The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

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Winter College on Optics in Environmental Science

2 - 18 February 2009

Atmospheric Monitoring, Differential Optical Absorption Spectroscopy – DOAS II, Applications

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University of Heidelberg
Germany

Atmospheric Monitoring, Differential Optical Absorption Spectroscopy – DOAS II, Applications

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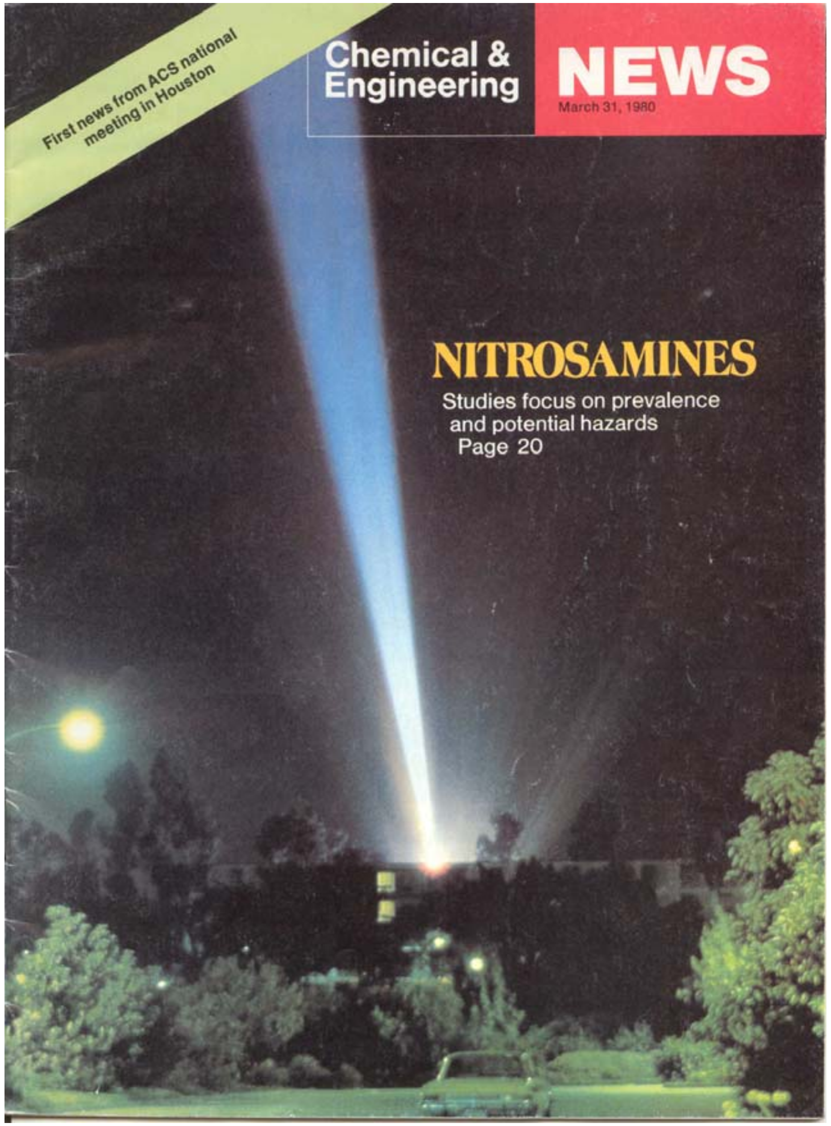
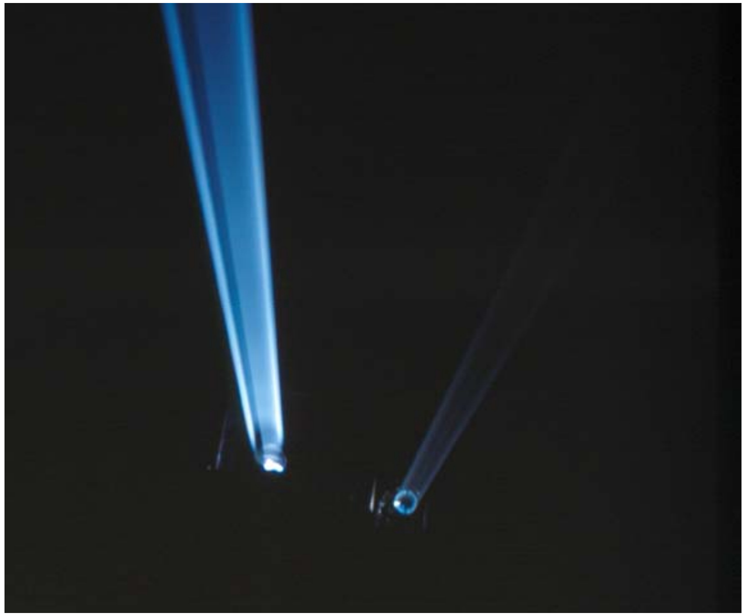
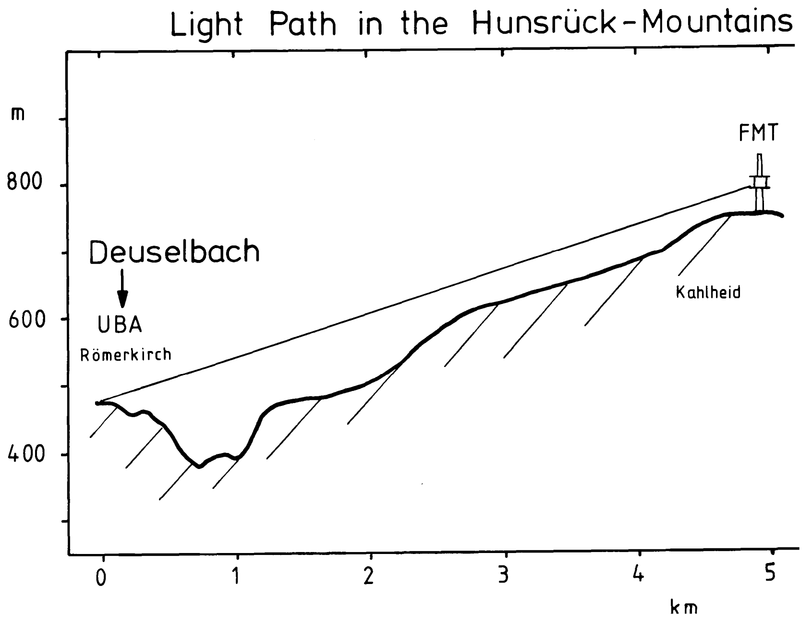
- Sample Applications Active DOAS
- Cavity Enhanced DOAS
- Examples Passive DOAS
- Summary

WINTER COLLEGE ON OPTICS IN ENVIRONMENTAL SCIENCE
2 – 13 February 2009, Triste, Italy

