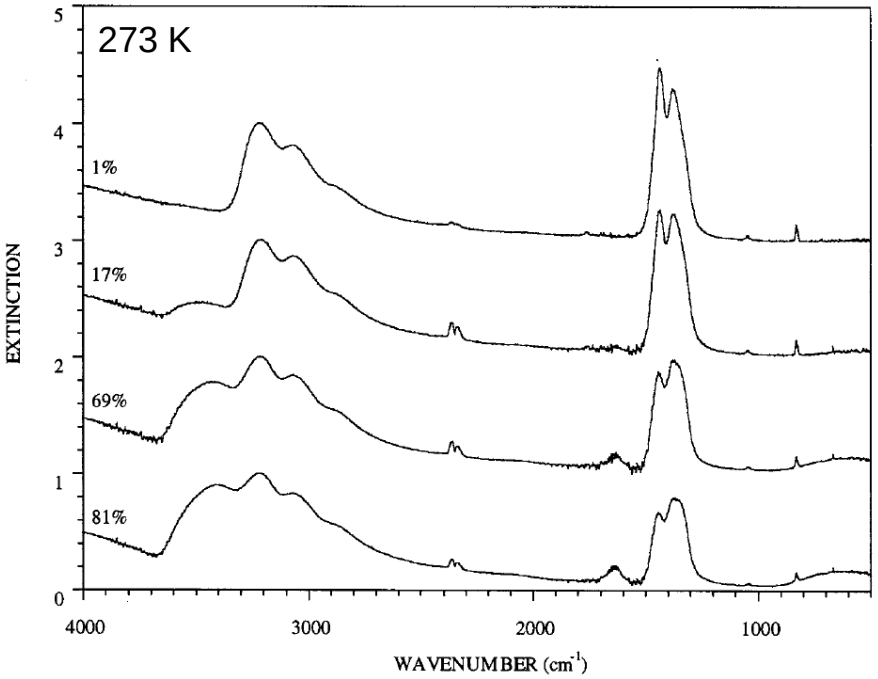
The $\nu_2(NO_3^-)$ band of NH_4NO_3 has been assigned in laboratory spectra to wavenumbers around 831 cm^{-1}:

- Théorêt and Sandorfy (1964): 830 cm^{-1} (phase IV)
- Fernandes et al. (1979): 833 cm^{-1} (phase V), 831 cm^{-1} (phase IV)
- Allen et al., 1994: 825-835 cm^{-1}
- Koch et al. (1996): 832 cm^{-1} (phase V), 830 cm^{-1} (phase IV)
- Schlenker and Martin (2005): 831 cm^{-1}

Literature overview

Cziczo & Abbatt (2000)
NH_4NO_3: strong inhibition to efflorescence down to 2% RH (298 – 238 K)
Aerosol flow tube equipped with FTIR spectrometer

