Combustion related nanoparticle formation in the atmosphere

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Talk given at 11 th ETH conference on *Combustion Generated Nanoparticles* , 13-15 August 2007 (Zuerich , Switzerland)

Atmospheric aerosol particles are of considerable current concern as they influence climate and human health. Particles scatter sunlight and if sufficiently large may also serve as water condensation nuclei in cloud formation and freezing nuclei in cloud droplet freezing.
The atmosphere contains primary and secondary aerosol particles. Primary particles are introduced into the atmosphere by external sources. Examples are soot from combustion, mineral dust from desserts, and sea salt from the oceans. Secondary particles are formed in the atmosphere by gas-to-particle conversion. Nascent secondary particles are initially very small (diameters around 1 nm) and hereafter may grow by condensation and mutual coagulation.

An important if not the most important gaseous precursor of secondary particles is sulphuric acid (H2SO4). It is formed by photochemical conversion of the atmospheric trace gas SO2 which in turn stems mostly from combustion. Gaseous H2SO4 induces new particle formation by nucleation and contributes to new particle growth by condensation.

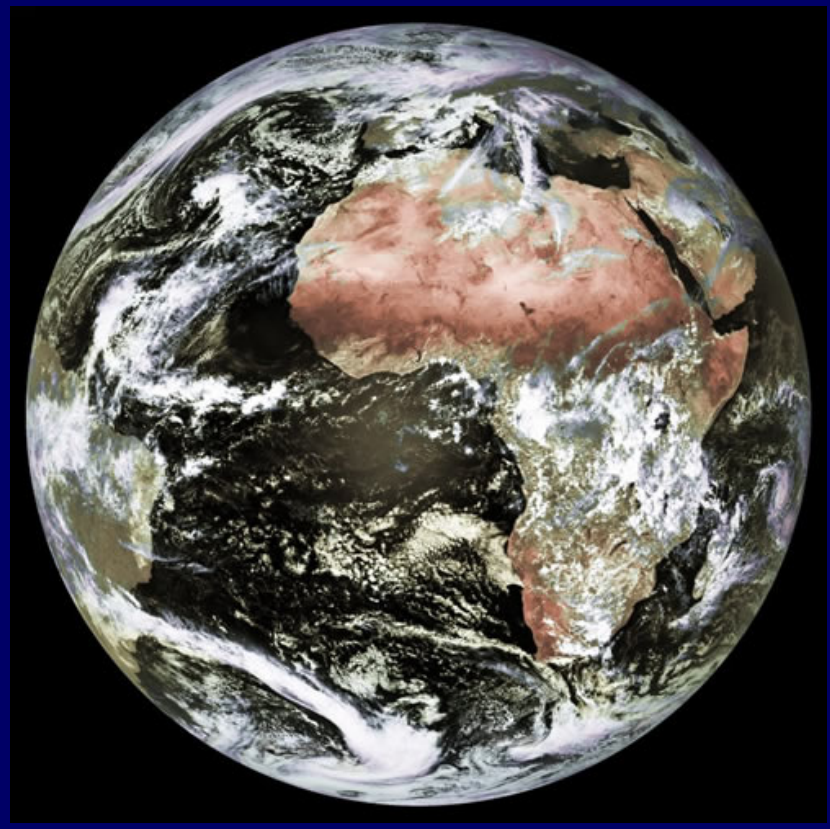
It is presently thought that sulphur containing aerosol particles have a strong influence on climate. They tend to increase the planetary albedo and thereby cool the planet. Hence they counteract the warming induced by anthropogenic greenhouse gases. Interestingly both SO2 and anthropogenic greenhouse gases stem mostly from combustion. Recently a climate engineering method has been proposed as an “ultima ratio therapy” of climate in case of a greenhouse warming disaster. The climate engineering method generates sulphur containing stratospheric aerosol particles in order to cool the planet and damp anthropogenic greenhouse warming. This proposal builds on the experience with the two recent major volcanic eruptions (1982 , 1992) which have cooled the planet by about 0.4 degrees for about 1-2 years.

This contribution reports on measurements of the atmospheric nano particle precursor gases H2SO4 and SO2. The measurements employed novel analytical tools (mass spectrometry-based) and have been made in a close cooperation between our MPIK-Heidelberg group and DLR-IPA (Deutsches Zentrum für Luft- und Raumfahrt- Institut für Physik der Atmosphäre). Measurements took place at altitudes between ground-level and 13000 m. Data have been obtained from various campaigns made in different parts of the globe including the northern and southern hemispheres, middle latitudes, the subtropics, the tropics, and the Arctic. Mass spectrometric instruments were deployed at ground-level, at high-altitude mountain sites, on a research ship, and on a research air craft (FALCON; operated by DLR).

Strong SO2 pollution has been observed at all heights covered by our measurements (0-13000 m). This implies that efficient vertical SO2 – transport takes place, particularly by convection in spite off some SO2 removal by clouds usually accompanying convection. Even long-range SO2 transport over thousands of kilometres has been observed particularly in the middle and upper troposphere where winds are very fast and within only about 7 days may transport SO2 around the globe. For example SO2 plumes released by fossil fuel combustion in China (where particularly sulphur-rich coal is burnt) have been observed over Europe.

This implies that photochemical SO2 conversion to gaseous H2SO4 followed by the formation and growth of nano particles can take place even thousands of kilometres downstream of major SO2 source regions.

Combustion related nano particle formation in the atmosphere



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Opening remarks

- Thanks to organizers of ETH conference
- Great pleasure to attend conference again
- 2005 air craft
- 2006 Diesel car
- 2007 Ocean ships and stationary sources
  (details of molecular processes can be found in power point hand out)

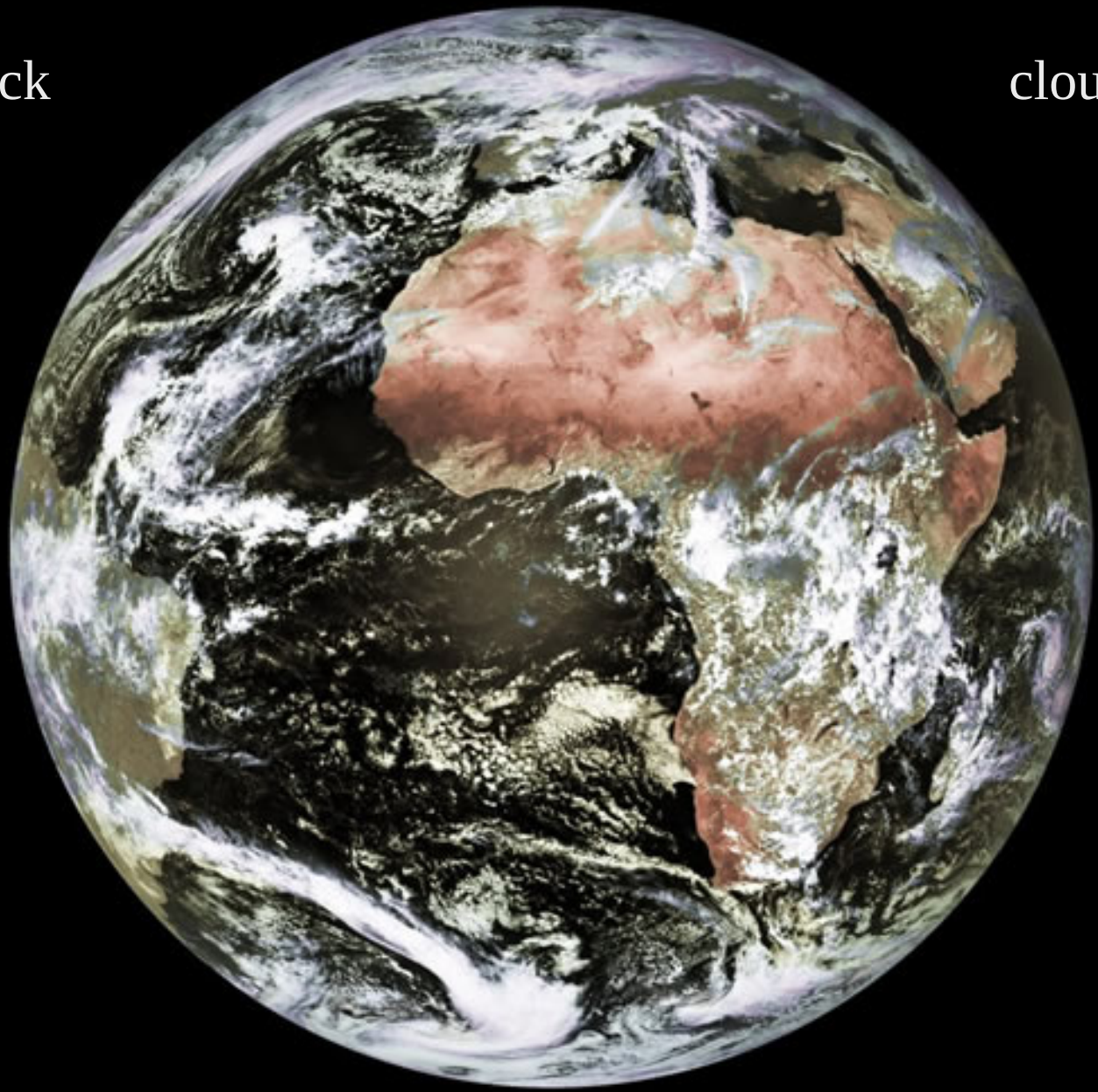
Perspective

Combustion related aerosol particle formation in the atmosphere

- influences **climate**
- potential adverse health effects

oceans black

clouds white



oceans black

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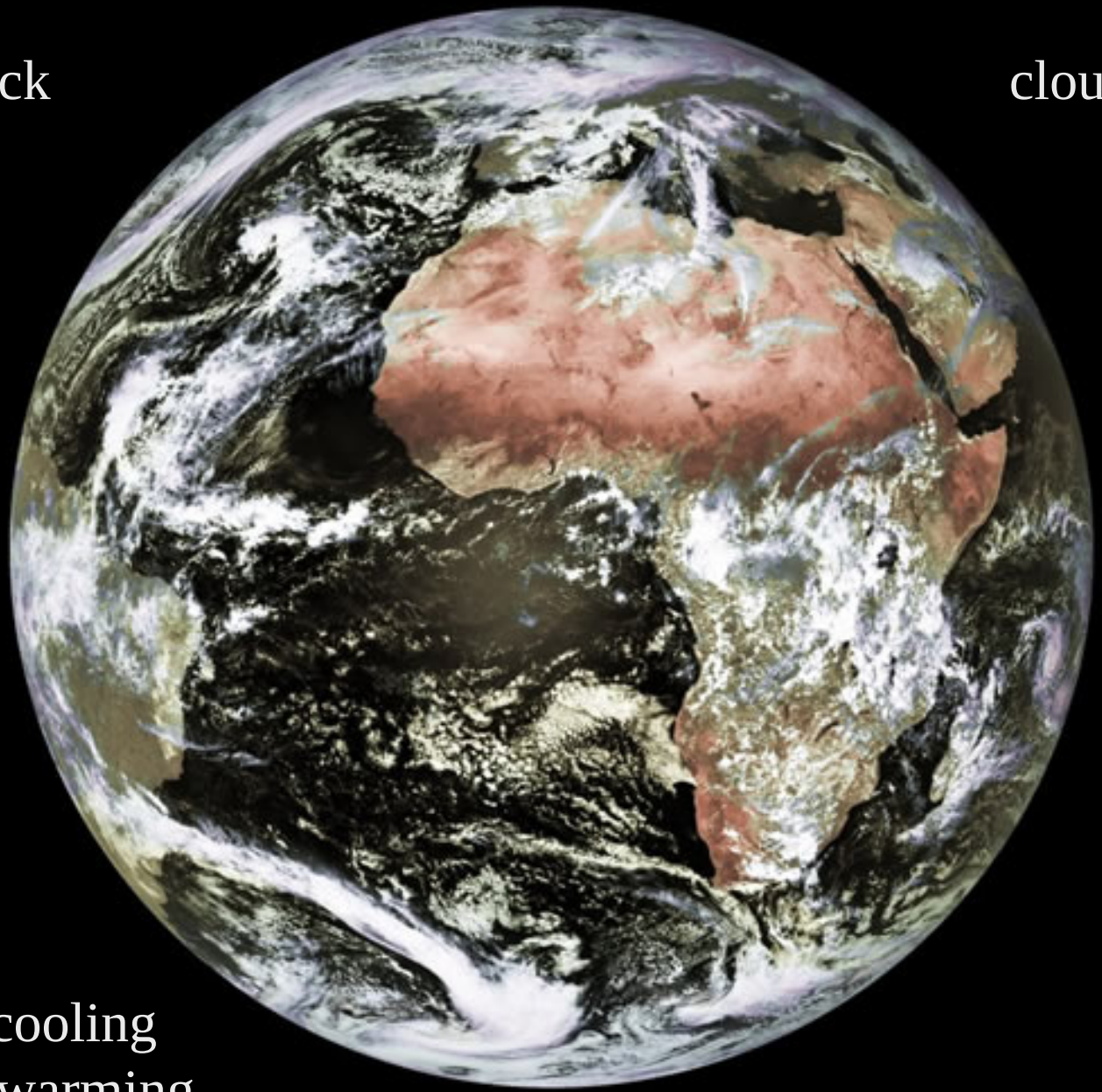


Aerosols
reflect → cooling
absorb → warming

An important if not the most important aerosol precursor gas is sulfuric acid

H_2SO_4

H_2SO_4

- Photochemically formed from SO_2 which stems mostly from combustion
- Induces new aerosol particle formation

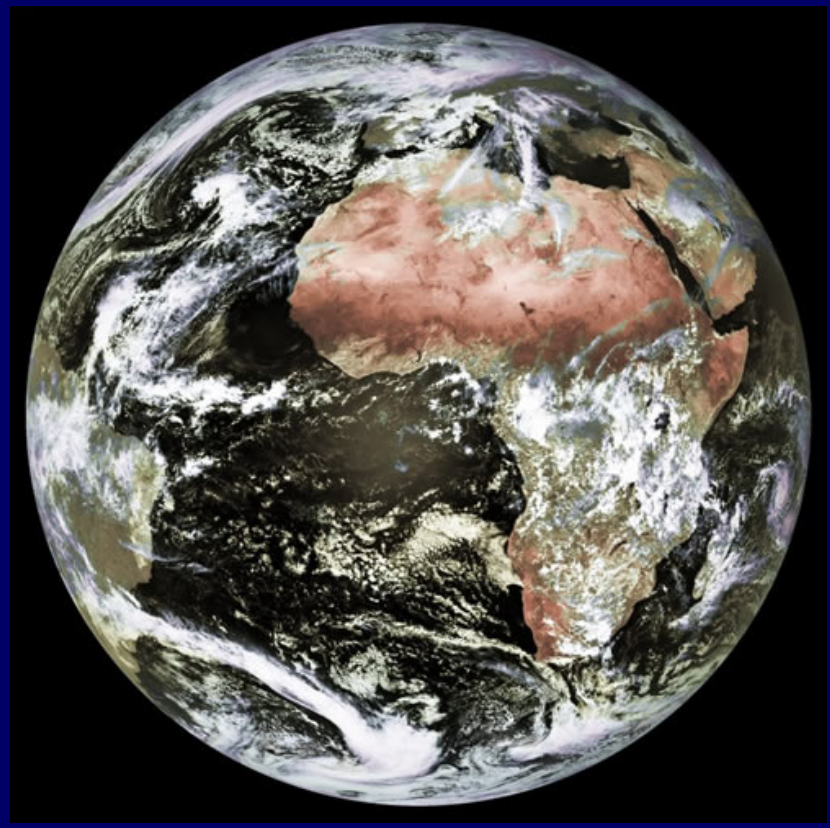
H2SO4

- Photochemically formed from SO2 which stems mostly from combustion
- Induces new aerosol particle formation
- In upper troposphere (UT) :
  SO2 conversion fast;
  H2SO4/H2O nucleation efficient;
  horizontal long – range transport fast

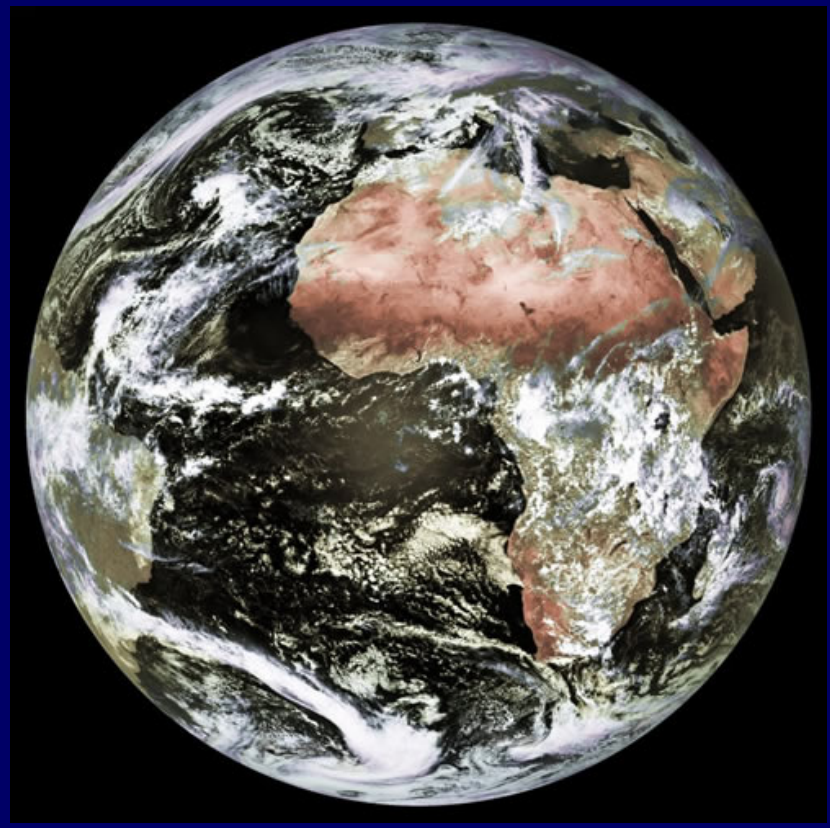
H2SO4

- Photochemically formed from SO2 which stems mostly from combustion
- Induces new aerosol particle formation
- In upper troposphere (UT) :
  SO2 conversion fast;
  H2SO4/H2O nucleation efficient;
  horizontal long – range transport fast
- But vertical SO2 transport from ground level SO2 sources to UT hindered by cloud processes ?

Atmospheric Gaseous Sulfuric Acid



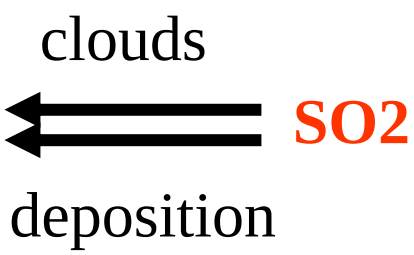
Sources and Sinks of Atmospheric H2SO4



Atmospheric H_2SO_4 Variations

which processes are controling
H_2SO_4
?