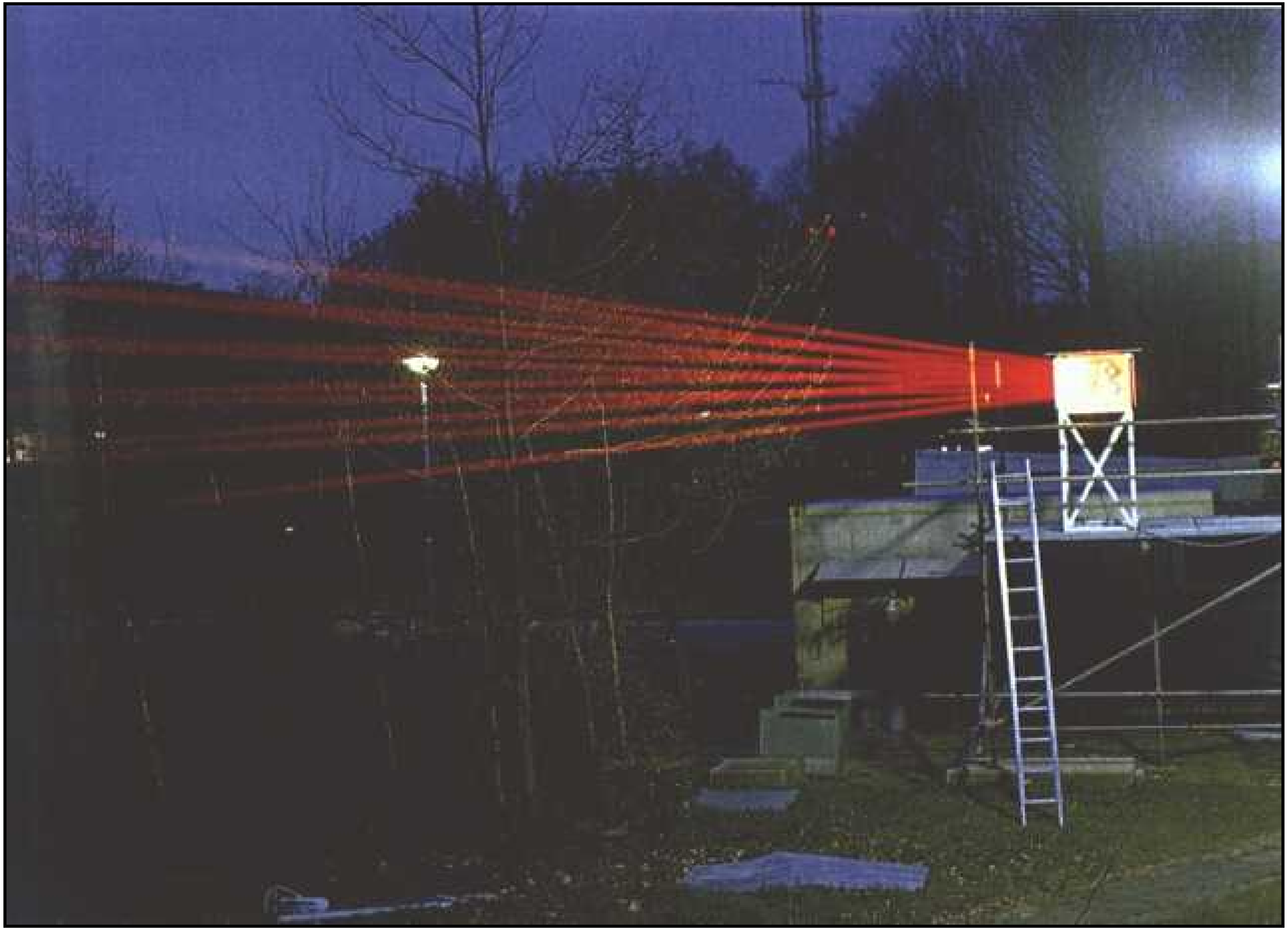
Sample Applications of DOAS ...



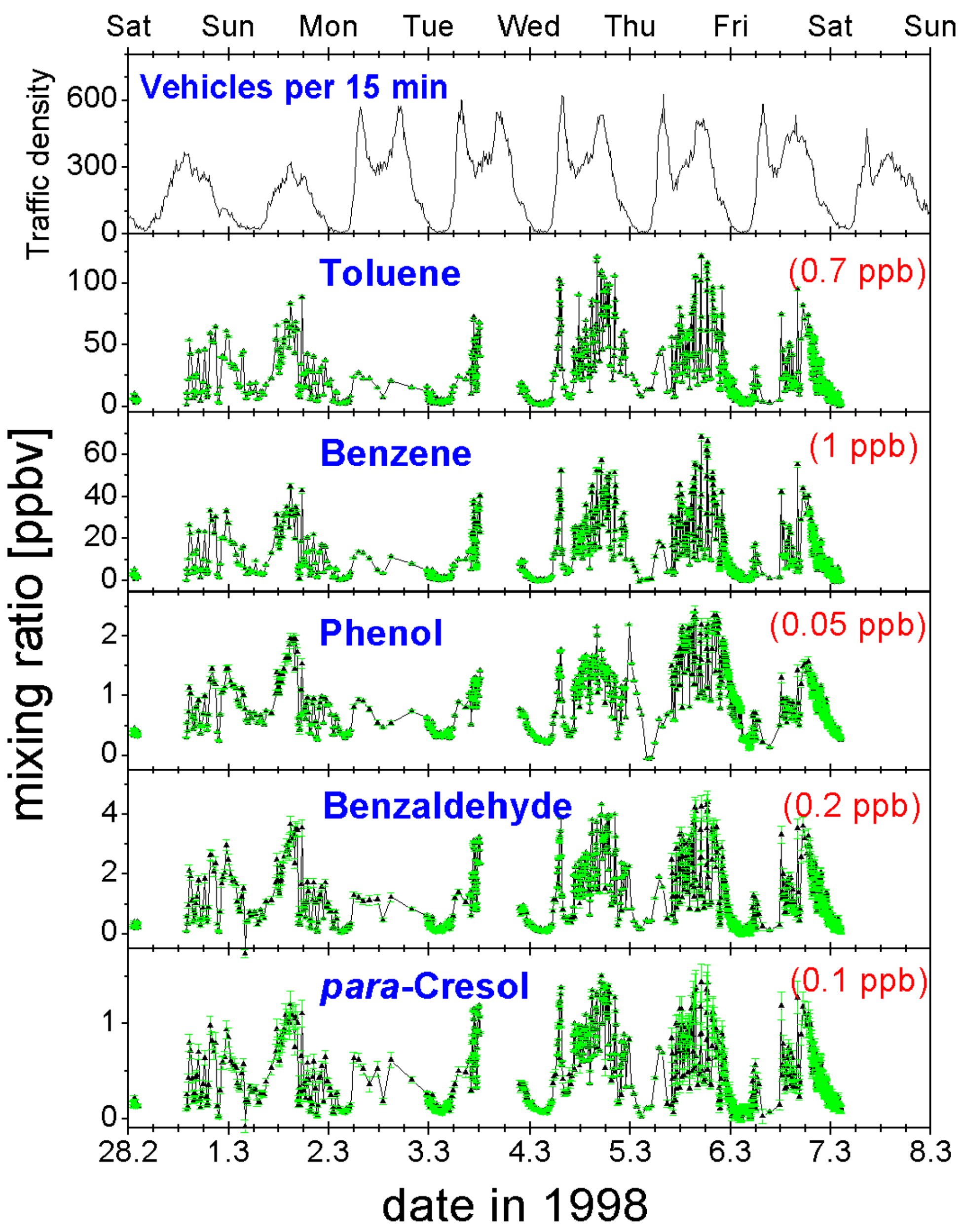




Multi - Reflection Cell (White System)