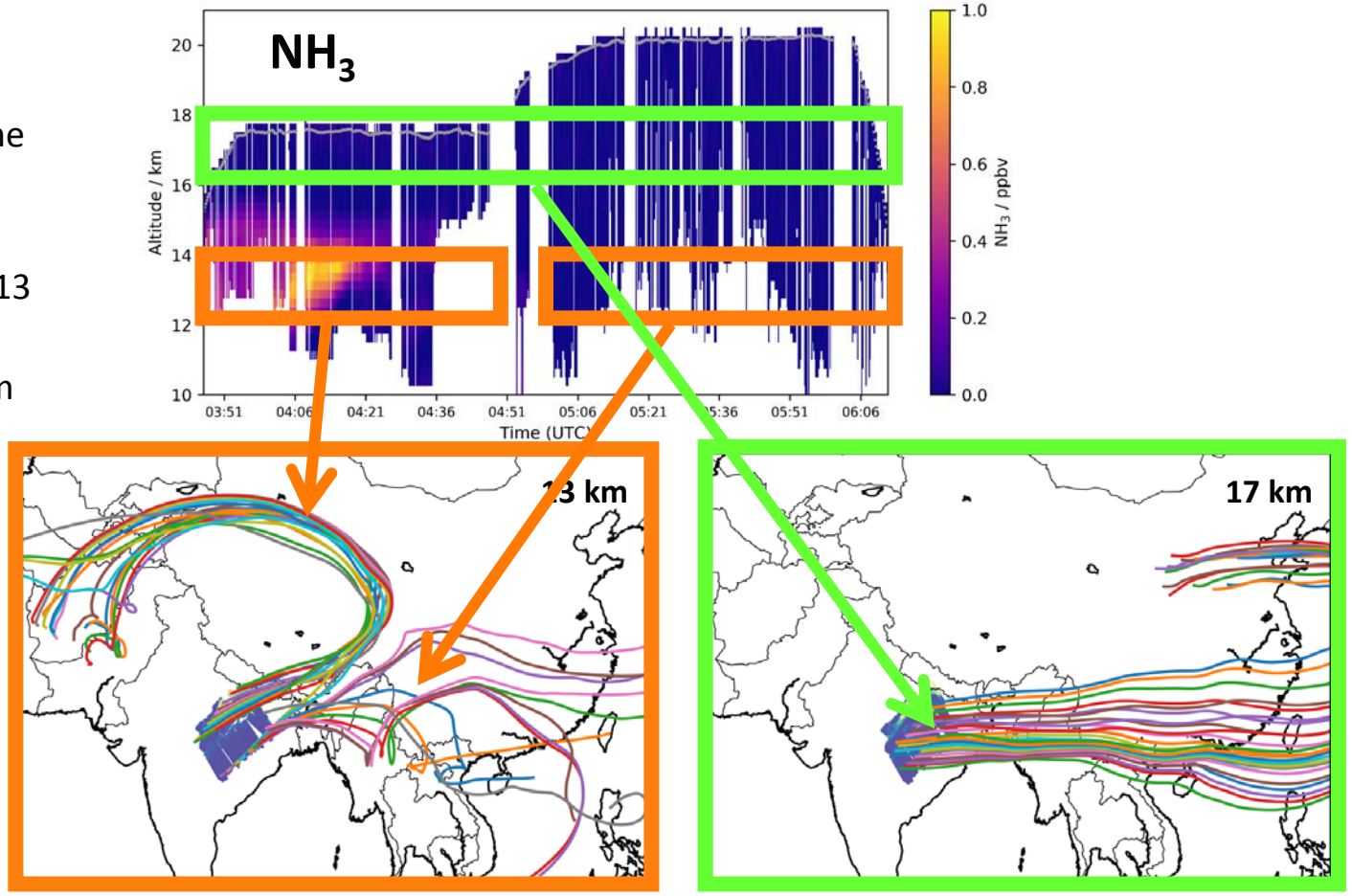
RH

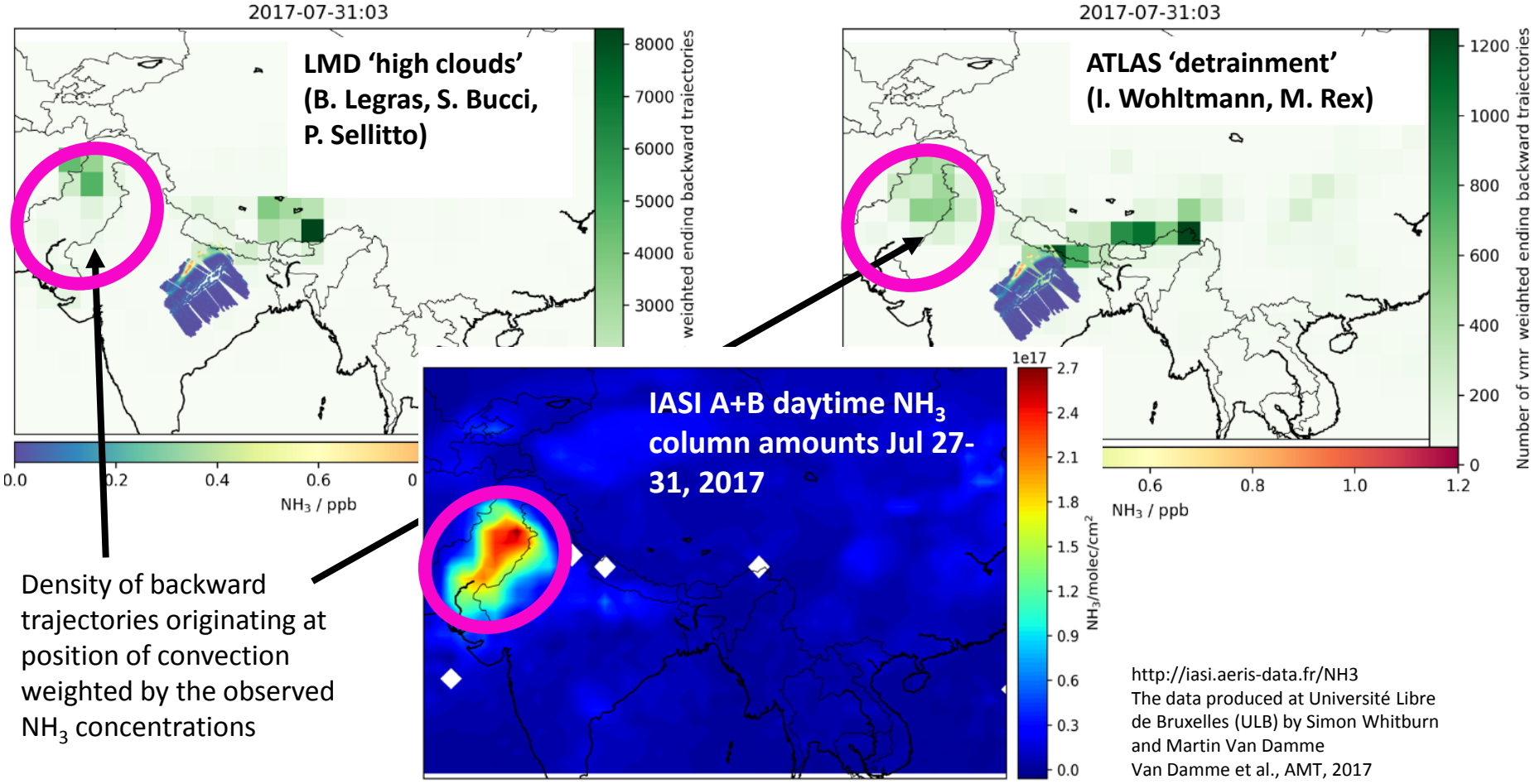


Deliquescence point:
61% RH

Backtrajectories 2017-07-31

- Different origin of the air encountered on the southbound vs. the northbound flight leg at 13 km altitude
- Same origin at 17 km





Density of backward trajectories originating at position of convection weighted by the observed NH_3 concentrations

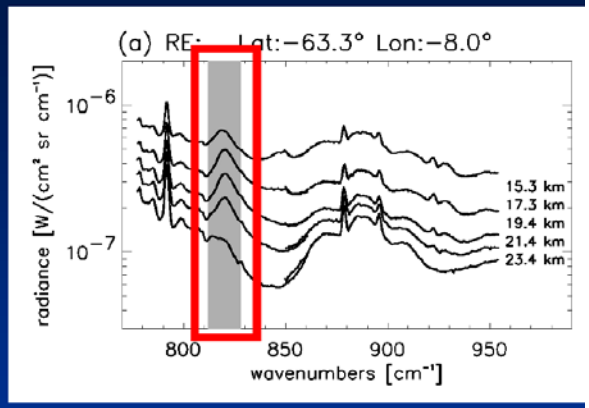
http://iasi.aeris-data.fr/NH3
The data produced at Université Libre de Bruxelles (ULB) by Simon Whitburn and Martin Van Damme
Van Damme et al., AMT, 2017

CRISTA and MIPAS observations of Polar Stratospheric Clouds: a peak at 820 cm^{-1}