Atmospheric Gaseous Sulfuric Acid Sources and Sinks



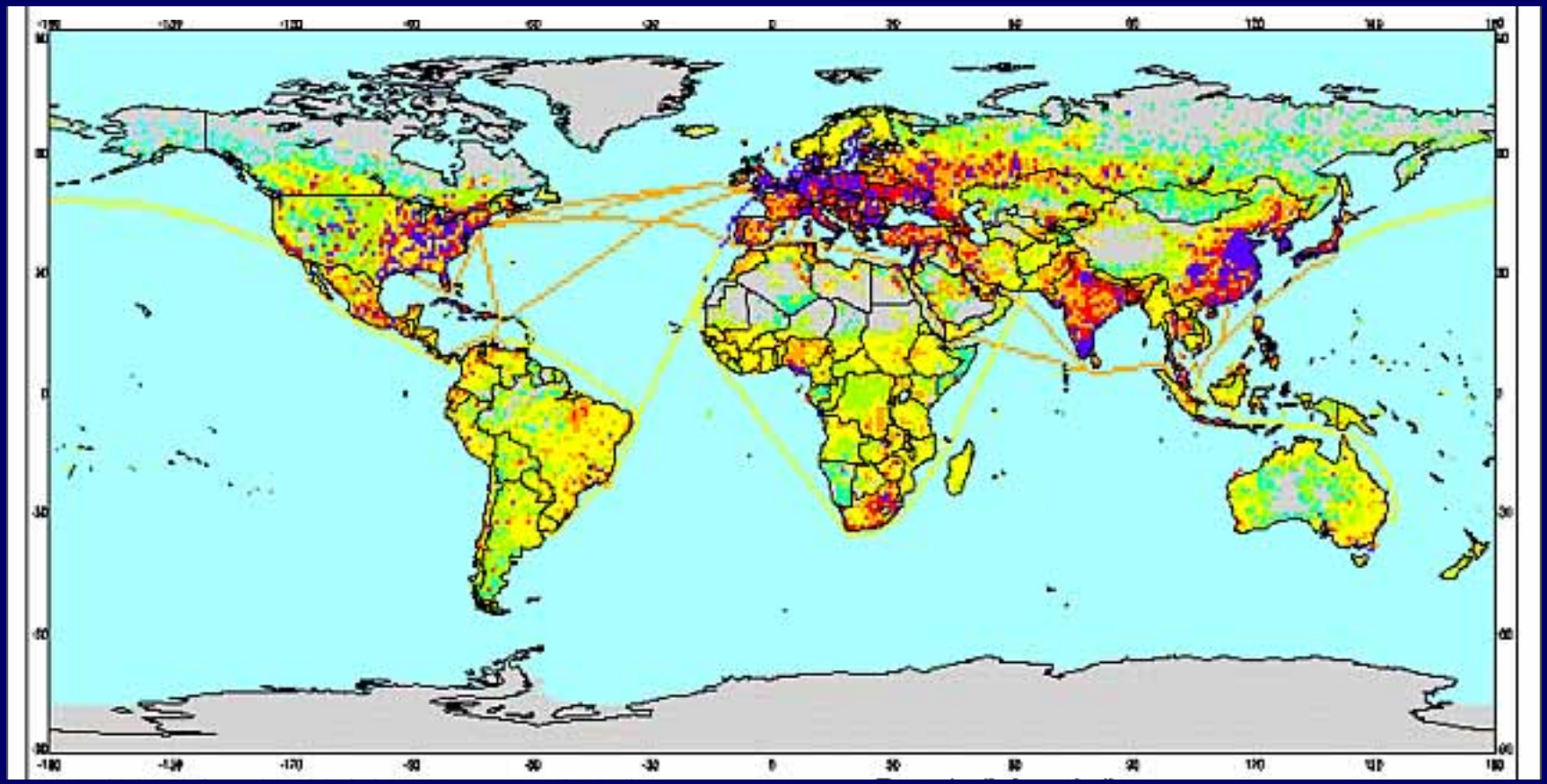
Global **SO2-Sources** (mT/a) :

Fossil Fuel combustion : 78.1

Oceanic Plankton : 15.4

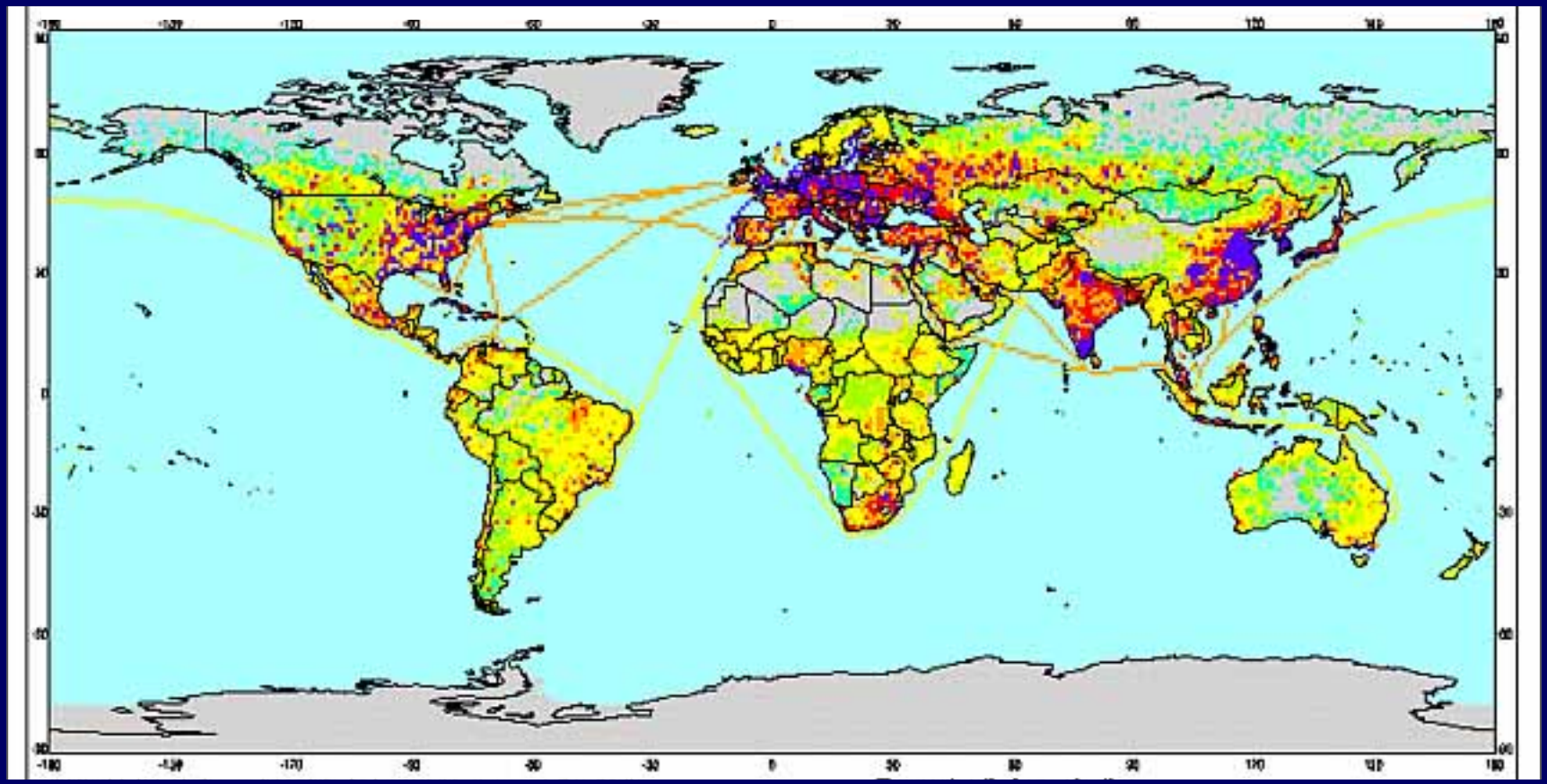
Volcanism : 9.4

Anthropogenic sulfur emissions



Emission rate: red (high) , blue (very high)

Anthropogenic sulfur emissions

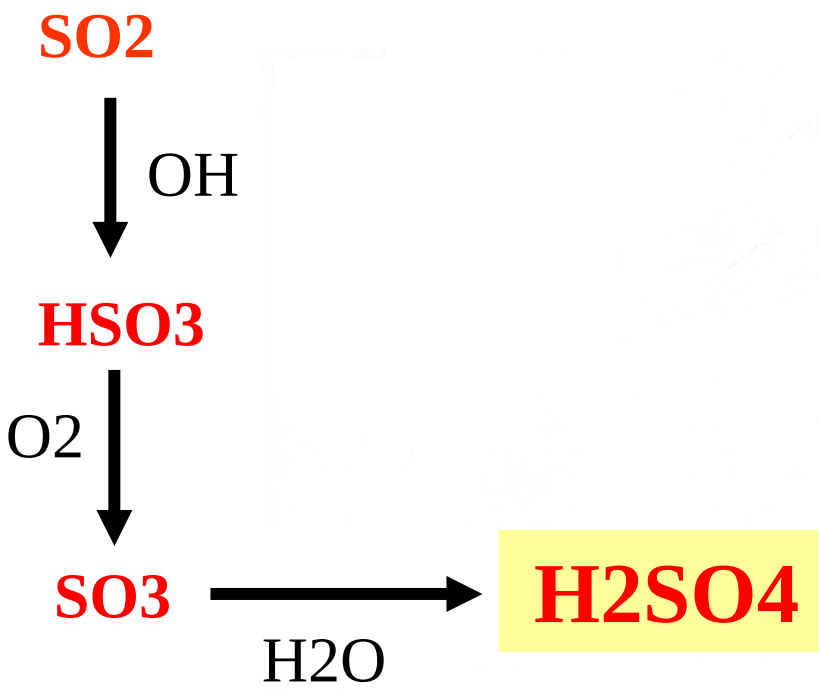


substantial SO2 pollution by ocean ships !

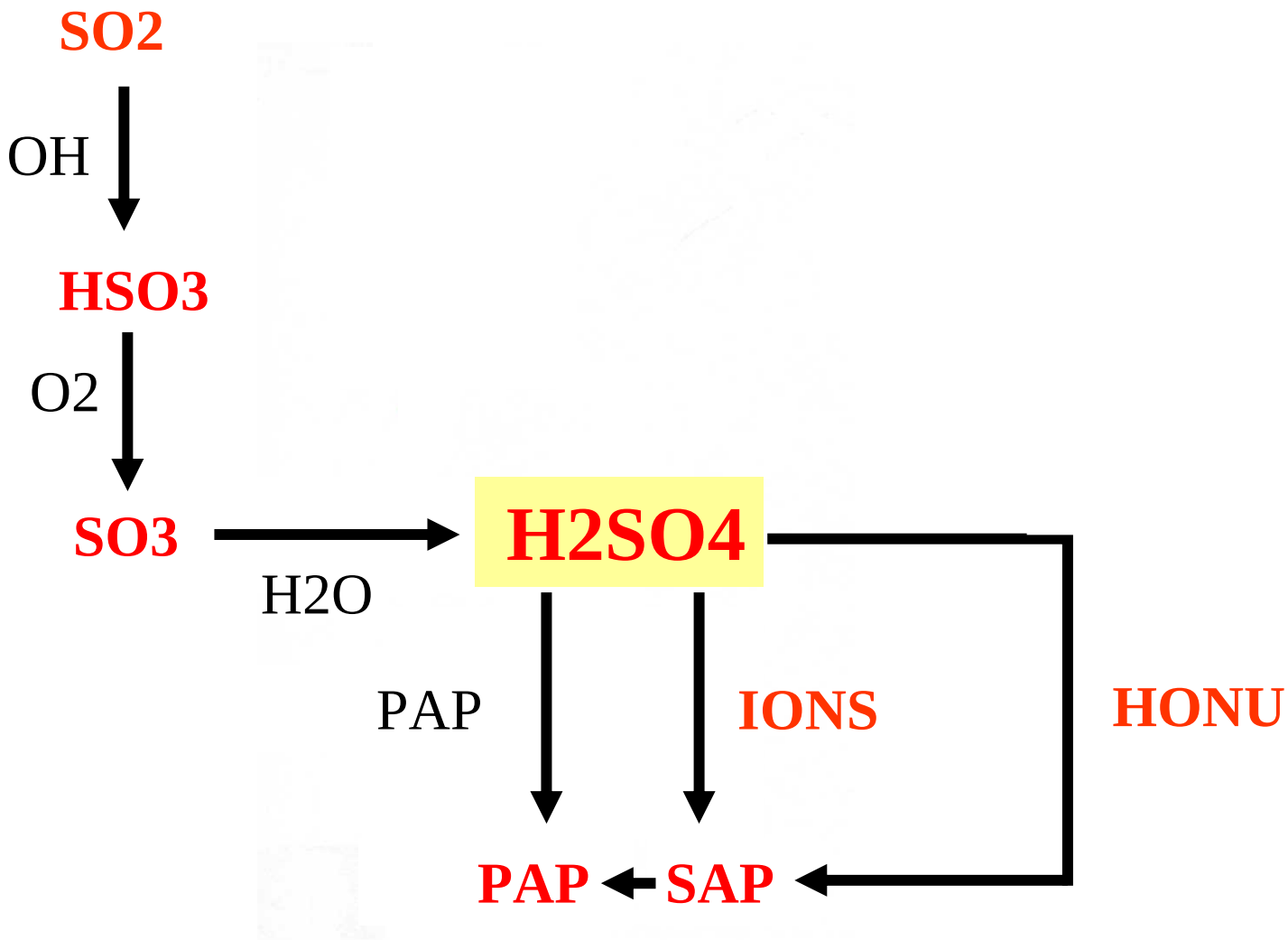
Ocean ship Diesel engines

- Are strong SO2 emitters
- Combust sulfur rich Diesel fuel

Atmospheric Gaseous Sulfuric Acid Sources and Sinks



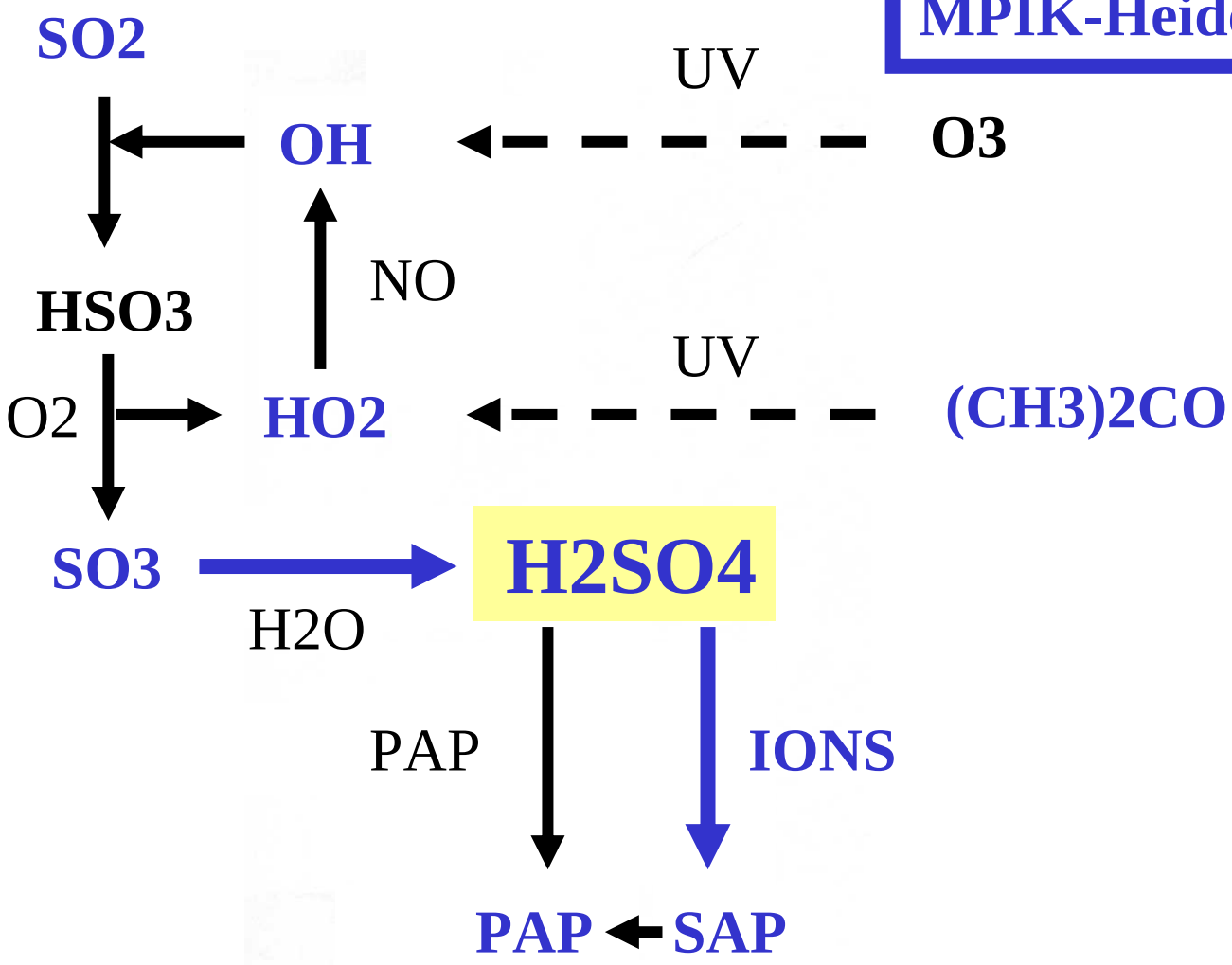
Atmospheric Gaseous Sulfuric Acid Sources and Sinks