Multi-Reflection-Cell DOAS Measurements of Aromatic Compounds



In the Kiesberg road traffic tunnel (Wuppertal, Germany) Feb. 28 - March 8, 1998;

Kurtenbach et al. 2002

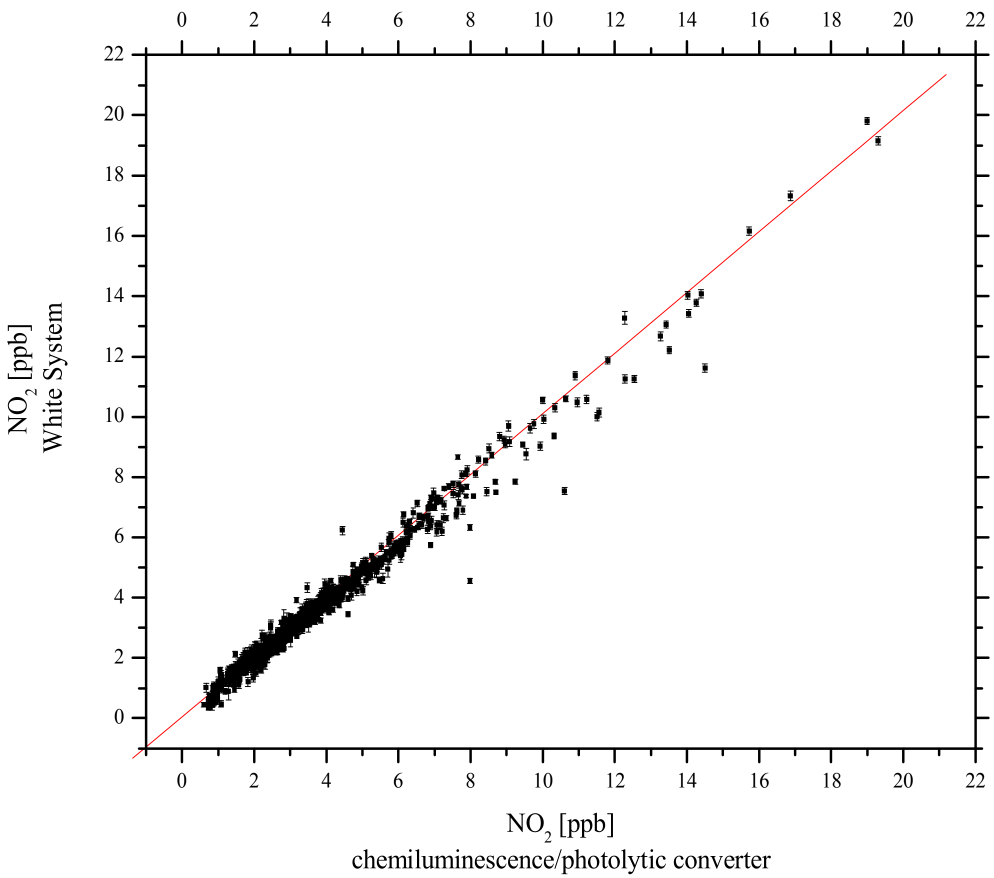
Intercomparisons DOAS - Other Techniques

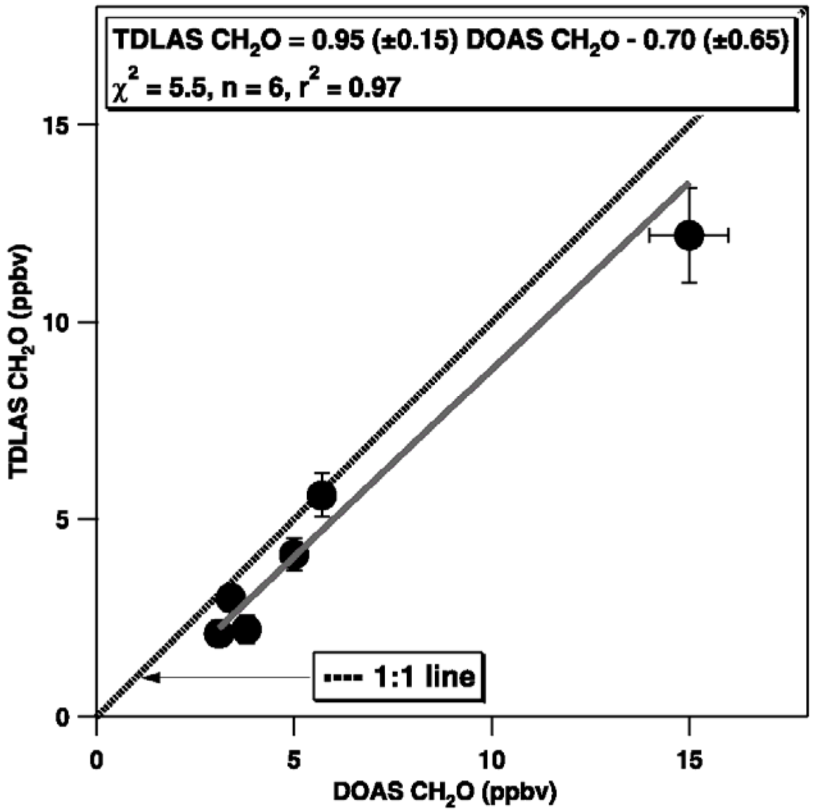
Active DOAS – NO_2 (Open Path Multi – Reflection System) vs. NO_2 – Measurements by Photolytic Converter + Chemoluminescence (BERLIOZ 1998)