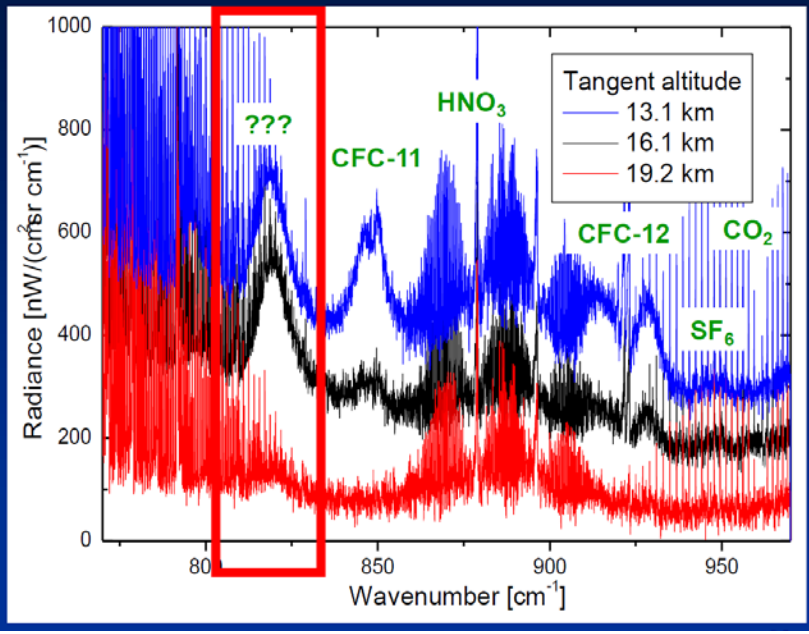
CRISTA PSC observations in August 1997

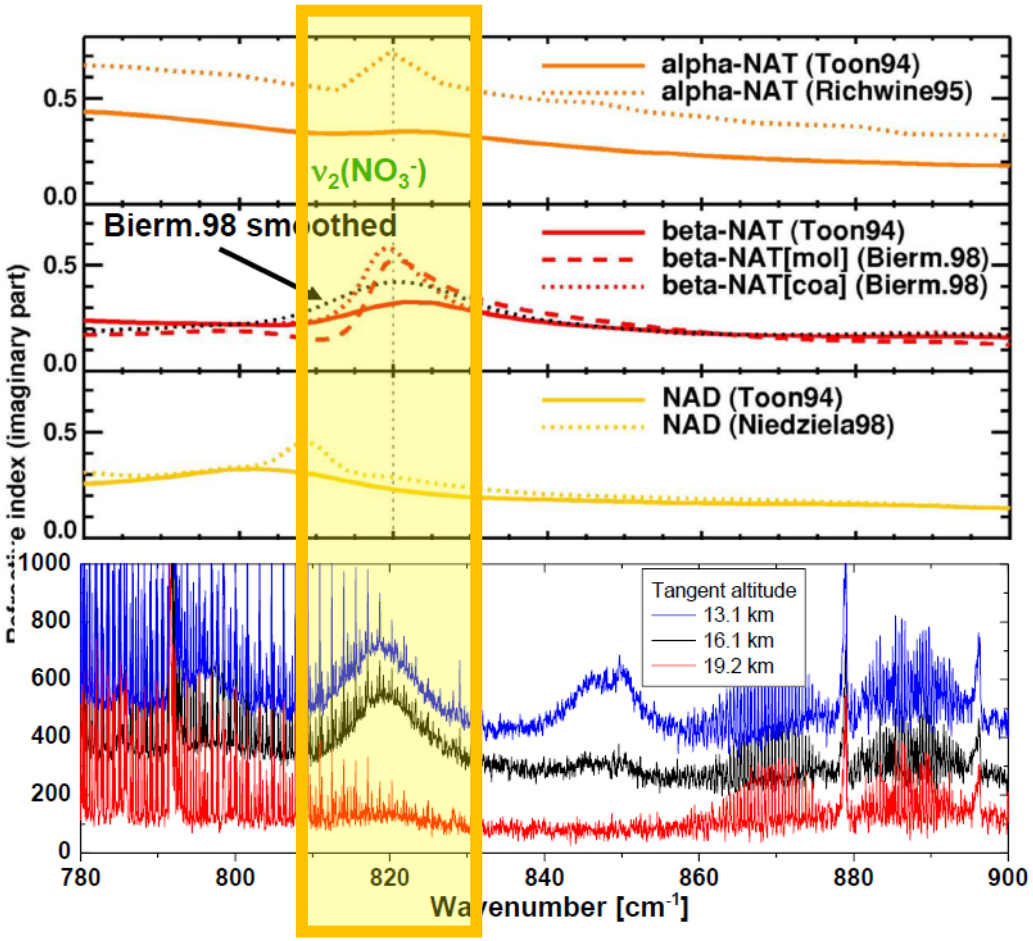
Spang and Remedios, 2003:

Spectral feature around 820 cm^{-1} attributed to NAT indirectly by HNO_3-temperature relationship and occurrence temperature of the band