Atmospheric Gaseous Sulfuric Acid Sources and Sinks

Measured by

MPIK-Heidelberg

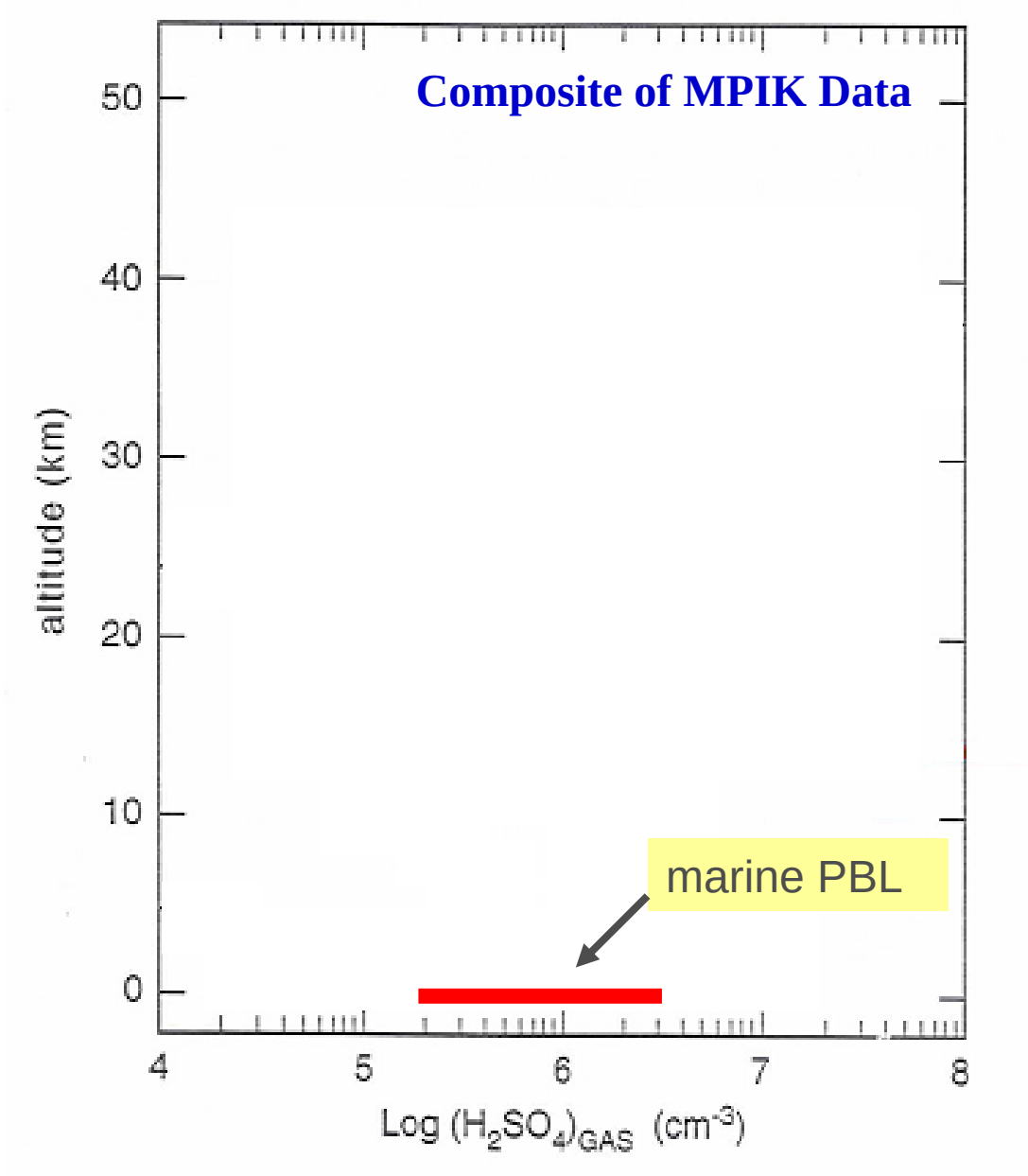


Measurements of Atmospheric

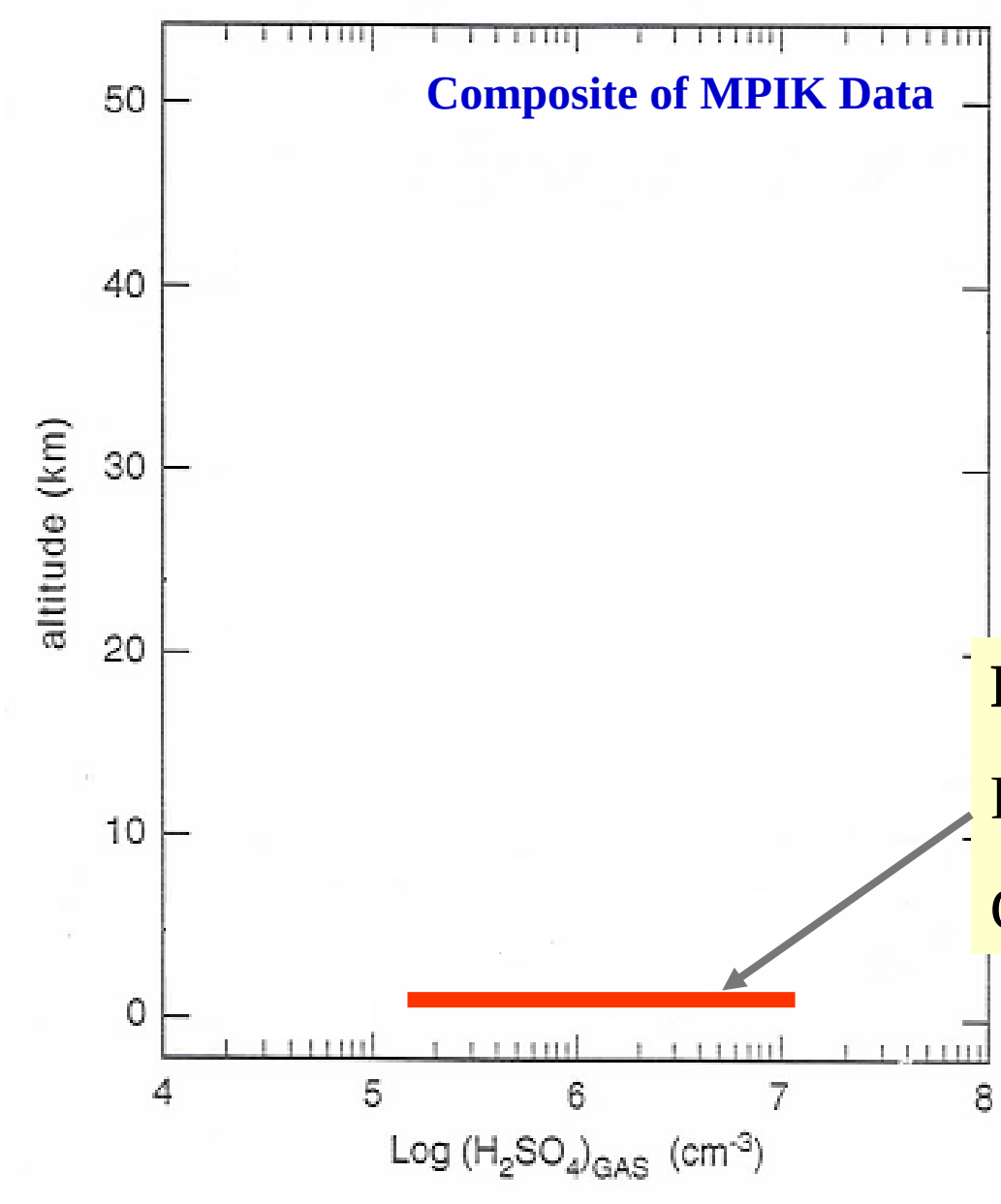
Gaseous Sulfuric Acid

by MPIK Heidelberg

Atmospheric gaseous H2SO4 measured by MPIK



Atmospheric gaseous H2SO4 measured by MPIK

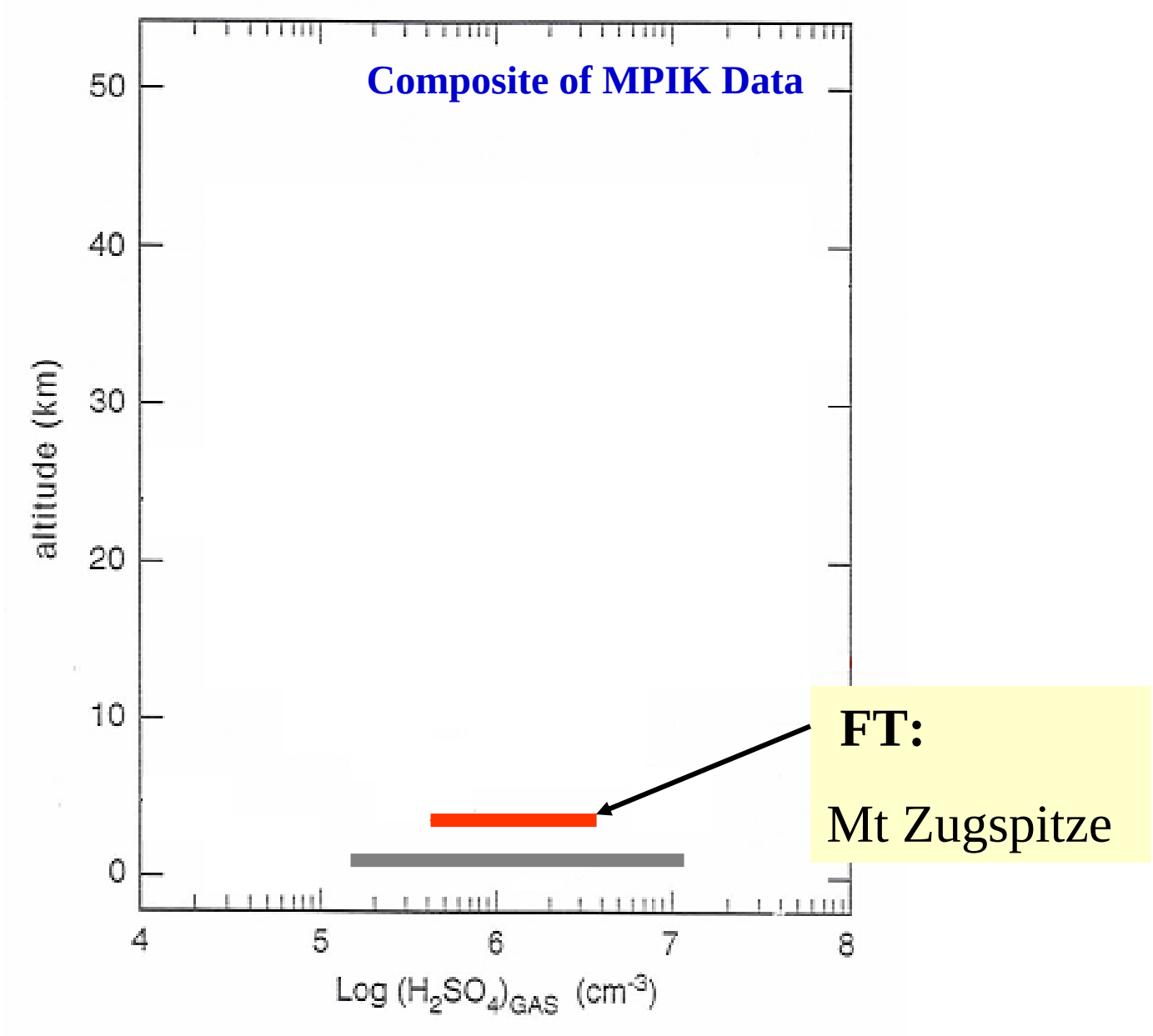


PBL:

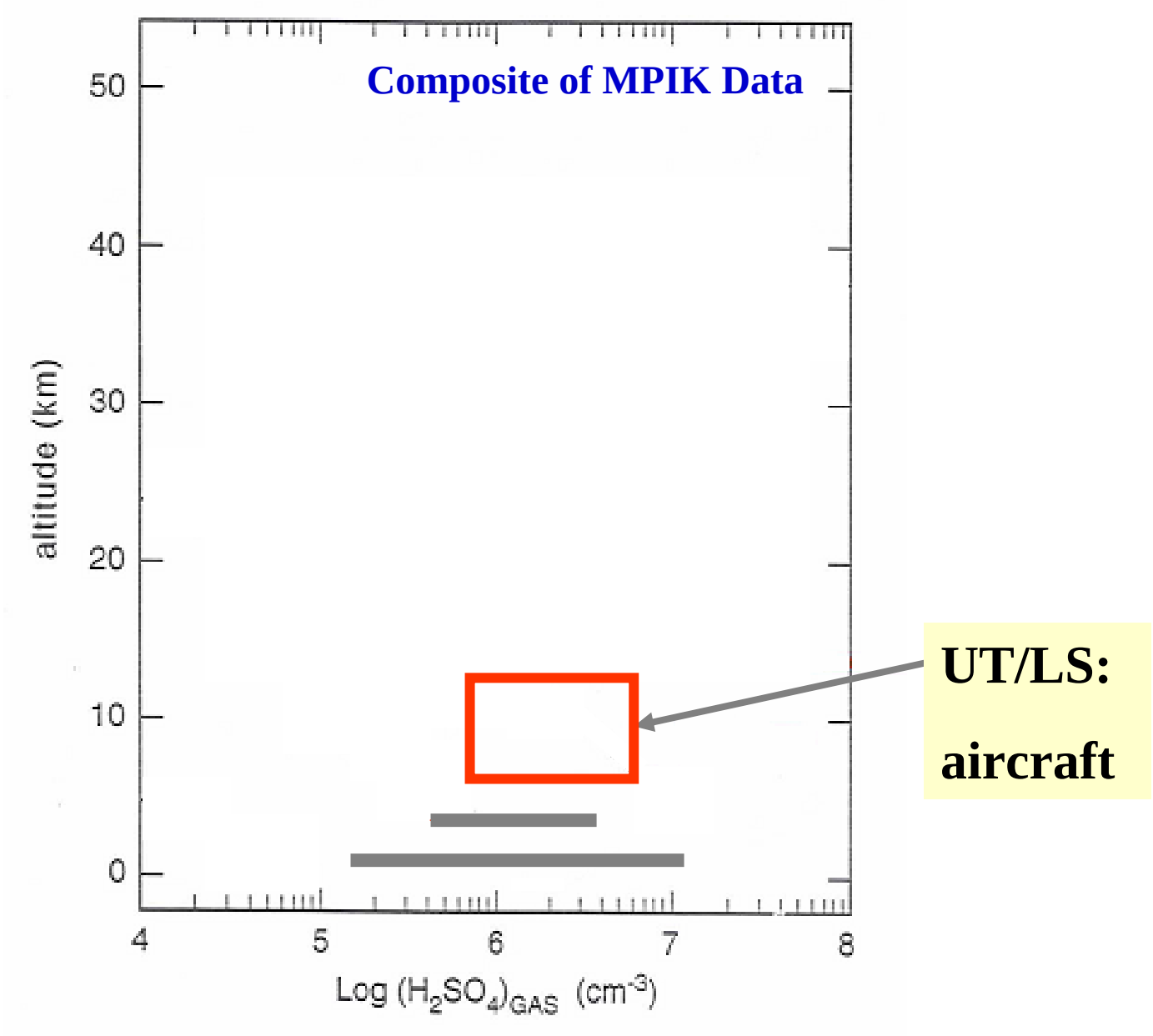
Finland (Hy)

Germany (HD)

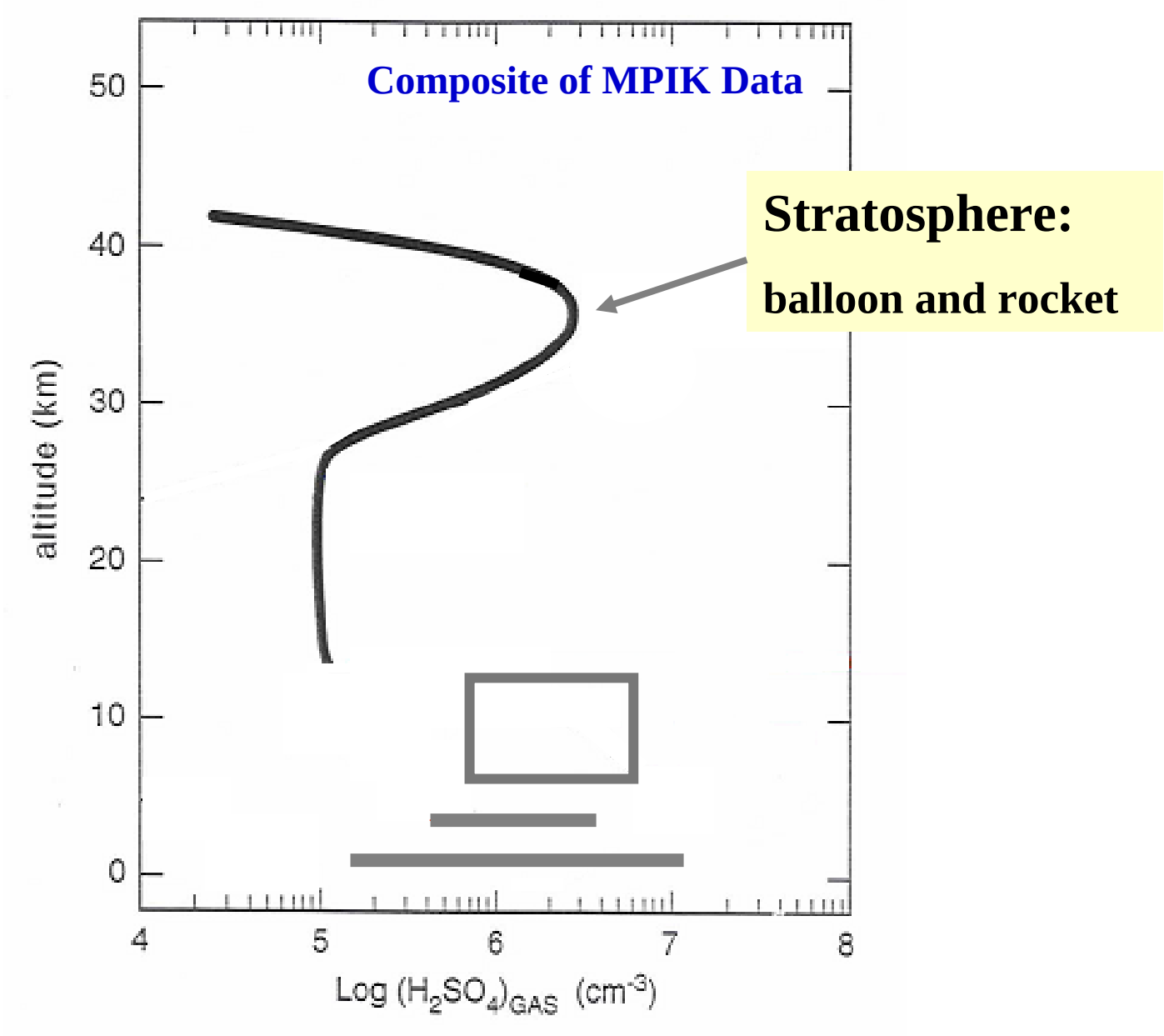
Atmospheric gaseous H2SO4 measured by MPIK



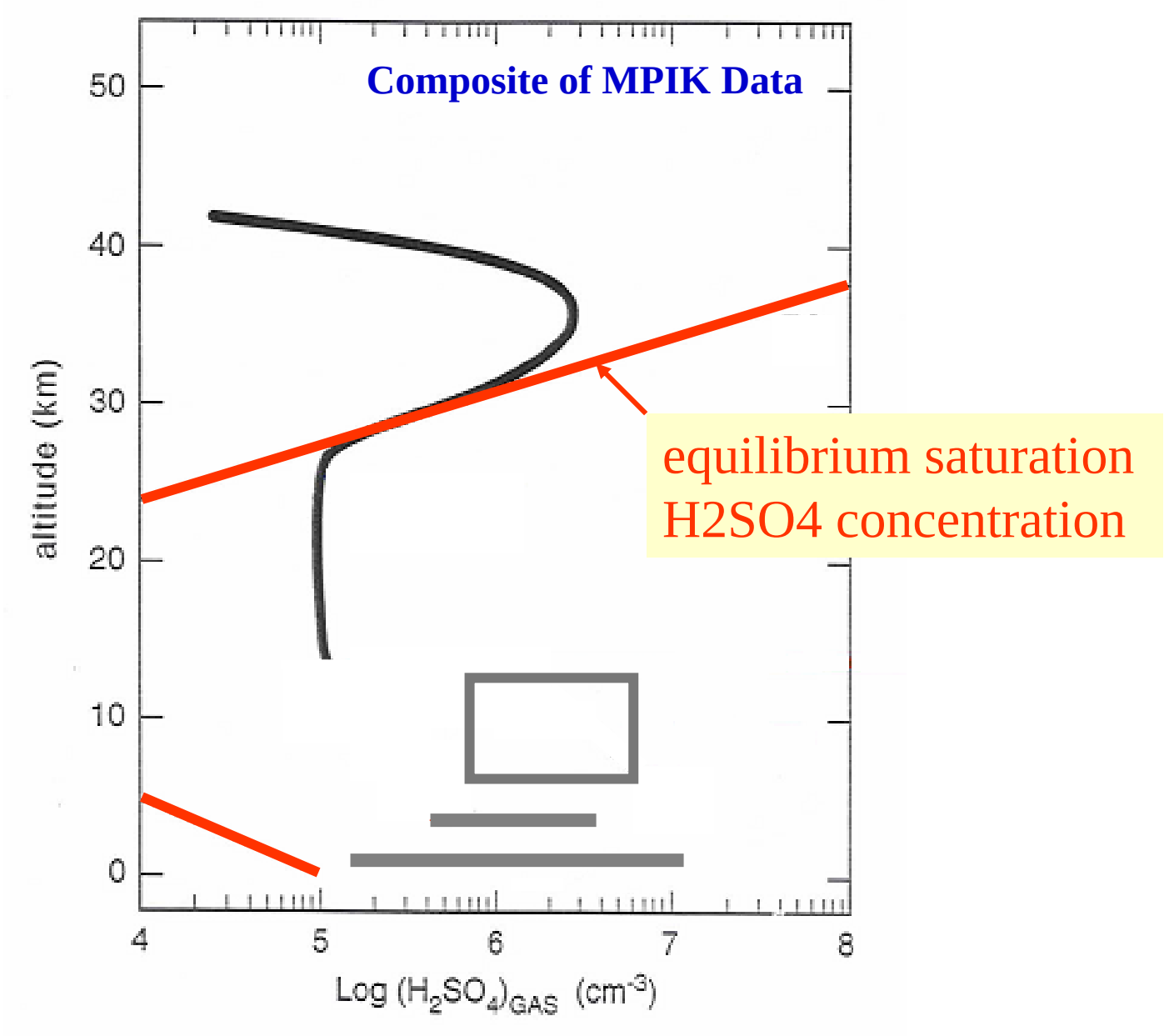
Atmospheric gaseous H2SO4 measured by MPIK