Alicke et al., J. Geophys. Res. 108, D4, 8247, doi: 10.1029/2001JD000579 , 2003

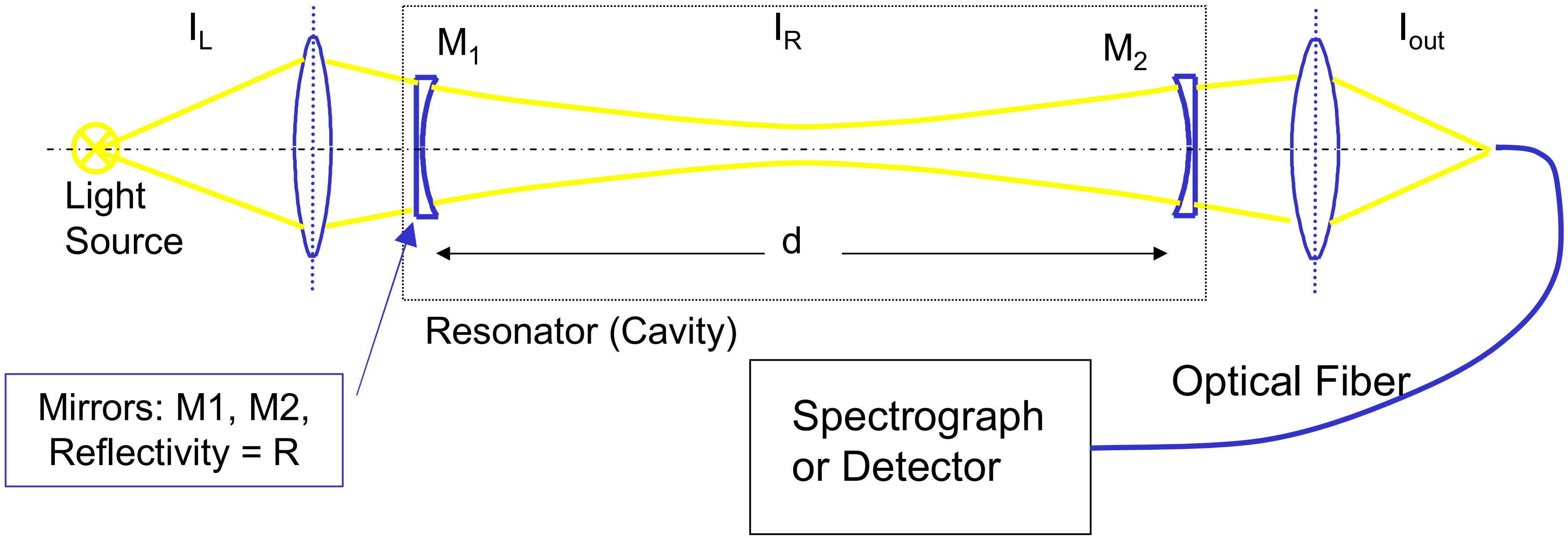
Active DOAS - CH_2O (Long Path) vs. TDLS (aircraft)

Wert et al. J. Geophys. Res. 108, D3, 4104, doi:10.1029/2002JD002502, 2003





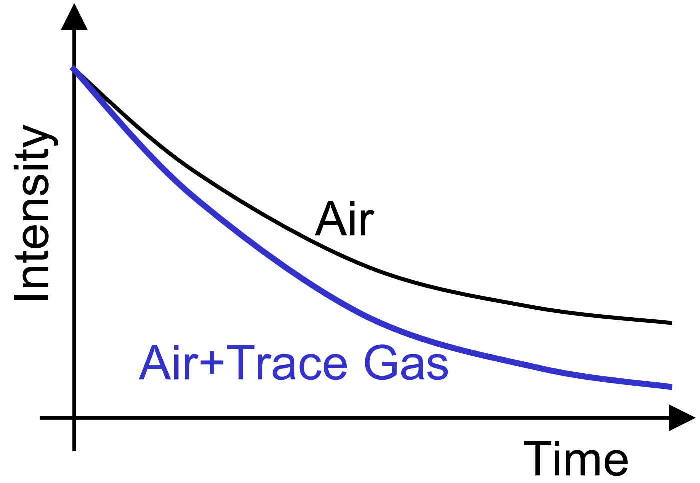
Cavity Ring-Down Spectroscopy (CRDS), Cavity Enhanced Absorption Spectroscopy (CEAS)



$$\text{Optical Path}: \ \bar{L} = n \cdot d = d \cdot \frac{1}{1-R} \quad \text{since} \quad n = \frac{1}{1-R}$$

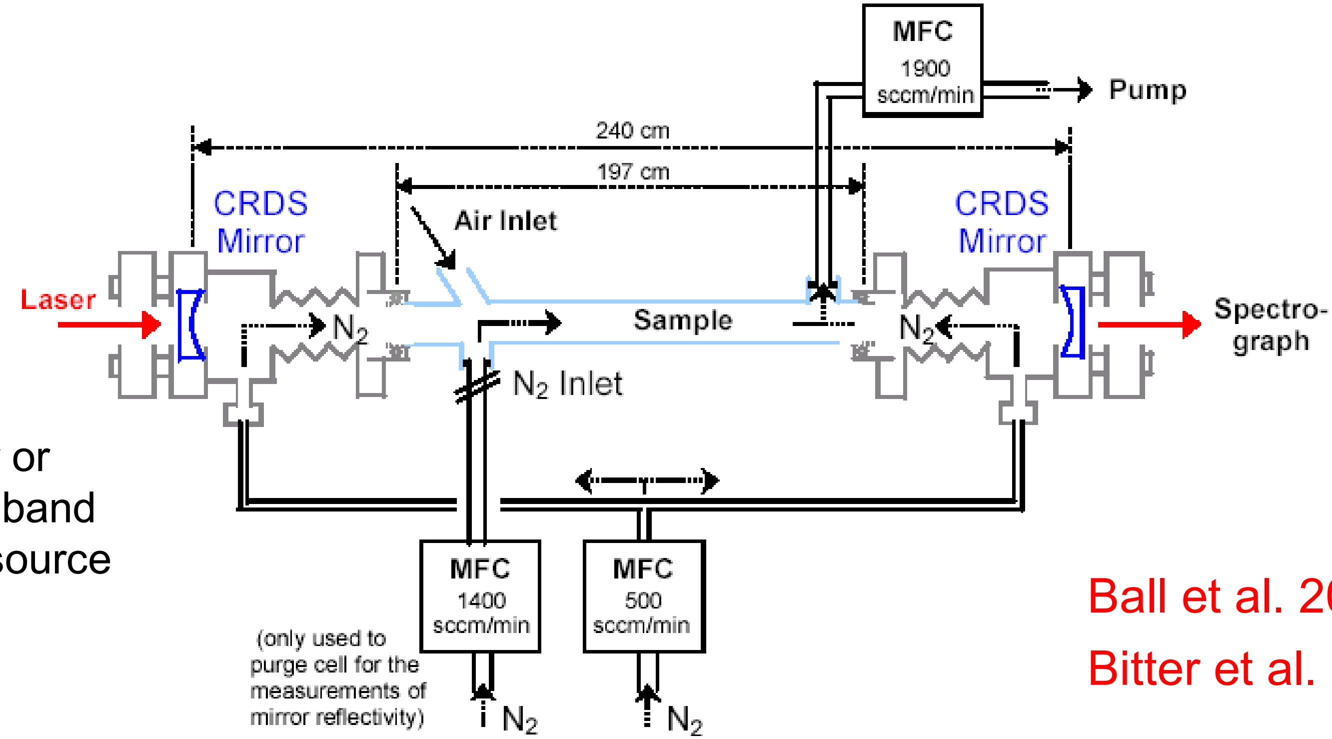
$$\text{Example}: \quad \bar{L} = \frac{1\text{m}}{1-0.99999} = 10\,\text{km}$$

$$\text{Continuous Input}: \ I_{out} = I_L \cdot \frac{(1-R)}{2} \approx 5 \cdot 10^{-6} \cdot I_L$$