MIPAS PSC observations over McMurdo on 4 Aug 2003





Atmos. Chem. Phys., 6, 1201–1219, 2006
www.atmos-chem-phys.net/6/1201/2006/

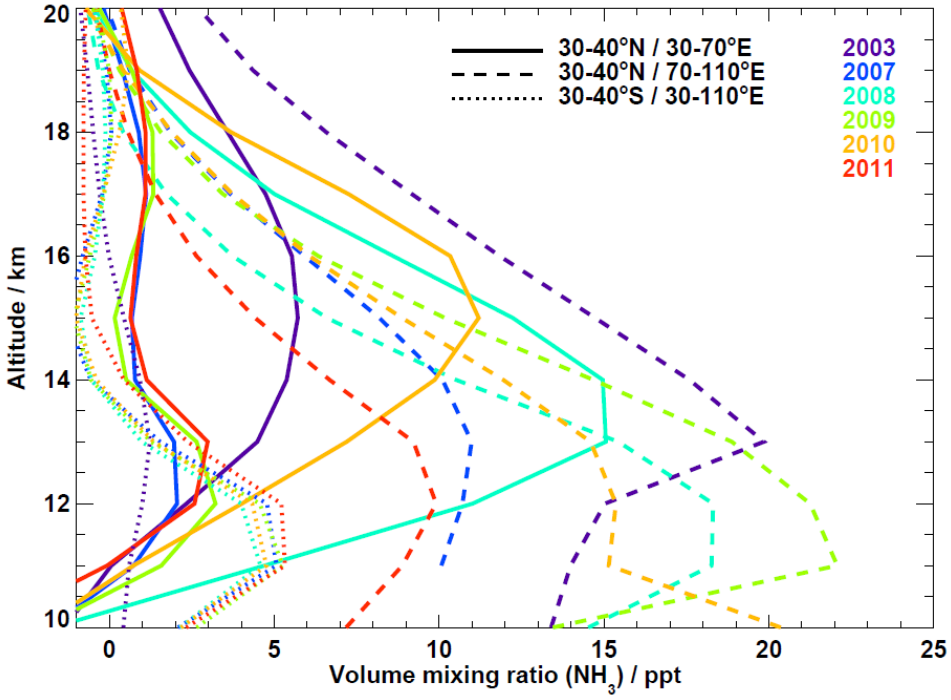
Atmospheric Chemistry and Physics

Spectroscopic evidence for NAT, STS, and ice in MIPAS infrared limb emission measurements of polar stratospheric clouds

M. Höpfner[1], B. P. Luo[2], P. Massoli[3,*], F. Cairo[3], R. Spang[4], M. Snels[3], G. Di Donfrancesco[5], G. Stiller[1], T. von Clarmann[1], H. Fischer[1], and U. Biermann[6,**]

- Infrared signature at 820 cm^{-1} explained as the $\nu_2(NO_3^-)$ band of β-NAT