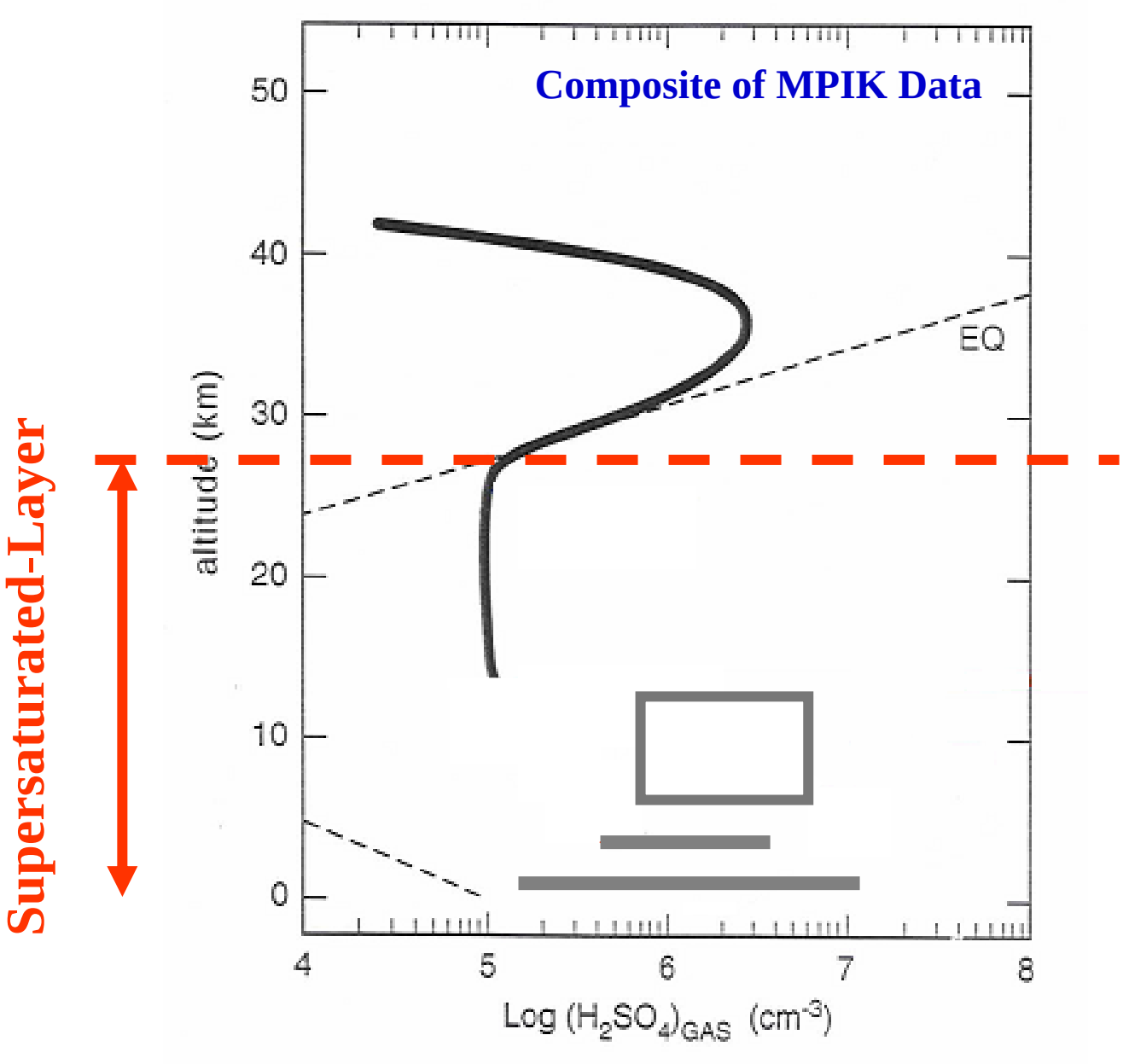
Atmospheric gaseous H2SO4 measured by MPIK



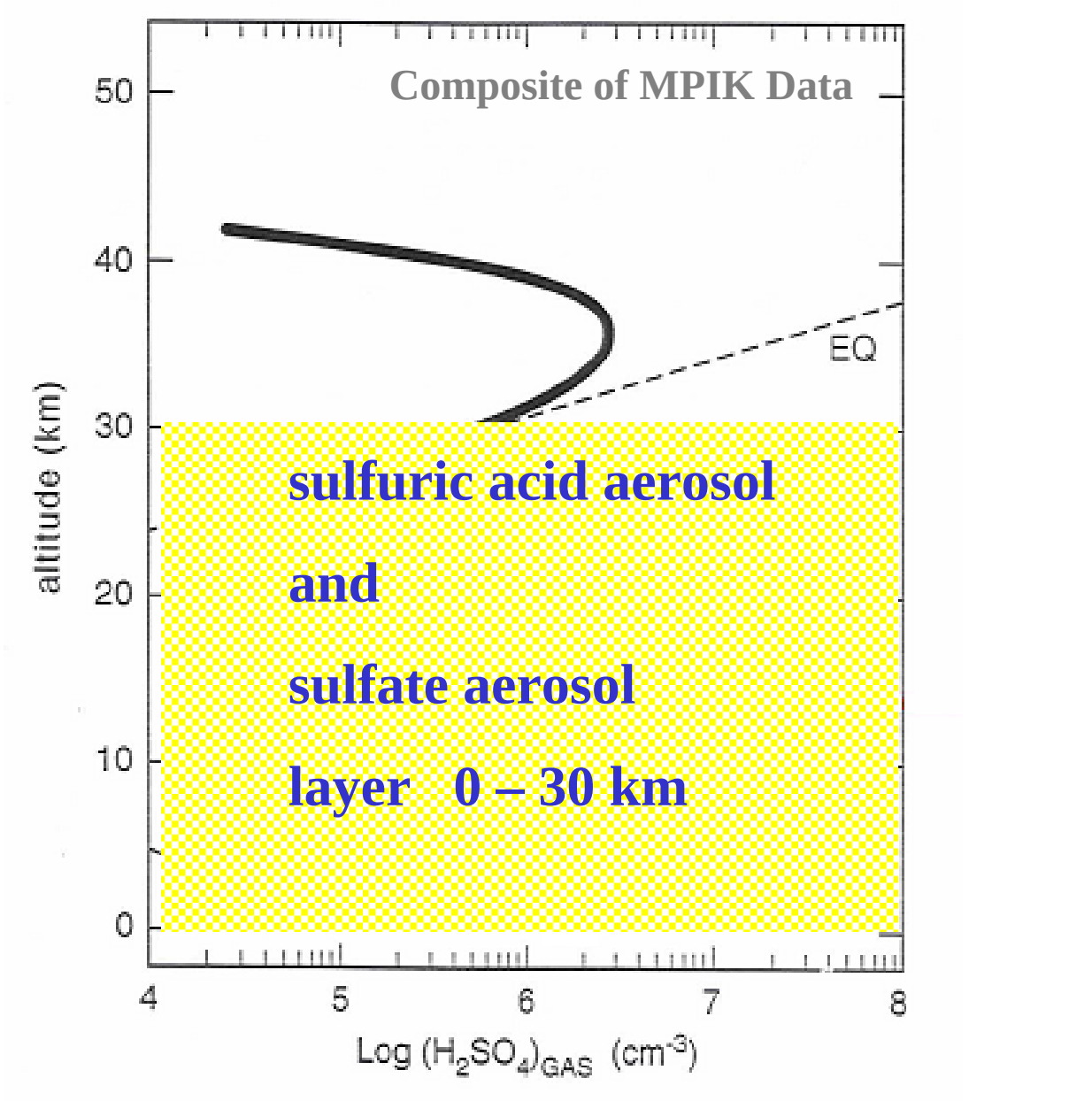
Atmospheric gaseous H2SO4 measured by MPIK



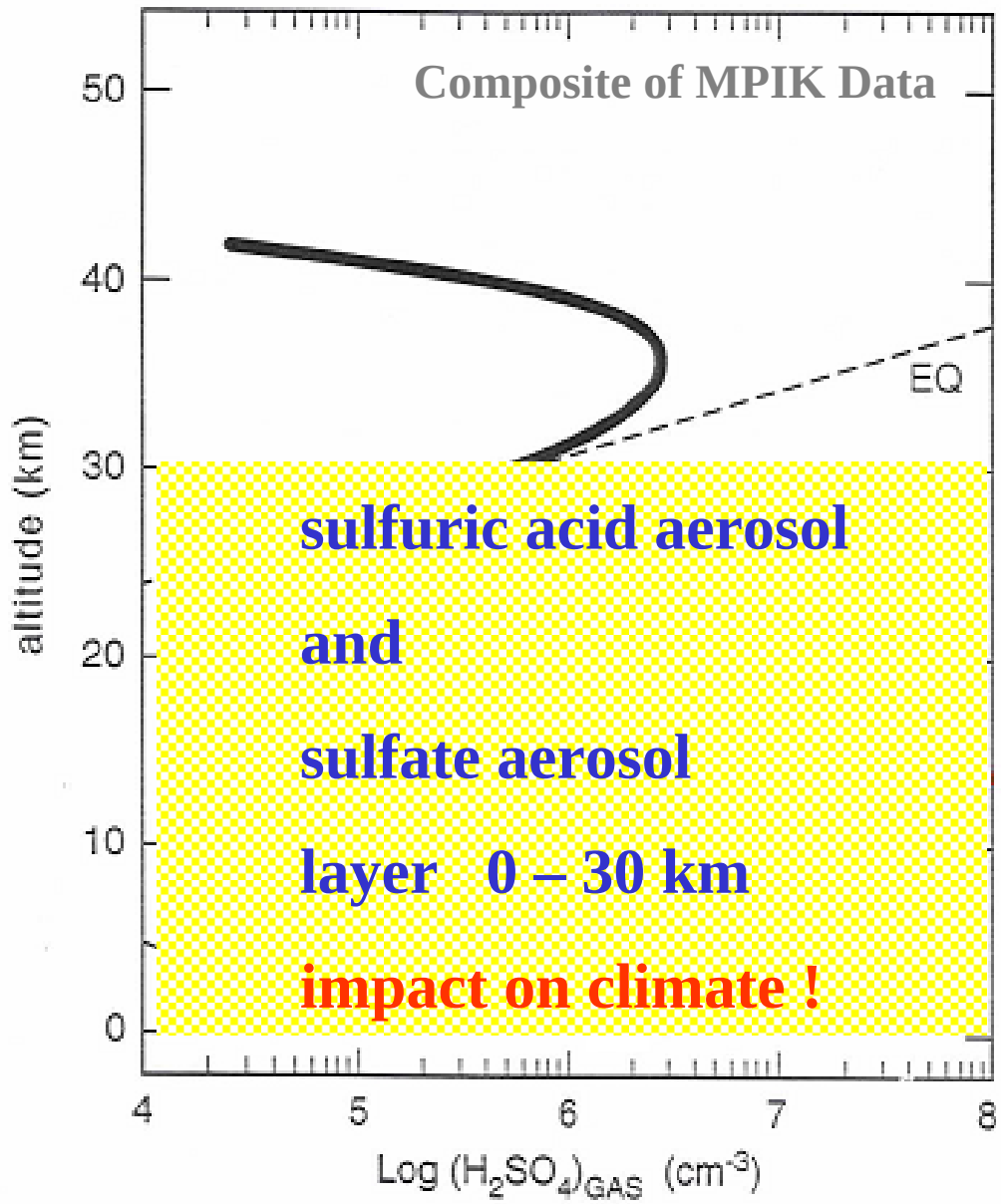
Atmospheric gaseous H2SO4 measured by MPIK



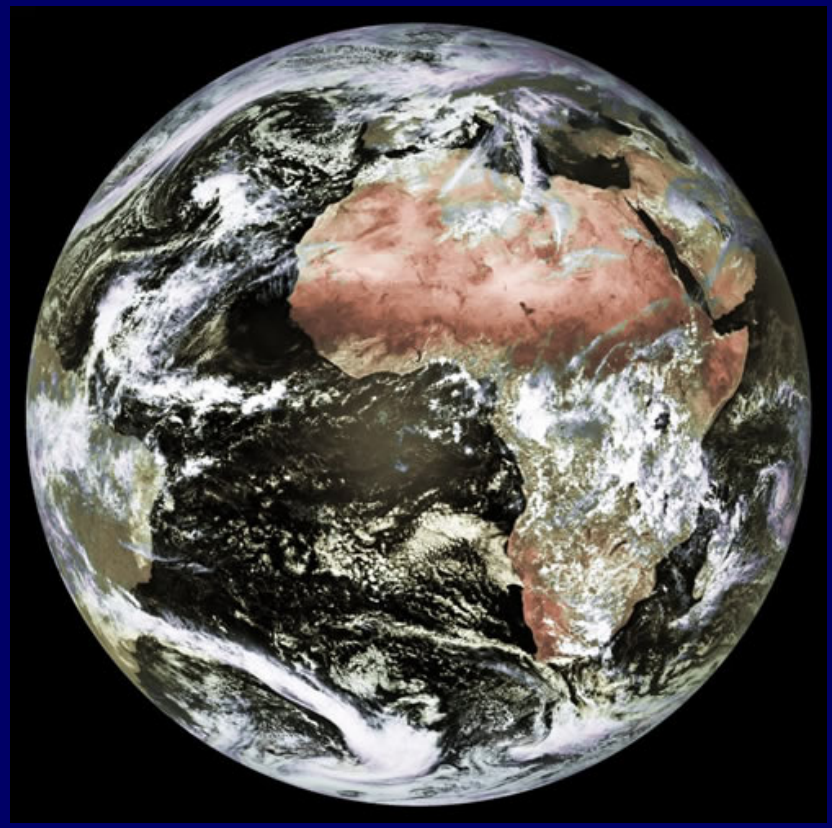
Atmospheric gaseous H2SO4 measured by MPIK