Cavity Ring-Down Spectroscopy (CRDS), Cavity Enhanced Absorption Spectroscopy (CEAS)

The idea: Use high finess optical cavity to provide long light path (kilometres) in a small volume)



Laser or broadband light source

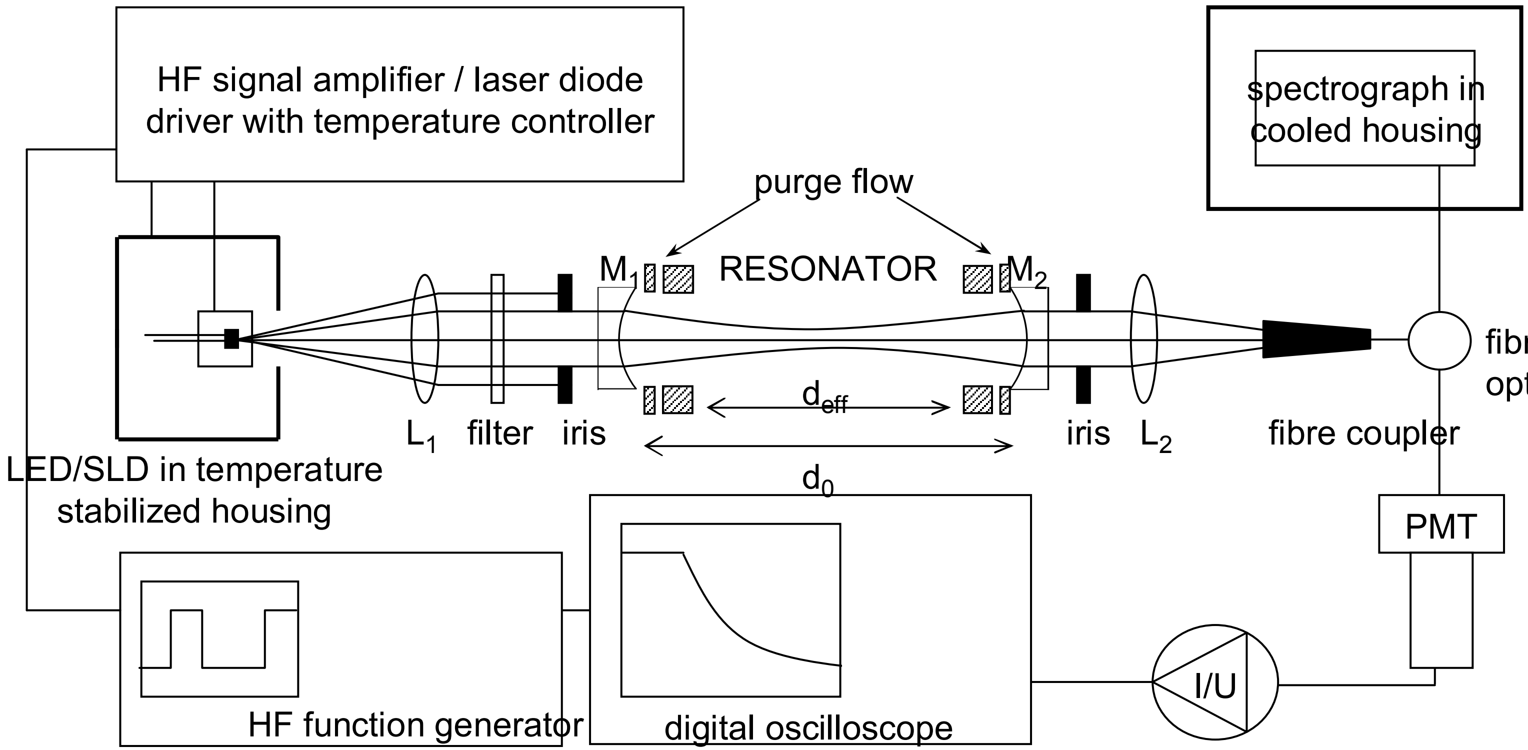
Ball et al. 2001

Bitter et al. 2005

CRDS: Determine monochromatic absorbance by ringdown time

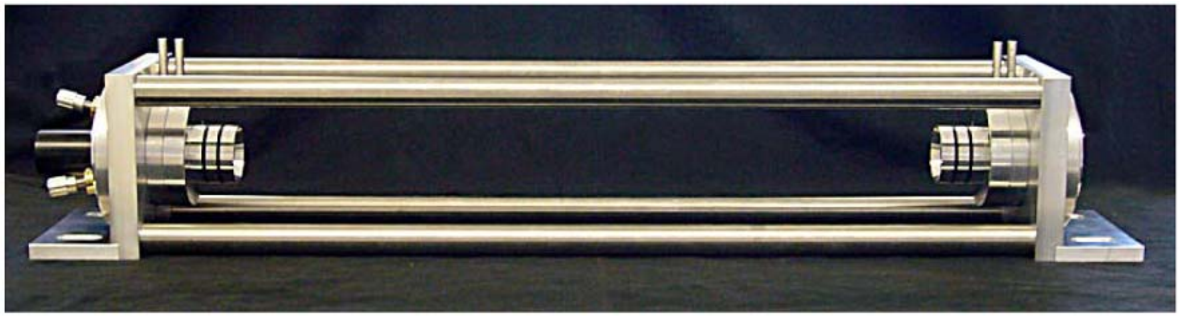
CEAS: Determine absorption using DOAS technology

Heidelberg CD-DOAS Instrument



Base path: $d \approx 0.5m$ $\rho \approx 10^{-5}$ (R ≈ 99.998%)