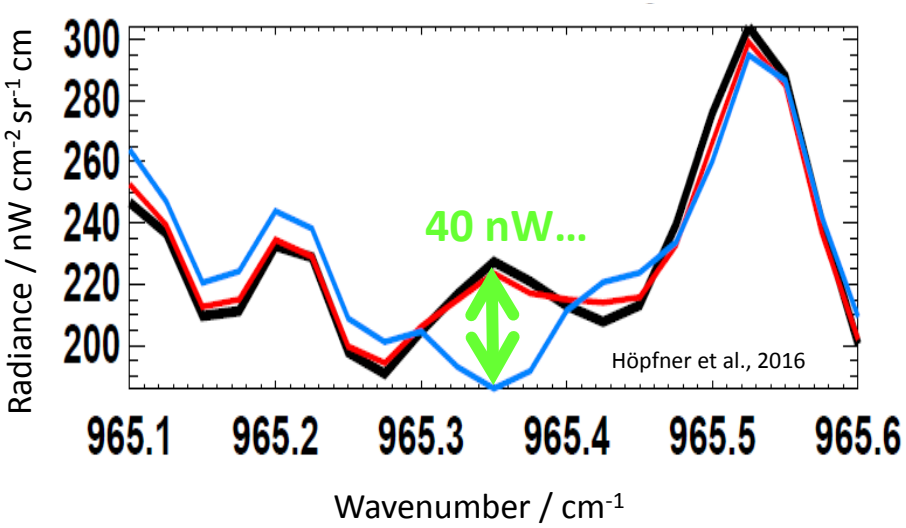
NH_3 profiles within the Asian monsoon



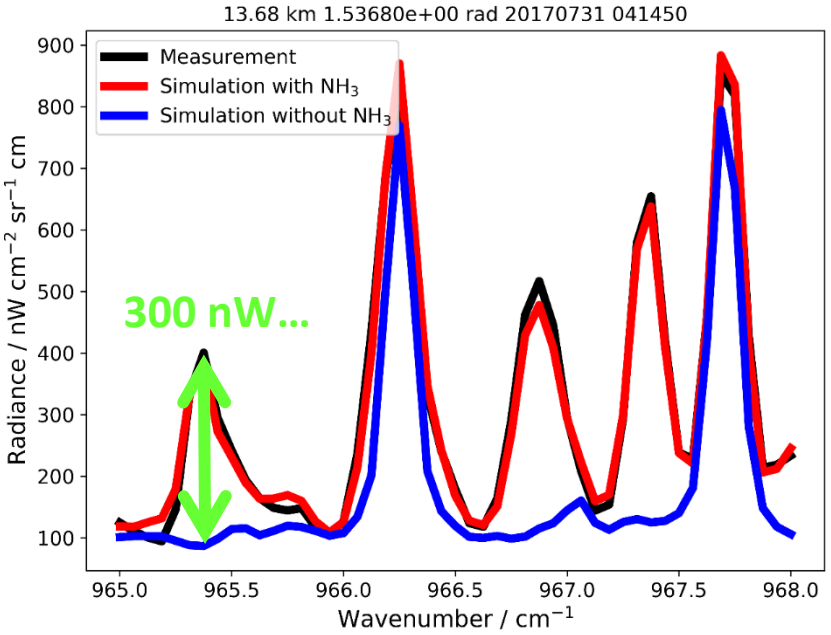
- NH_3 maximum larger and at lower altitudes in the eastern part of the monsoon area
- Much more variable and peaking at higher altitudes in the western part
- Maximum in southern hemisphere indicates detection limit of ~5 ppt

Spectral detection of NH_3

MIPAS/Envisat

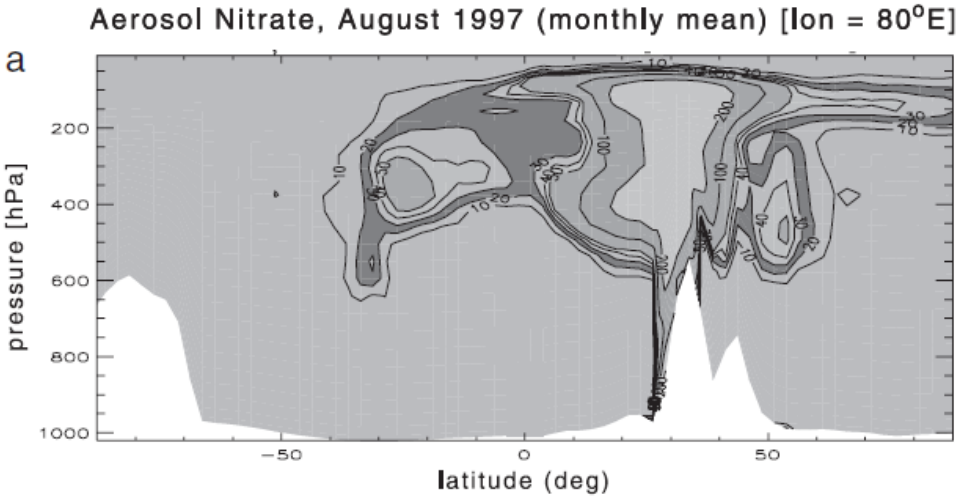


GLORIA/Geophysica



NH_3 and the Asian Tropopause Aerosol Layer

- Model simulates extended plume of ammonium nitrate in the upper troposphere
- Aerosols formed in the UT through neutralization of nitric acid (in the model present in higher amounts than sulfuric acid) by a surplus of NH_3



Metzger et al., JGR, 2002