Atmospheric gaseous H2SO4 measured by MPIK

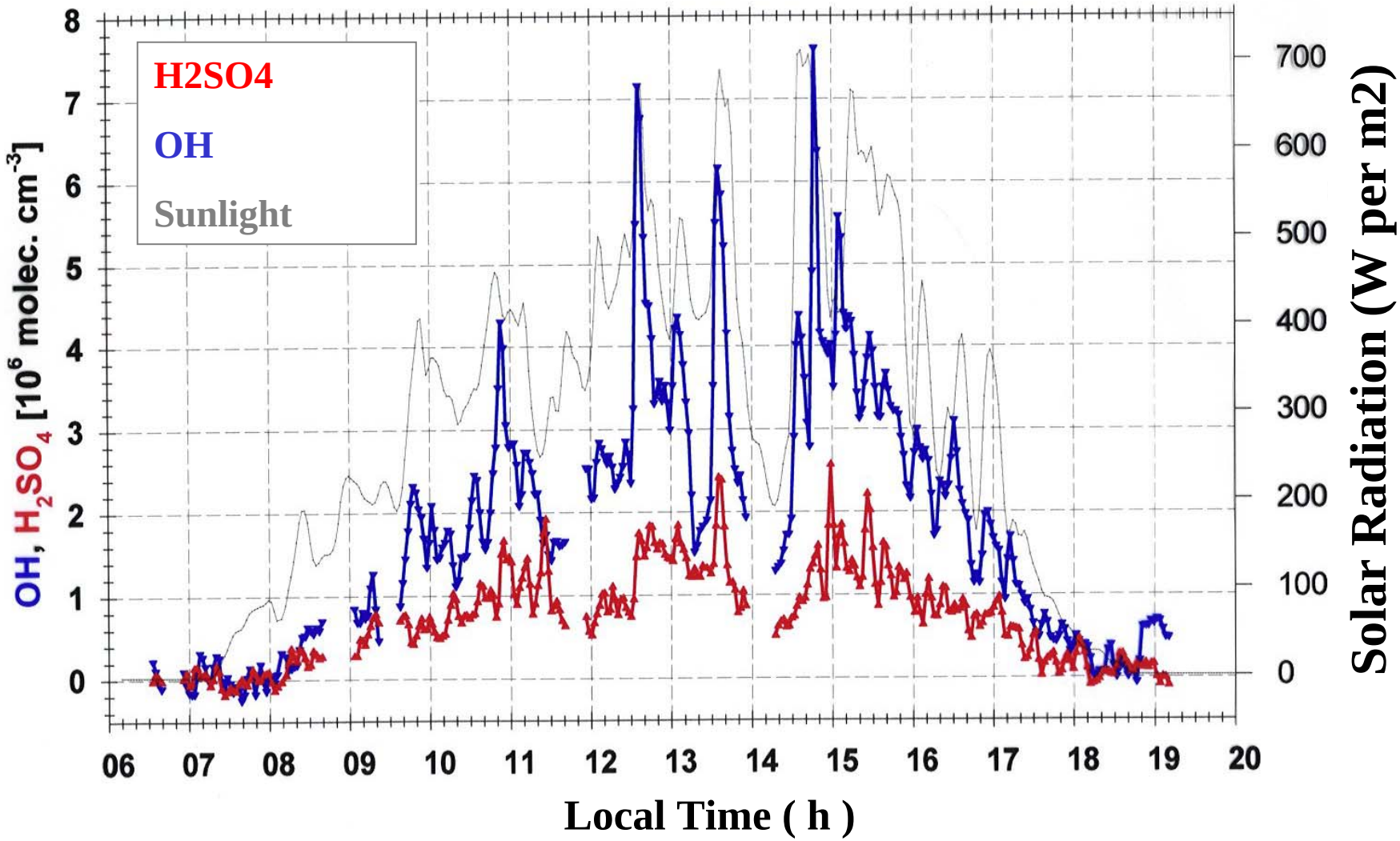


OH and H2SO4 measurements

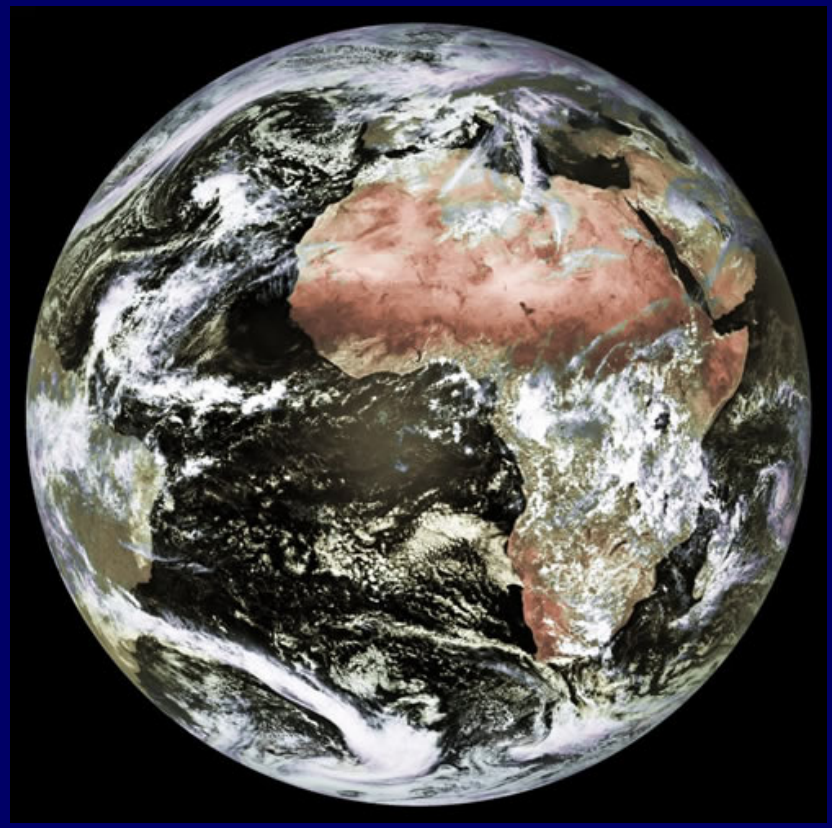


On Mount Zugspitze

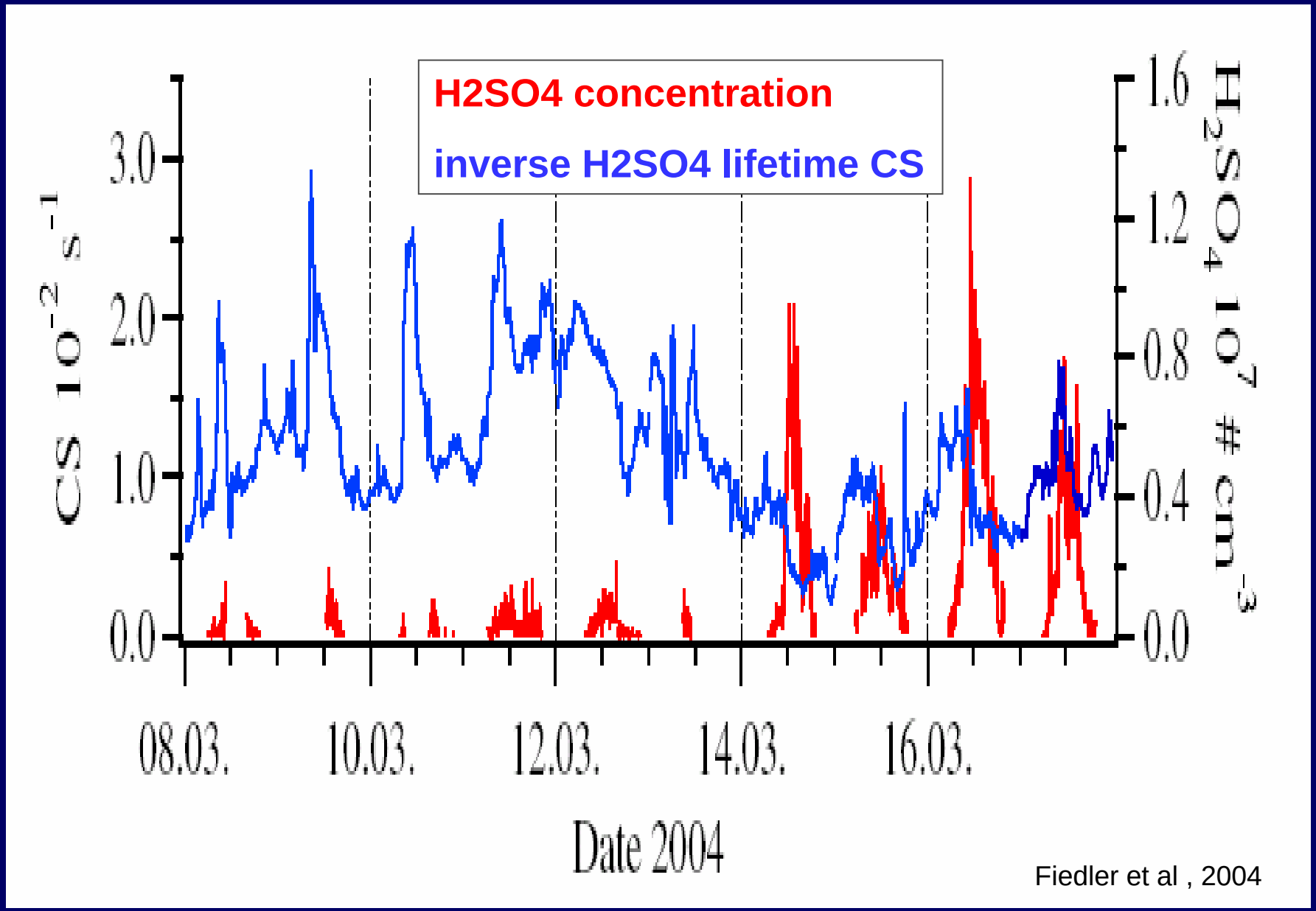
Mount Zugspitze SFH 2300 m altitude



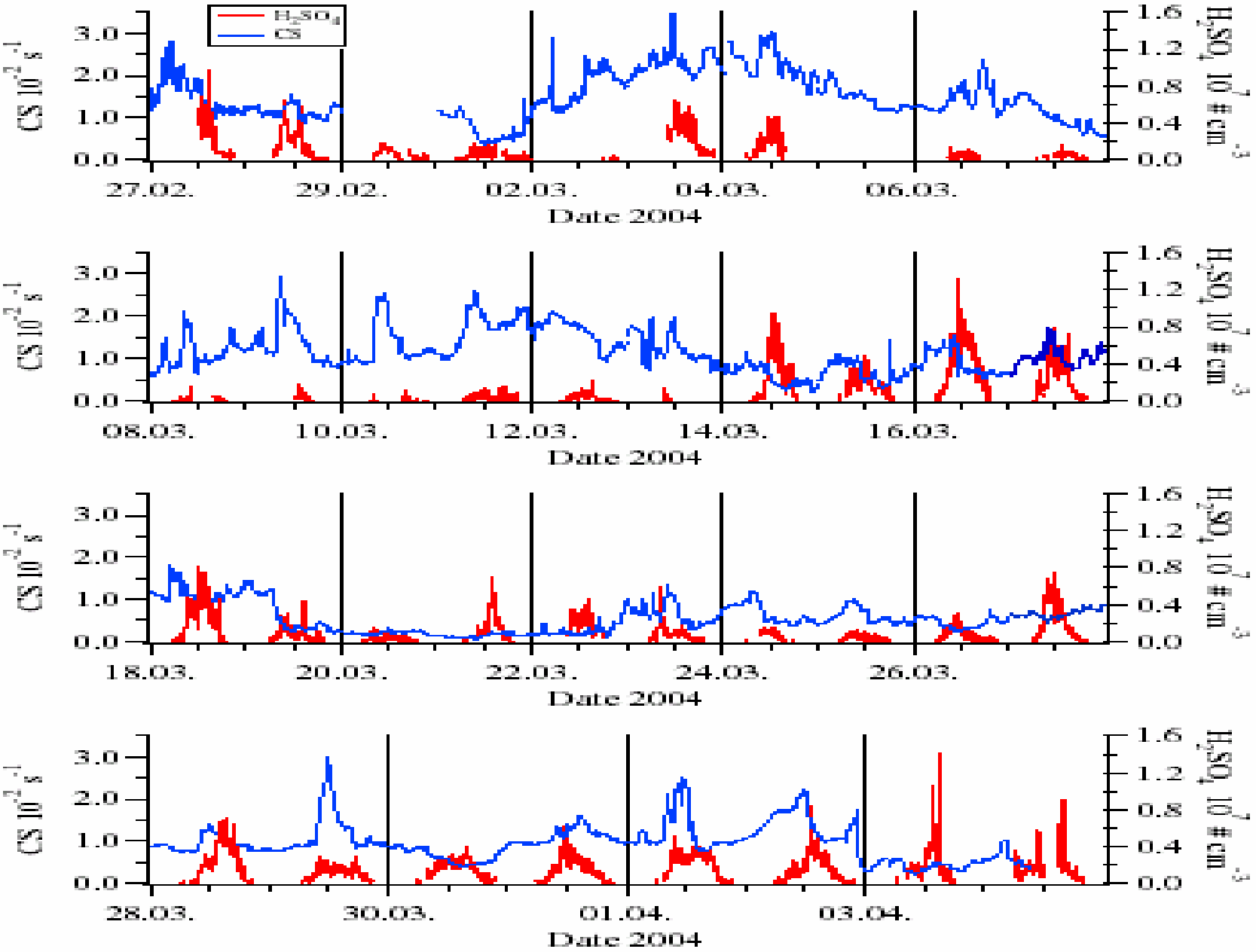
H2SO4 measurements



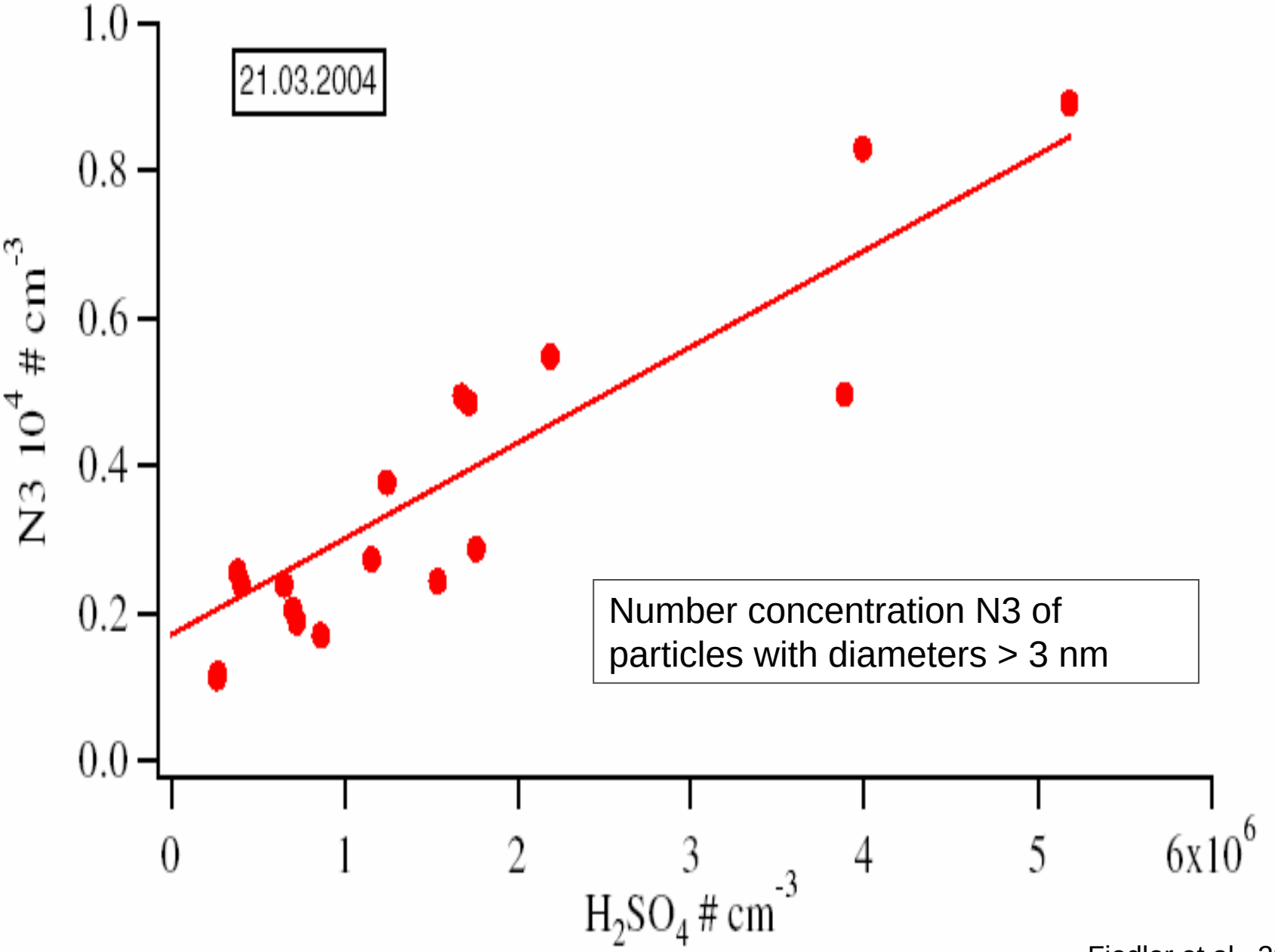
In ground-level air inFinland



Fiedler et al , 2004



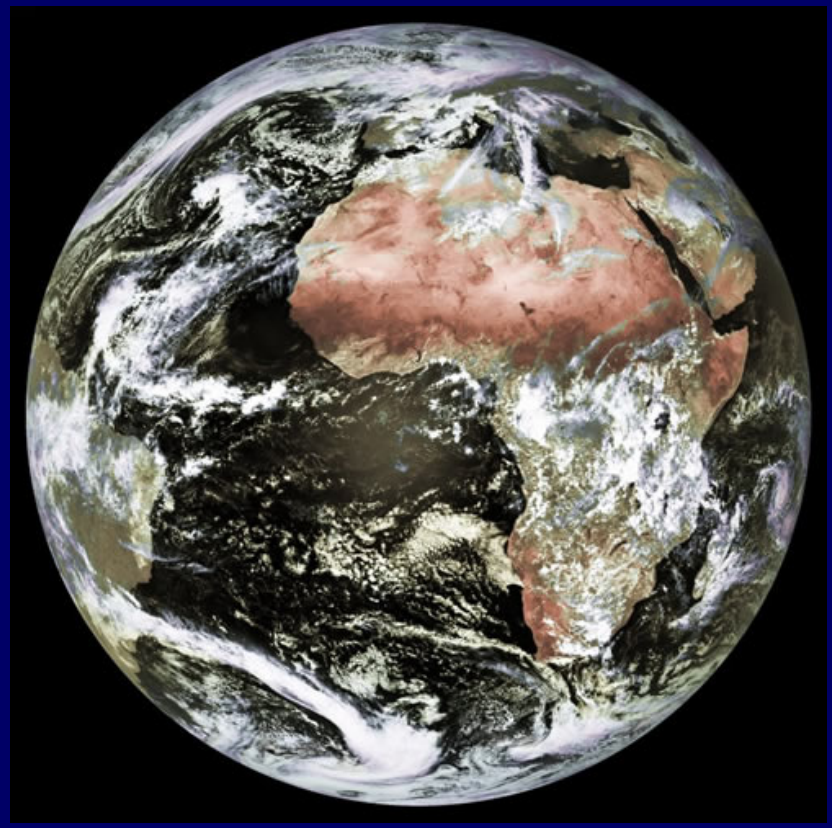
Fiedler et al , 2004



Fiedler et al , 2004

H2SO4 variability is to a large part due to SO2 variability

Air craft-based SO2 measurements



cooperation MPIK/ DLR

Research air craft FALCON (DLR)

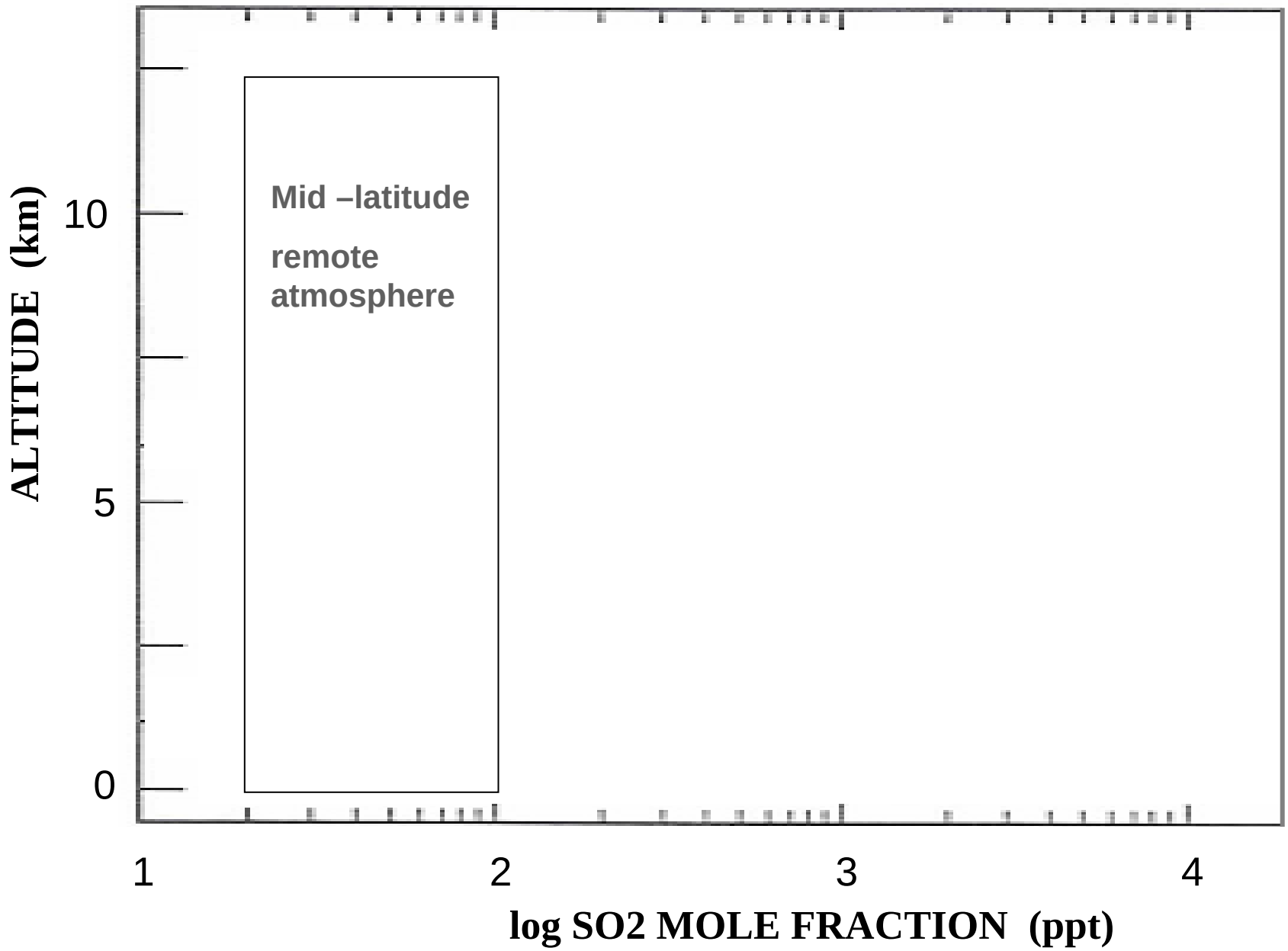
Research air craft FALCON (DLR)

SO2 Measurements
(MPIK/DLR-IPA cooperation)

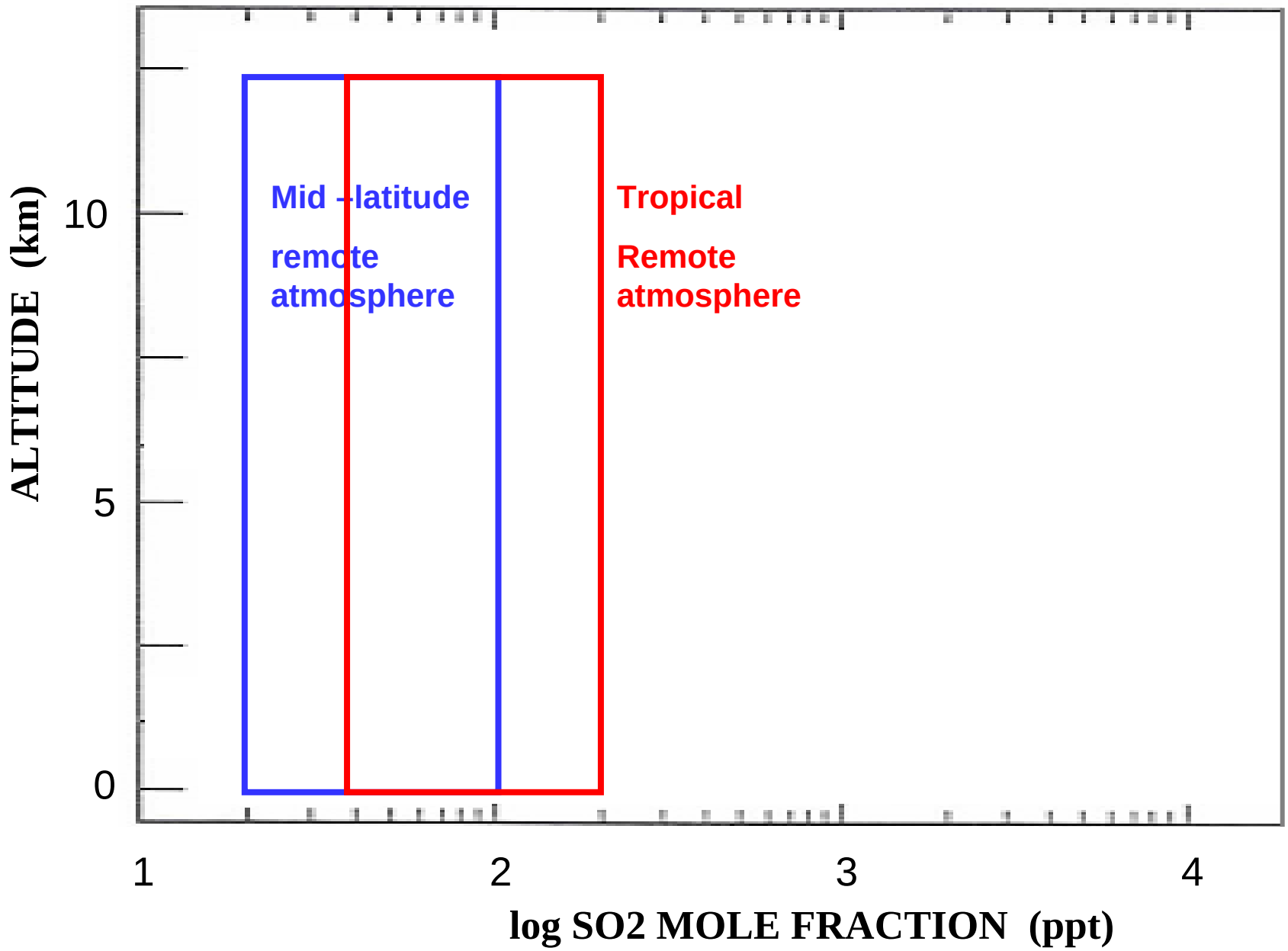
Atmospheric mole fraction ranges

(schematic)