Meinen et al. 2008



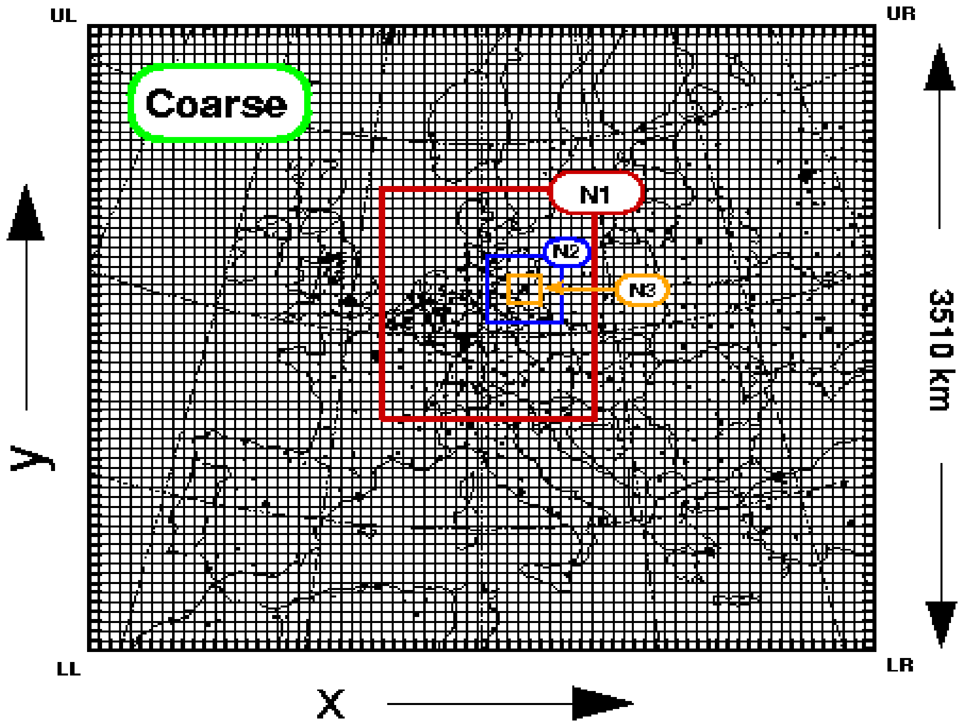
Spatially Resolved Measurements Why and How?

Option	Advantages	Problem(s)
Many (10^3 – 10^5) instruments	true in-situ measurements	Technology must be developed (cheap mini x-meter?)
LIDAR	proven spatial resolution for some species	Combination of spatial resolution and sufficient sensitivity problematic Expensive solution
Spectroscopy	High sensitivity Relatively cheap solution (depending on technique)	Daytime only (passive techniques) Limited spatial resolution

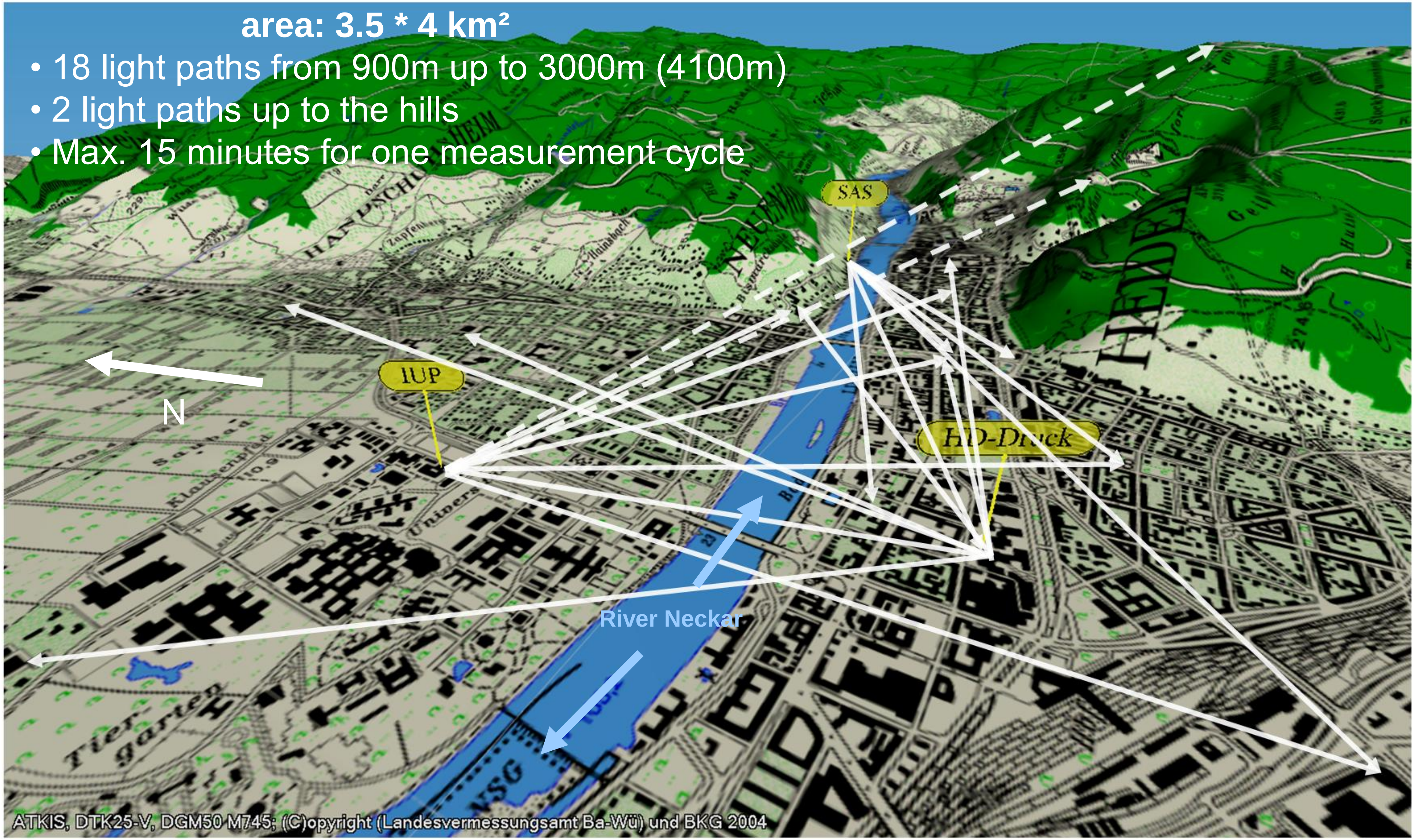
Example:

EURAD-Model during BERLIOZ

75 x 55 = 3850 grid points (coarse grid)



Tomographic Measurement Geometry in Heidelberg



The Principle of Tomography

Reconstruct 2D image from series of 1D projections
(i.e. of column densities)