Atmospheric **sulfur dioxide** measured by MPIK-DLR



Atmospheric **sulfur dioxide** measured by MPIK-DLR



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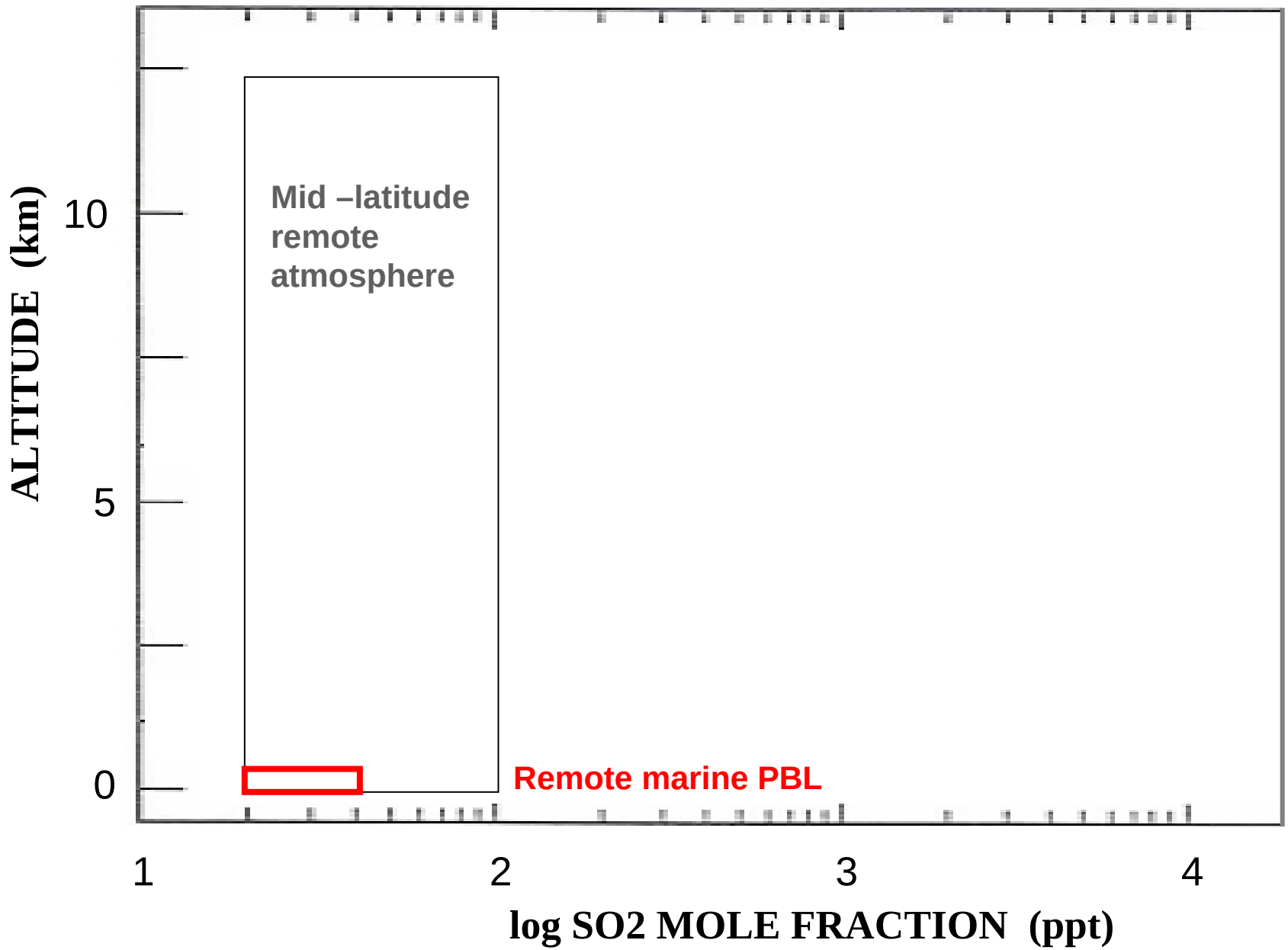

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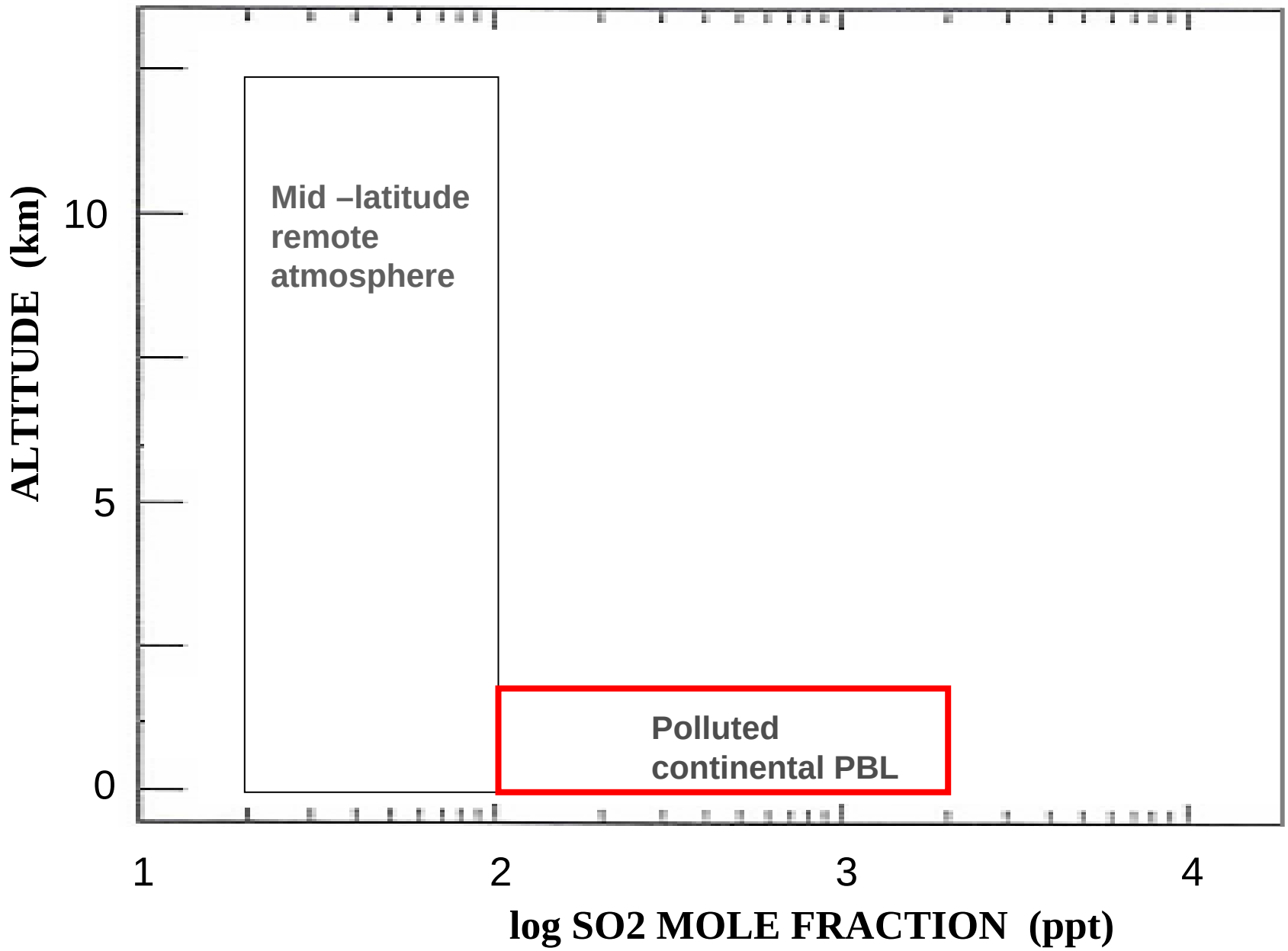

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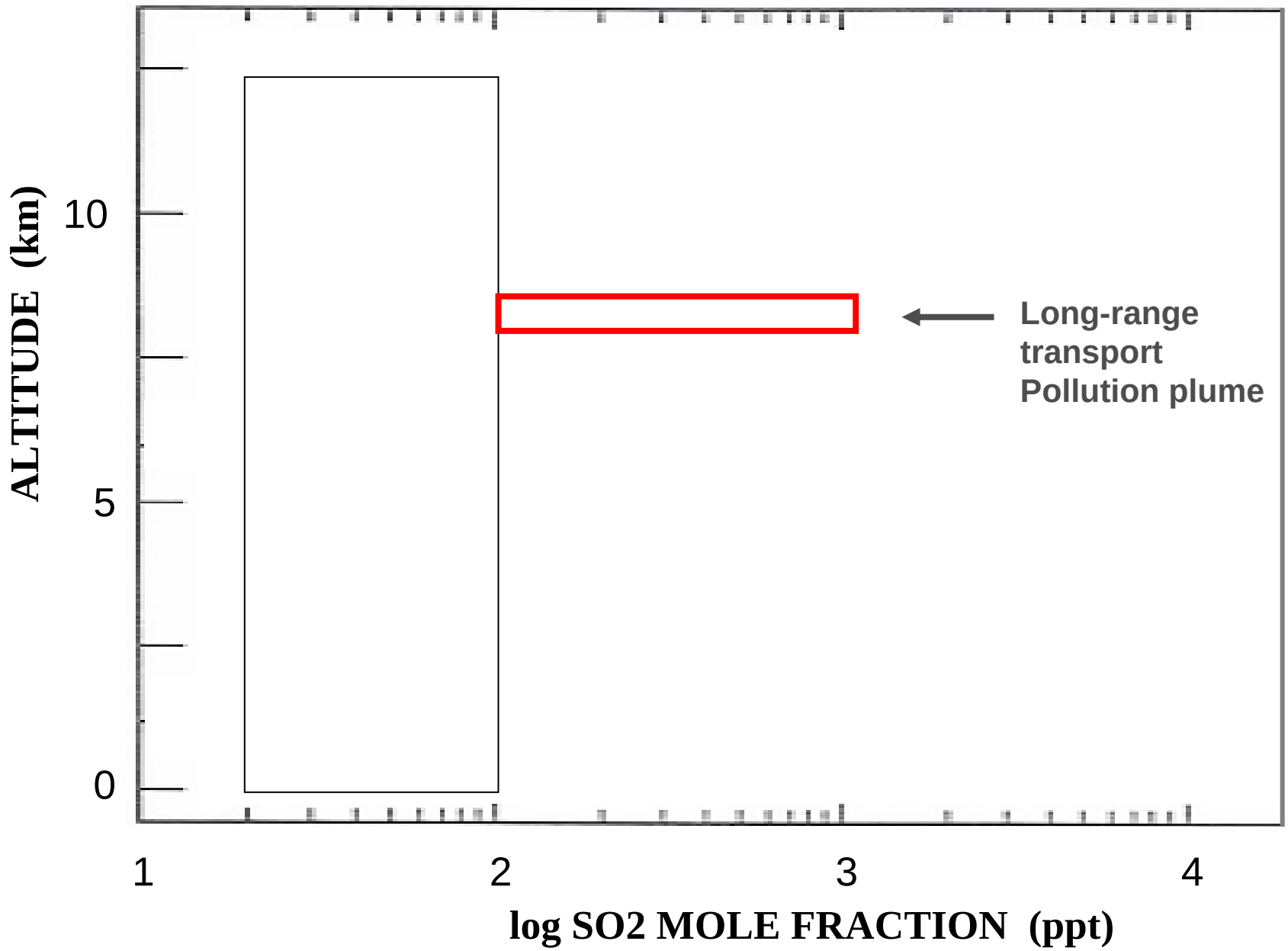

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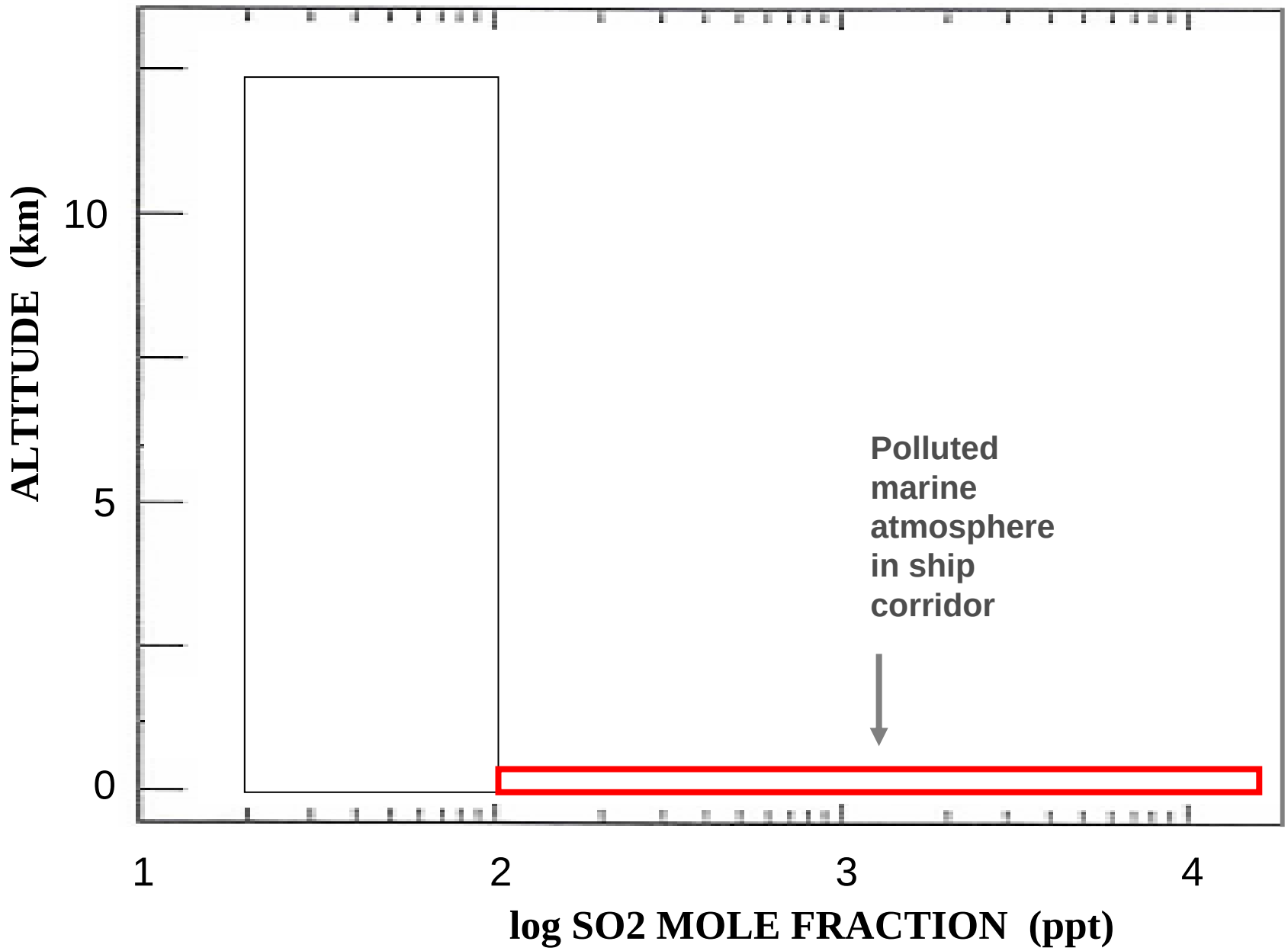
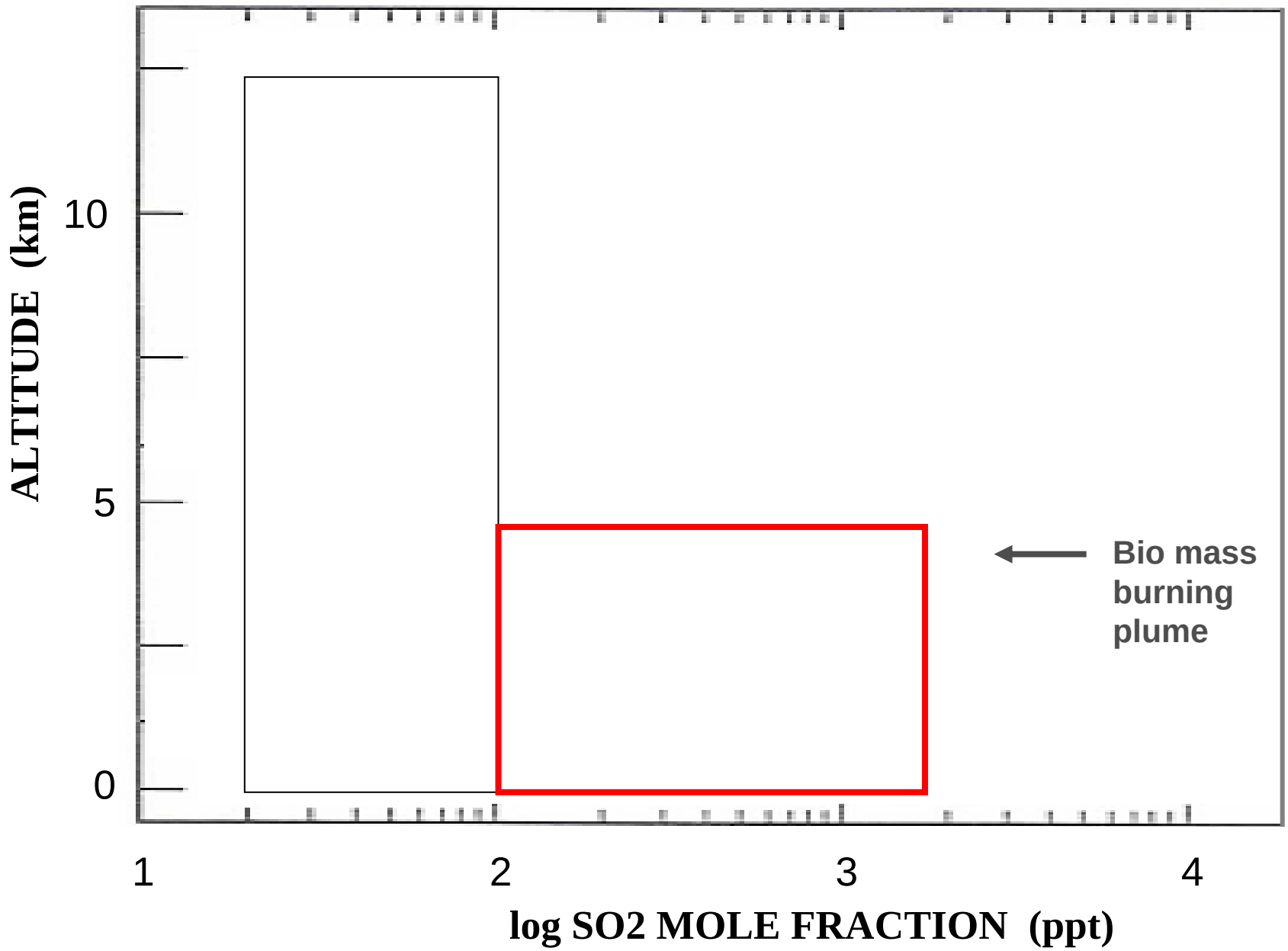
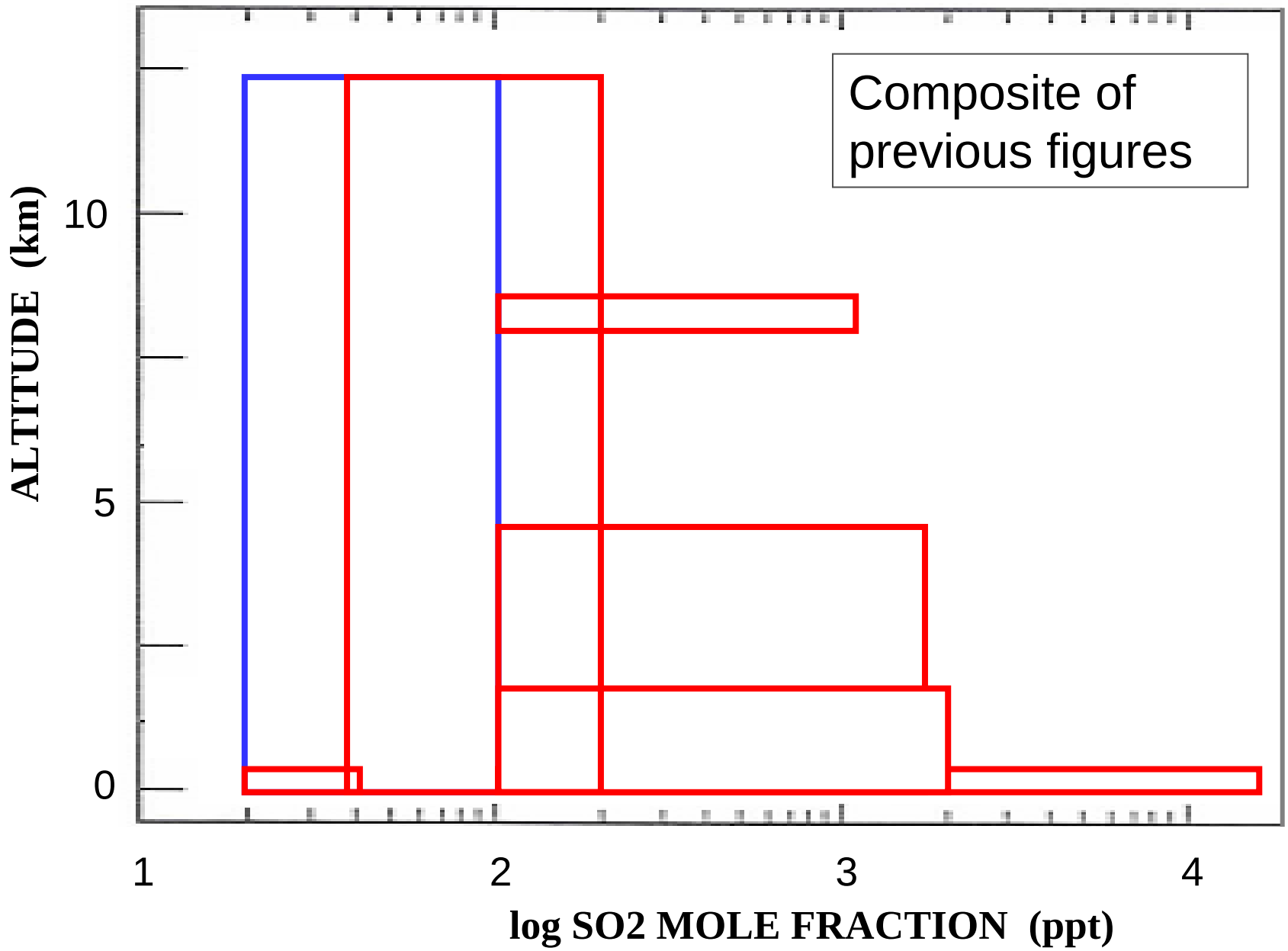


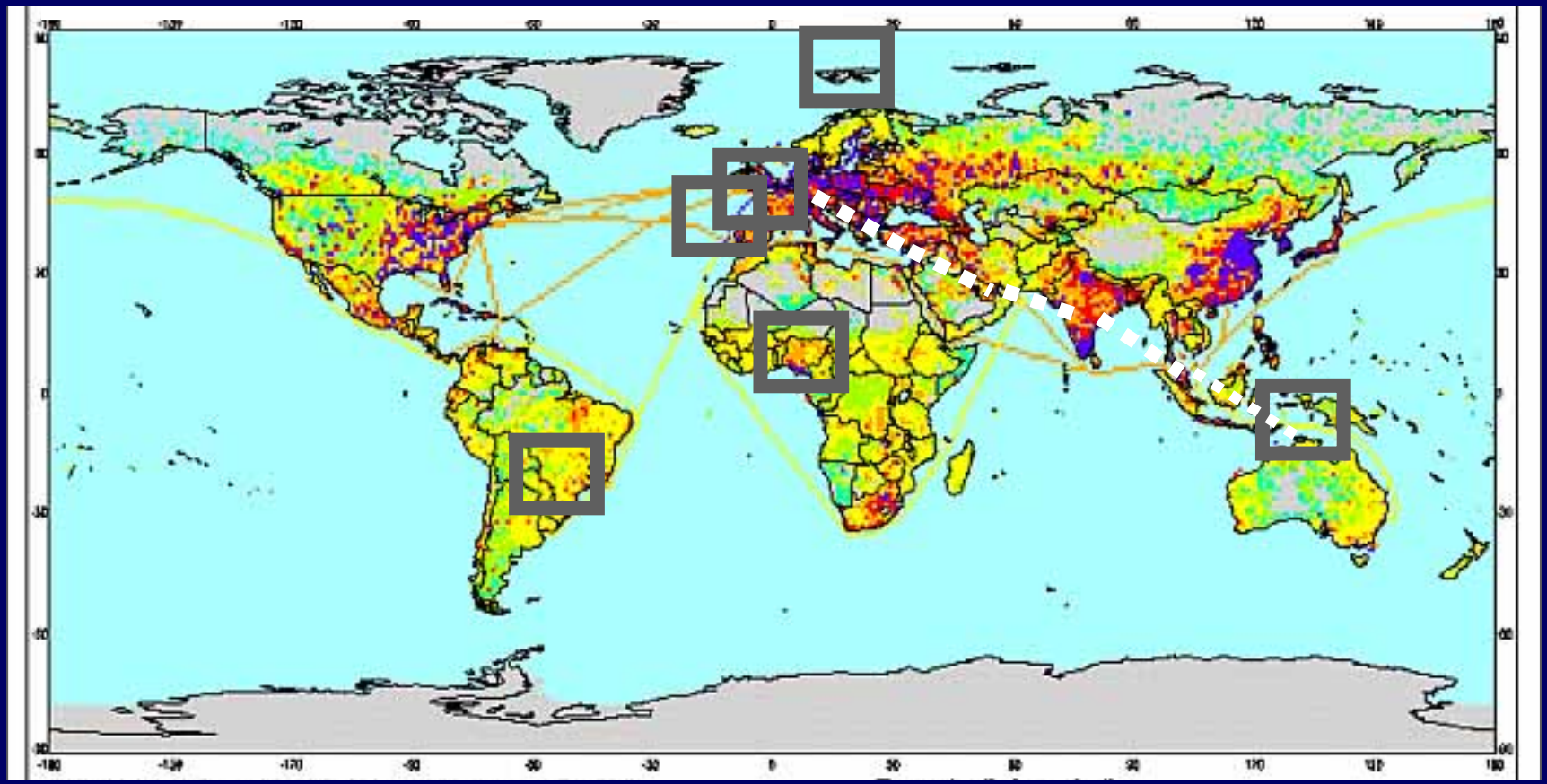
Atmospheric **sulfur dioxide** measured by MPIK-DLR



Atmospheric **sulfur dioxide** meqasured by MPIK-DLR

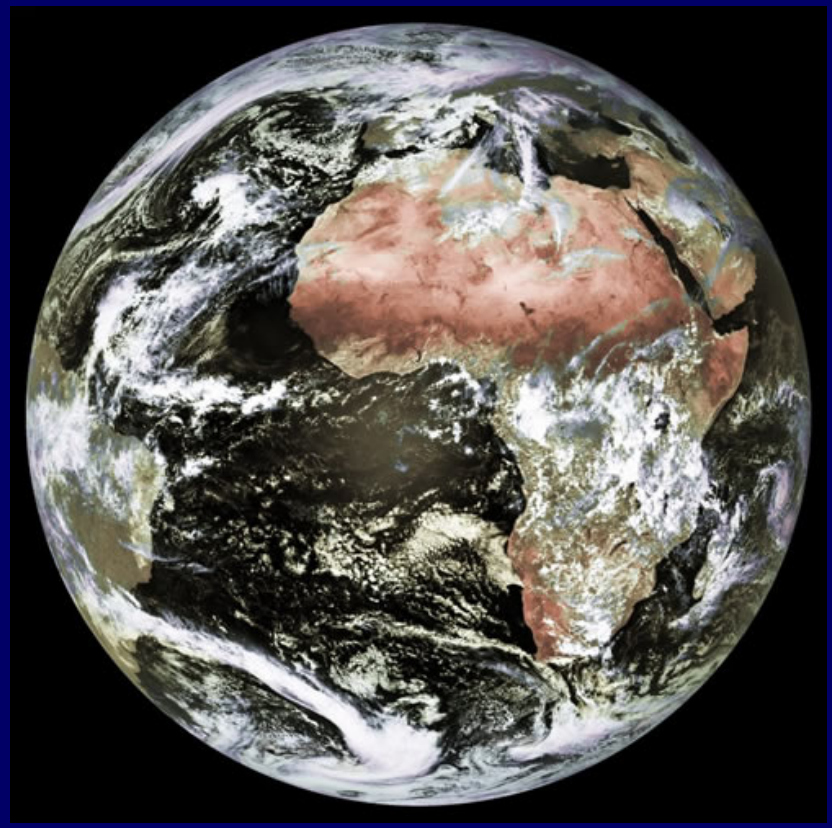


Aircraft Campaigns 2005-2007

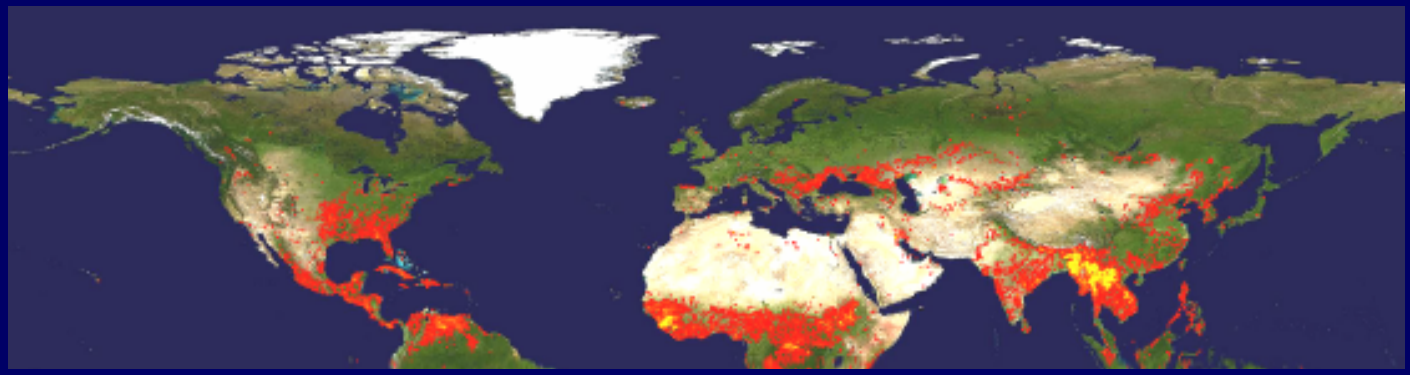


CIMS measurements (cooperation MPIK/DLR)

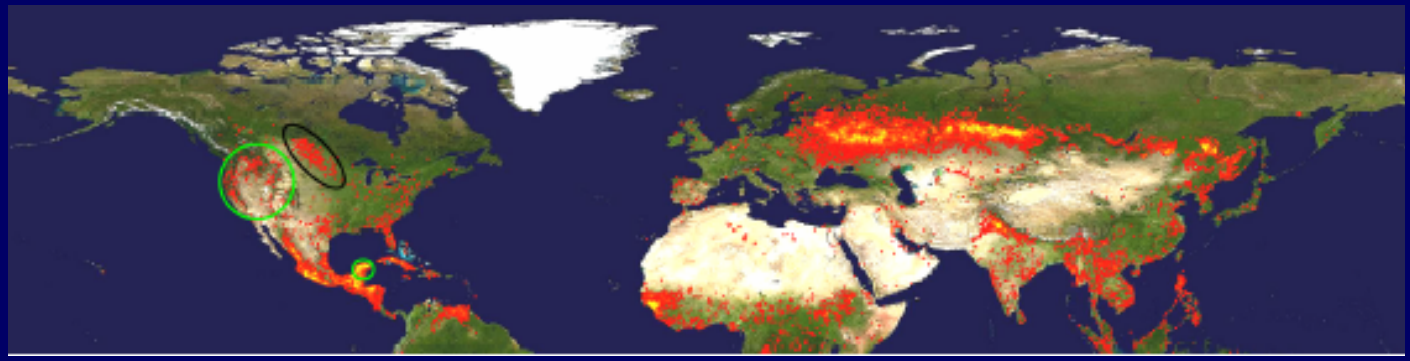
Bio mass burning plume measurements



colaboration MPIK/ DLR



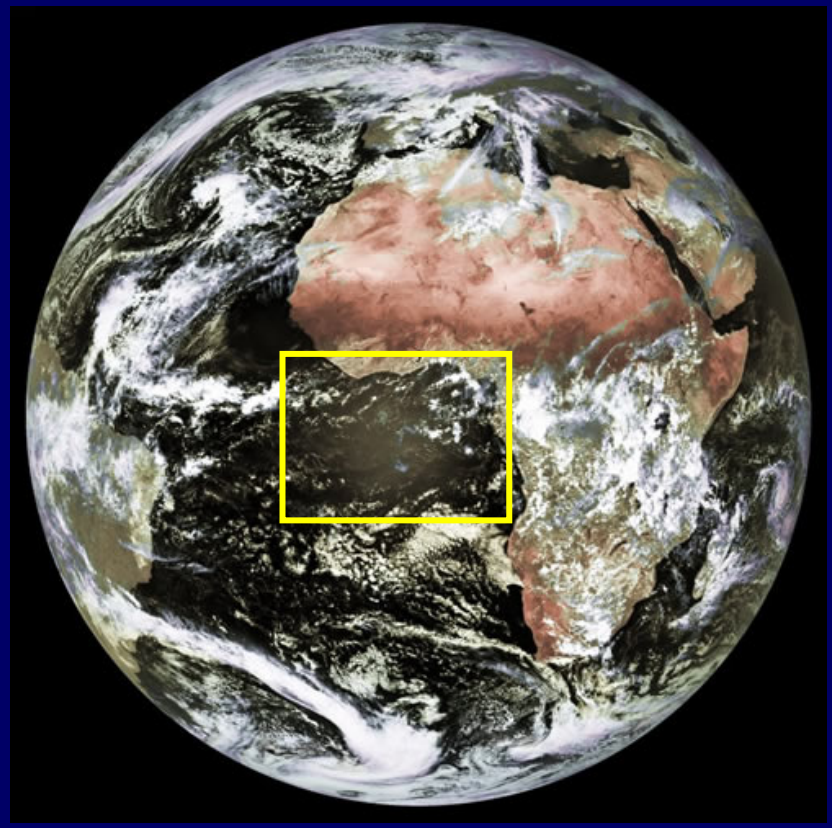
MODIS fire map : 22 – 31 Mar 06



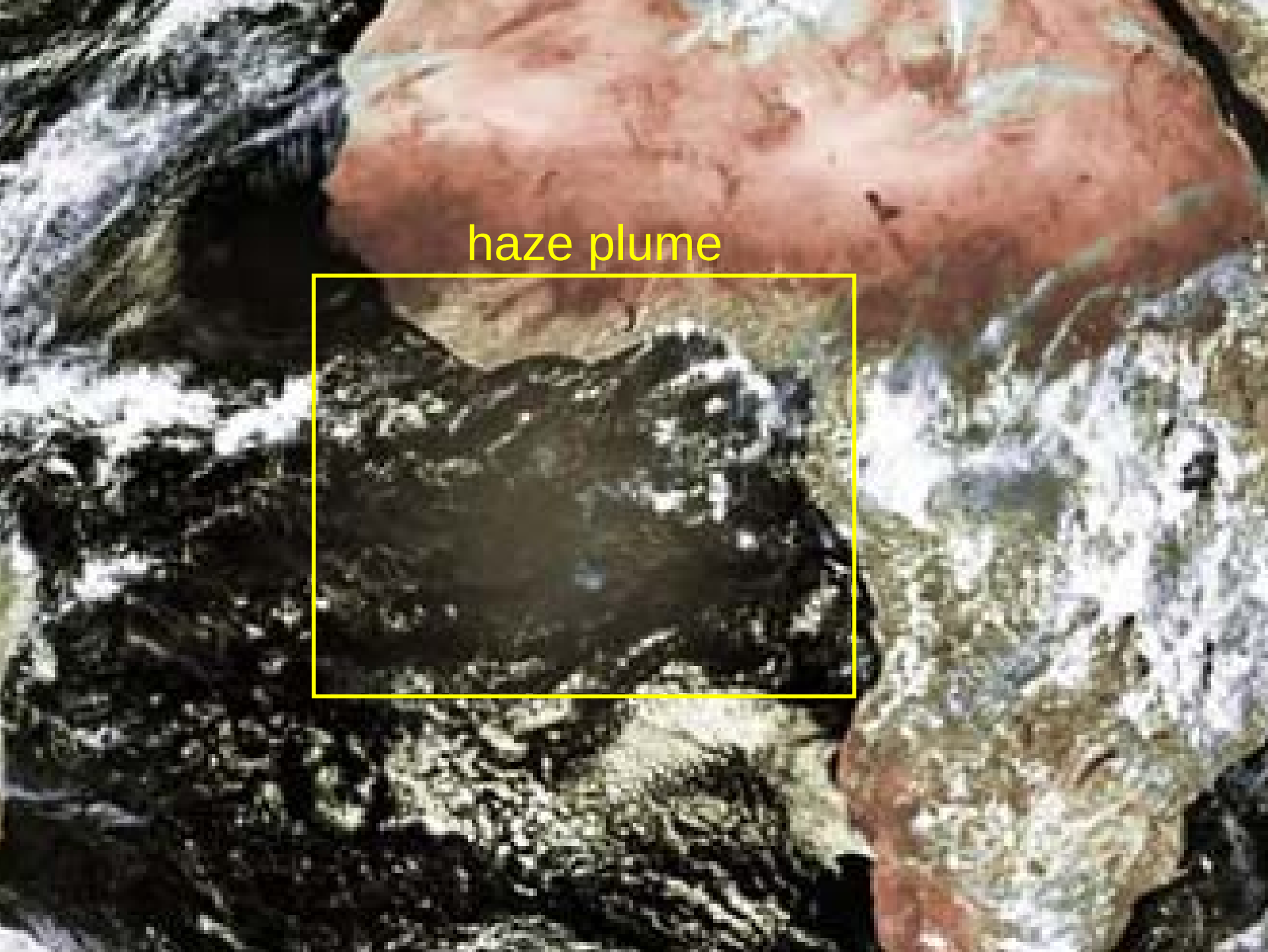
MODIS fire map : 01 - 10 May 06

Fires indicated by red and yellow

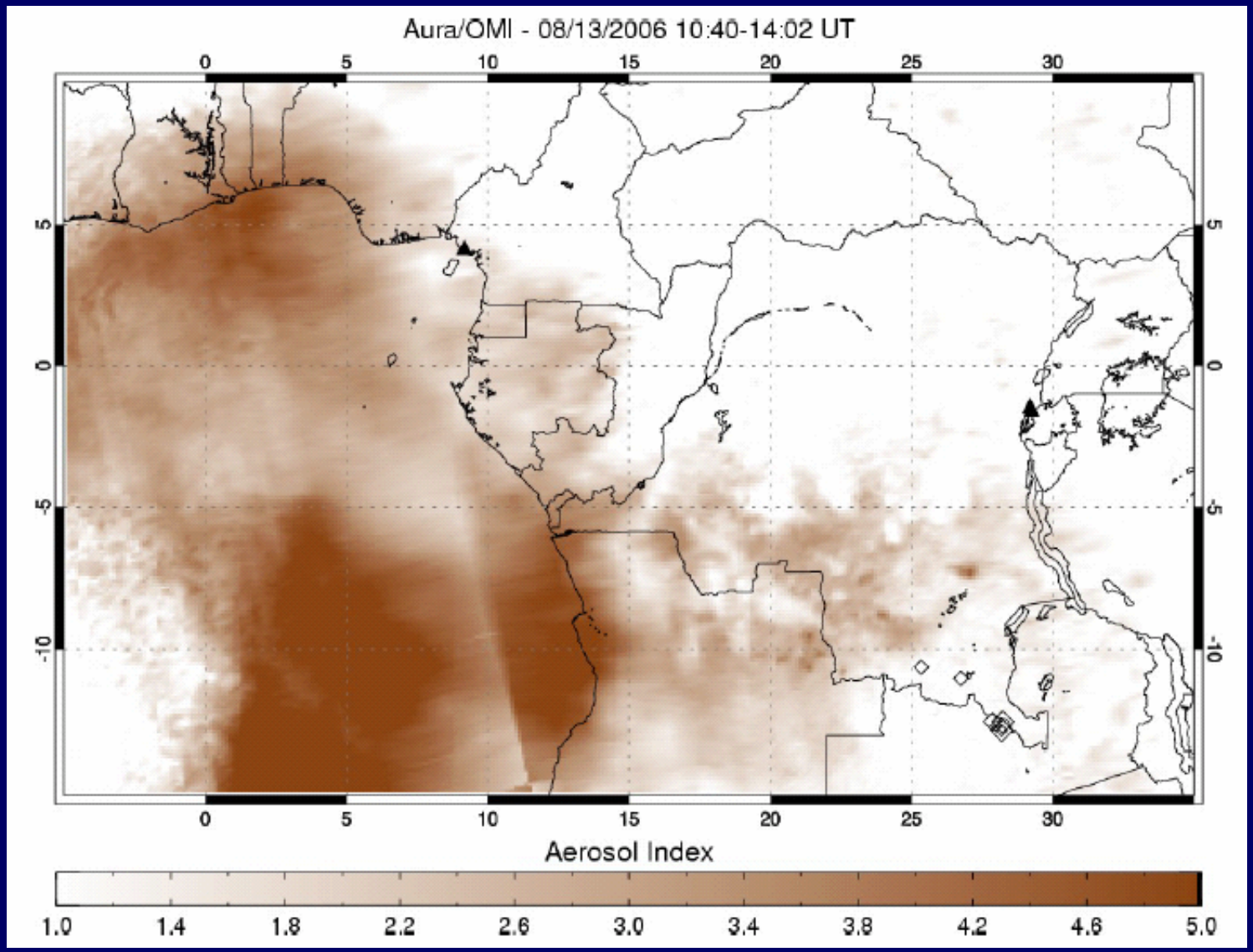
Bio mass burning plume measurements



colaboration MPIK/ DLR


haze plume

Absorbing aerosol measured by OMI (on AURA satellite)