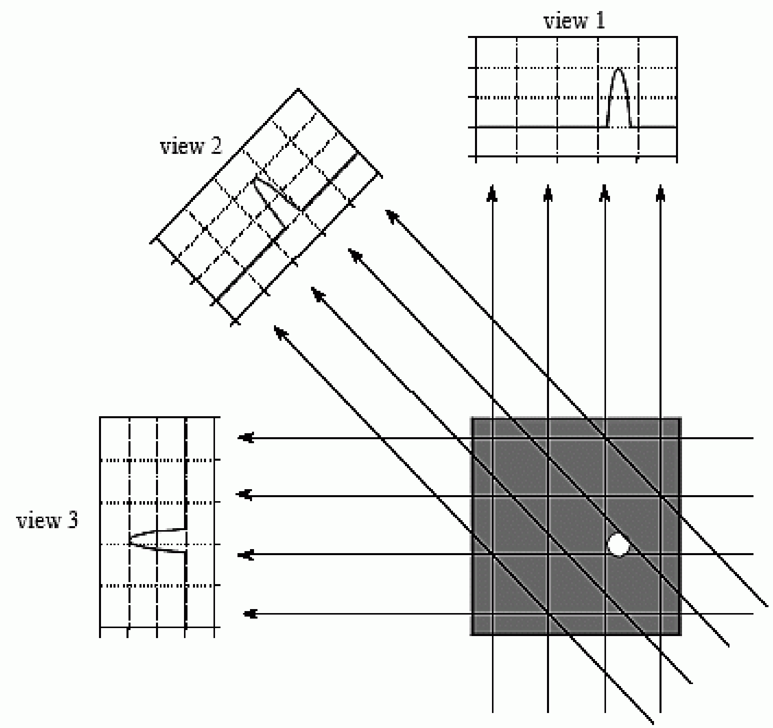


FIGURE 25-15
CT views. Computed tomography acquires a set of views and then reconstructs the corresponding image. Each sample in a view is equal to the sum of the image values along the ray that points to that sample. In this example, the image is a small pillbox surrounded by zeros. While only three views are shown here, a typical CT scan uses hundreds of views at slightly different angles.

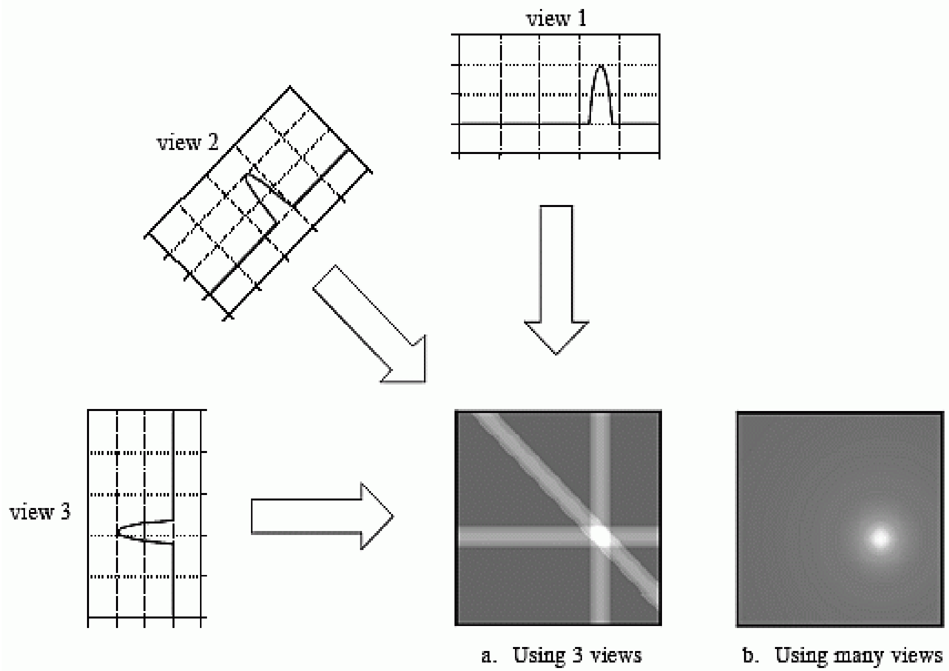
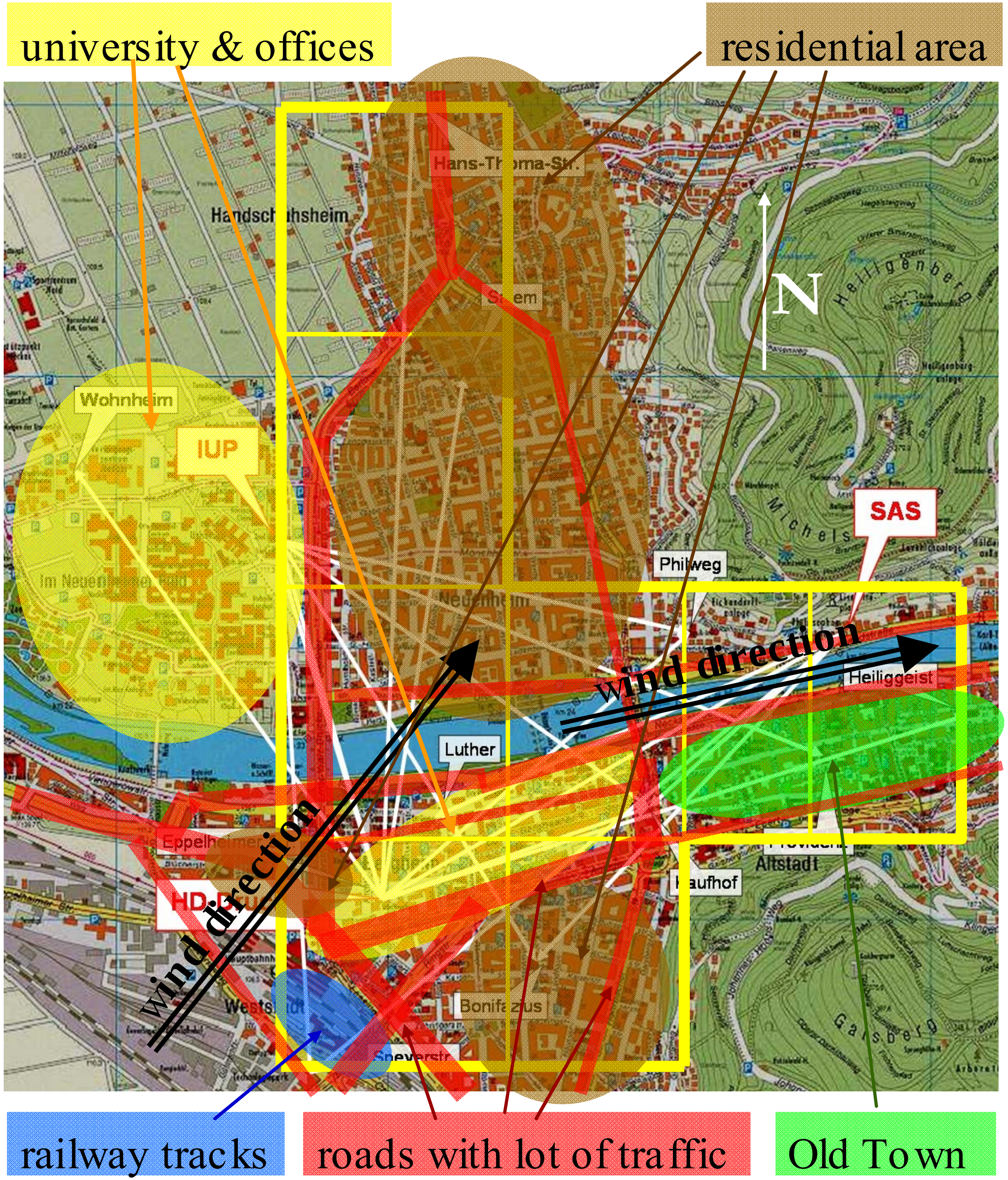


FIGURE 25-16
Backprojection. Backprojection reconstructs an image by taking each view and *smearing* it along the path it was originally acquired. The resulting image is a blurry version of the correct image.