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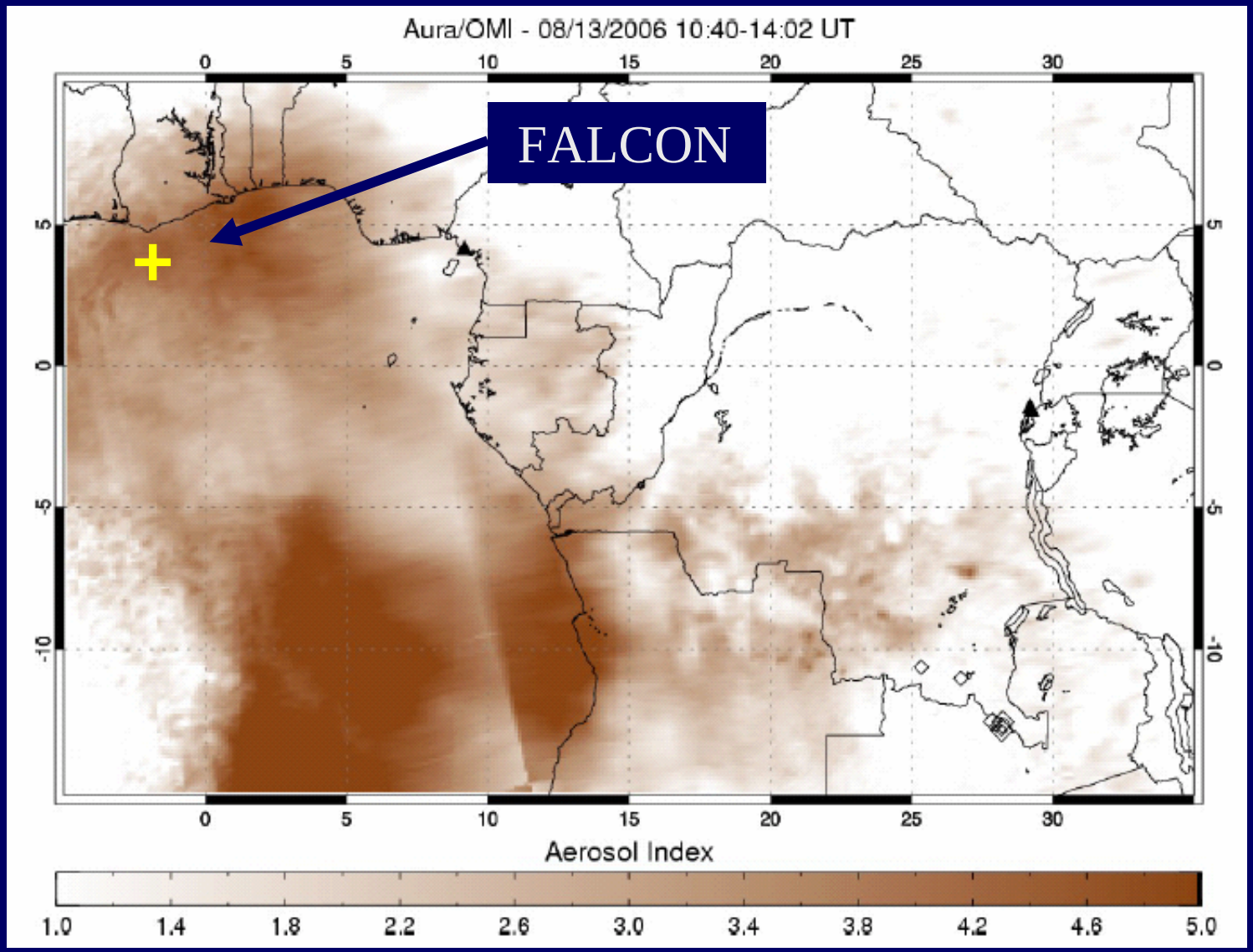
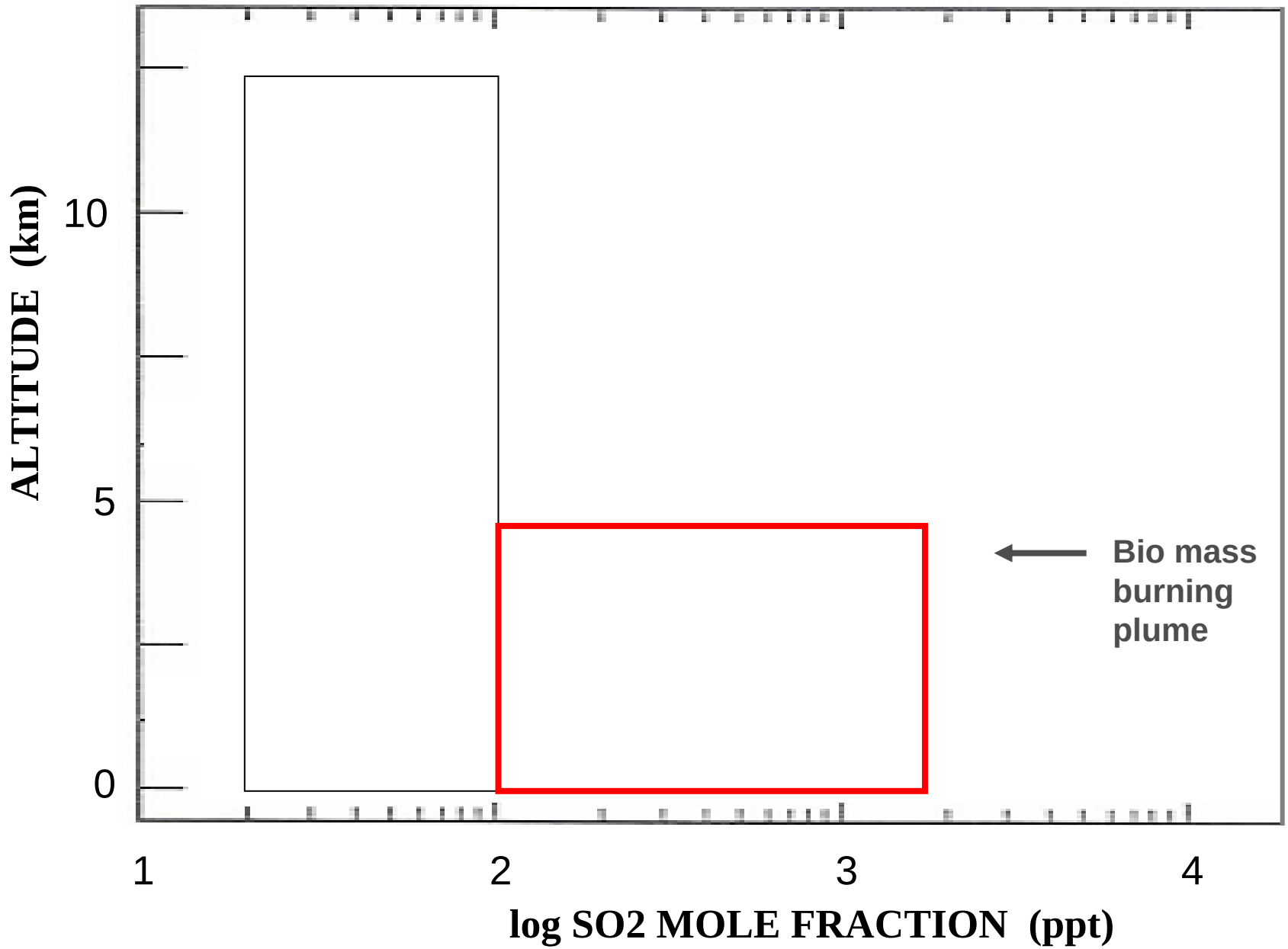


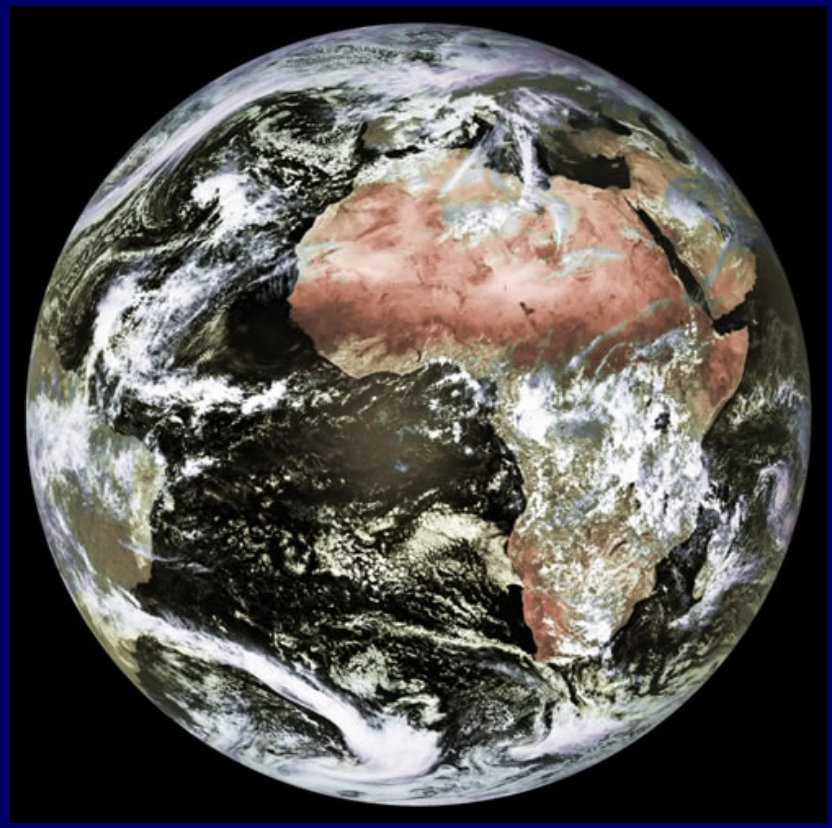
ATMOSPHERIC SULFUR DIOXIDE



Biomass burning plume

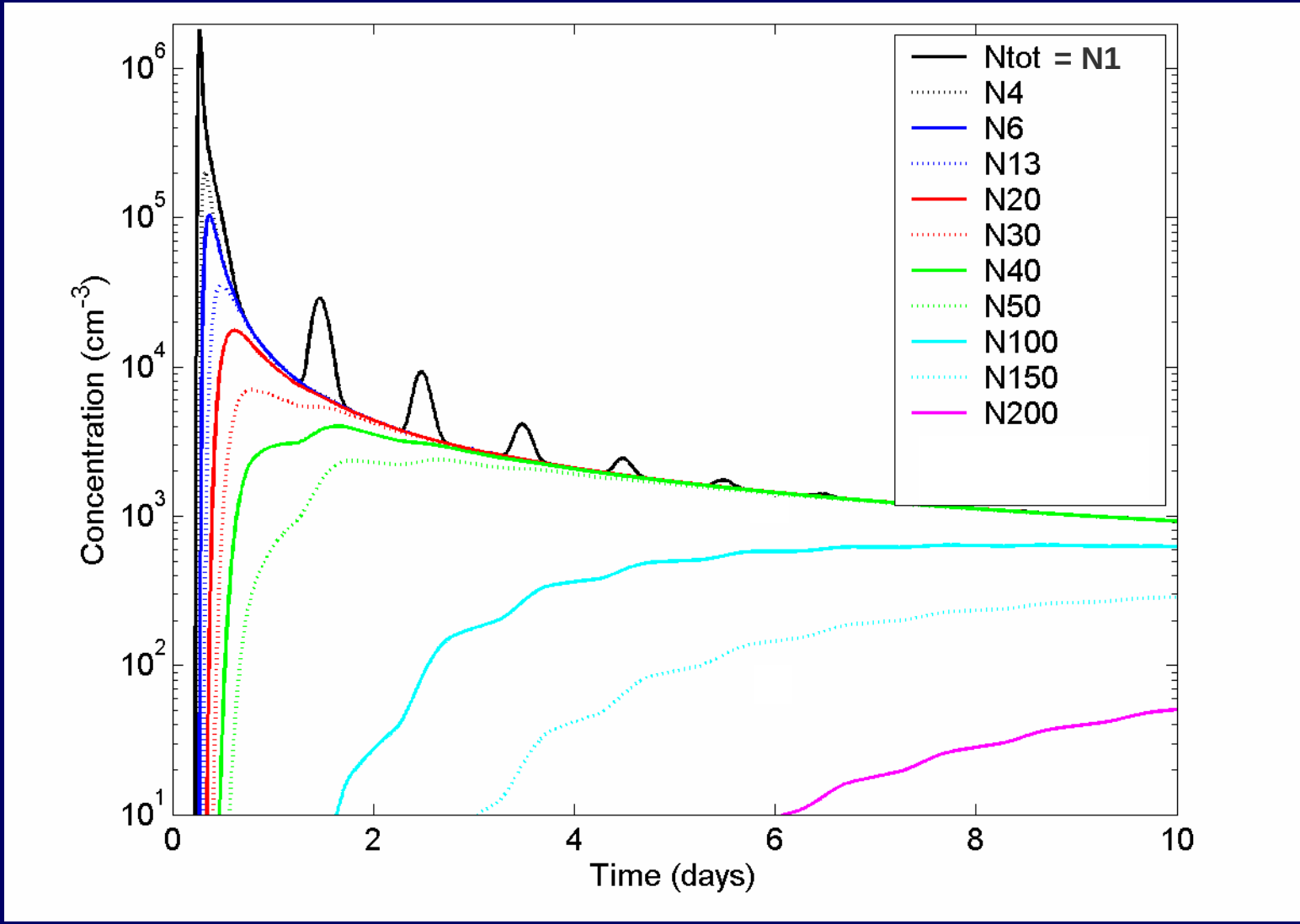
- Efficient NOx conversion to HNO3
- Suggests high OH
- appreciable SO2 conversion to gaseous H2SO4
- H2SO4 coating of soot → hygroscopicity increases

Aerosol model simulations



AEROFOR model (cooperation with L. Pirjola, UH)

AEROFOR model: 10 day simulation of number concentrations Nx of particles with diameters > x nm



F.Arnold, L. Pirjola, et al. 2007

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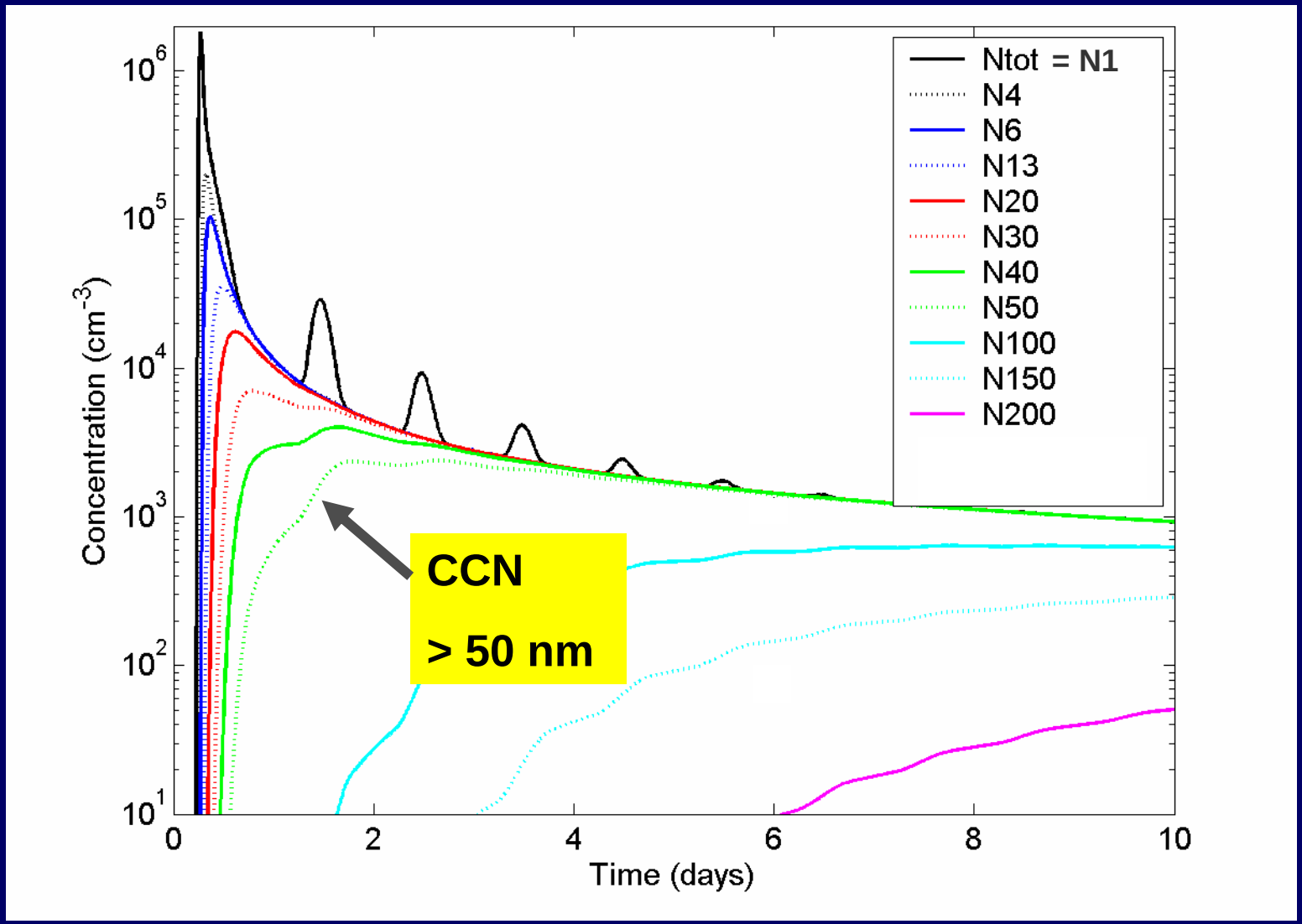

F.Arnold, L. Pirjola, et al. 2007

Conclusions

- Aerosol precursor gas SO2 (main sources: combustion and smelters; other sources: plankton and volcanoes) can be efficiently transported vertically and horizontally
- Rapid long – range transport in UT
- Rapid photochemical conversion to gaseous H2SO4 in UT
- Efficient formation of nanoparticles by H2SO4 nucleation in UT
- Growth of nanoparticles to **CCN** size by H2SO4 condensation followed by coagulation is possible

Acknowledgements

- Organizers of ETH conference
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  (DLR , MAN , UH , NILU , ….)

Thank you for your interest