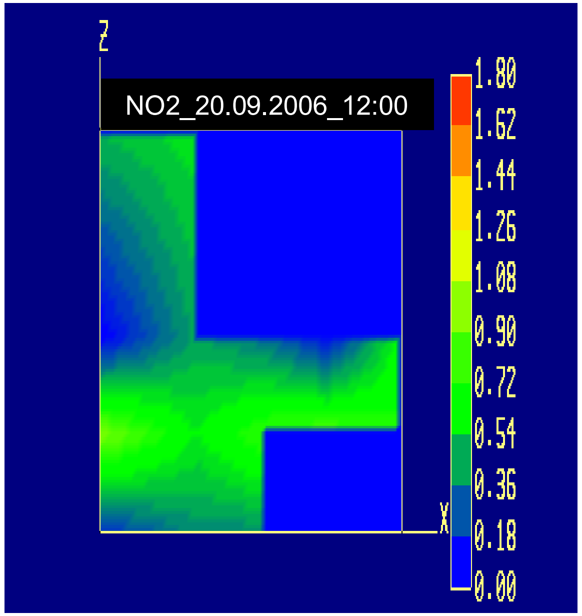
NO_2 and SO_2 Sources in Heidelberg

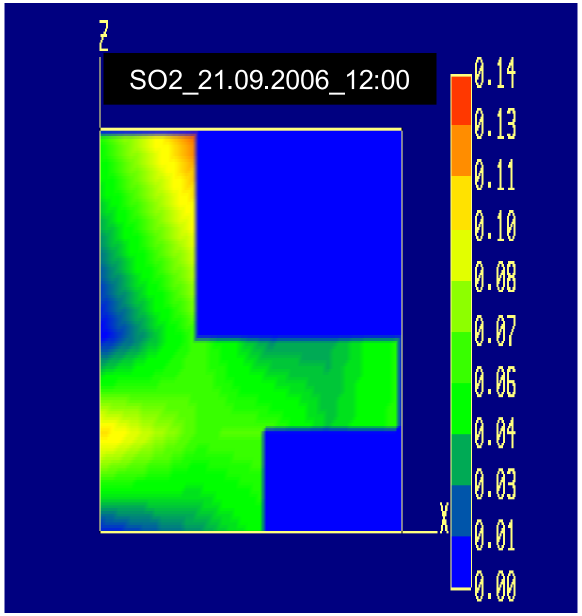
D. Pöhler, I. Pundt
K.U. Mettendorf

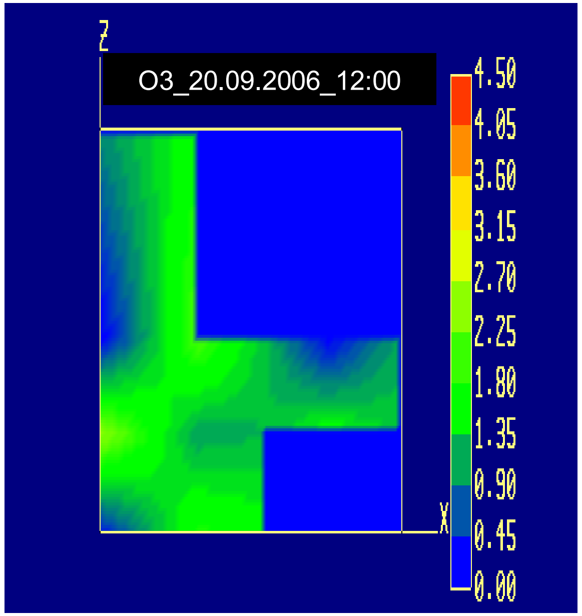


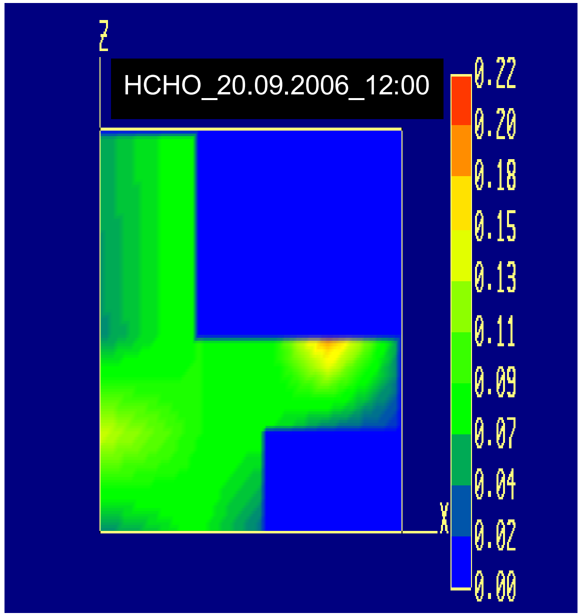
2D-Reconstructions in Heidelberg, Sept. 20, 2006; 3h Averages

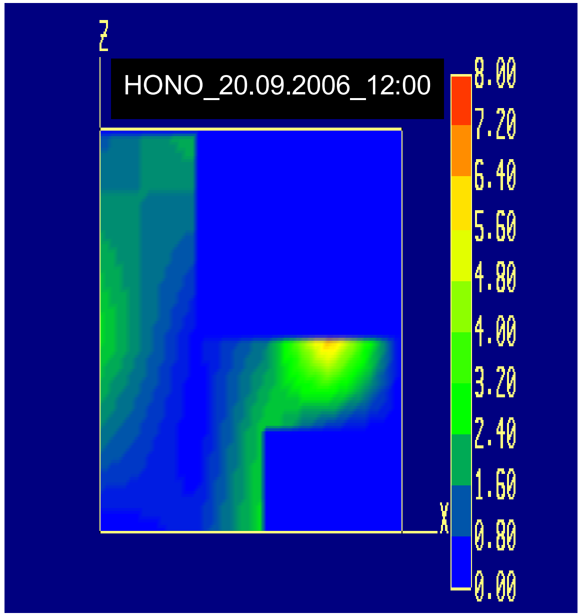
1 unit = $5 \cdot 10^{11}$ Molecules / cm^3
$\approx$ 19 ppbv





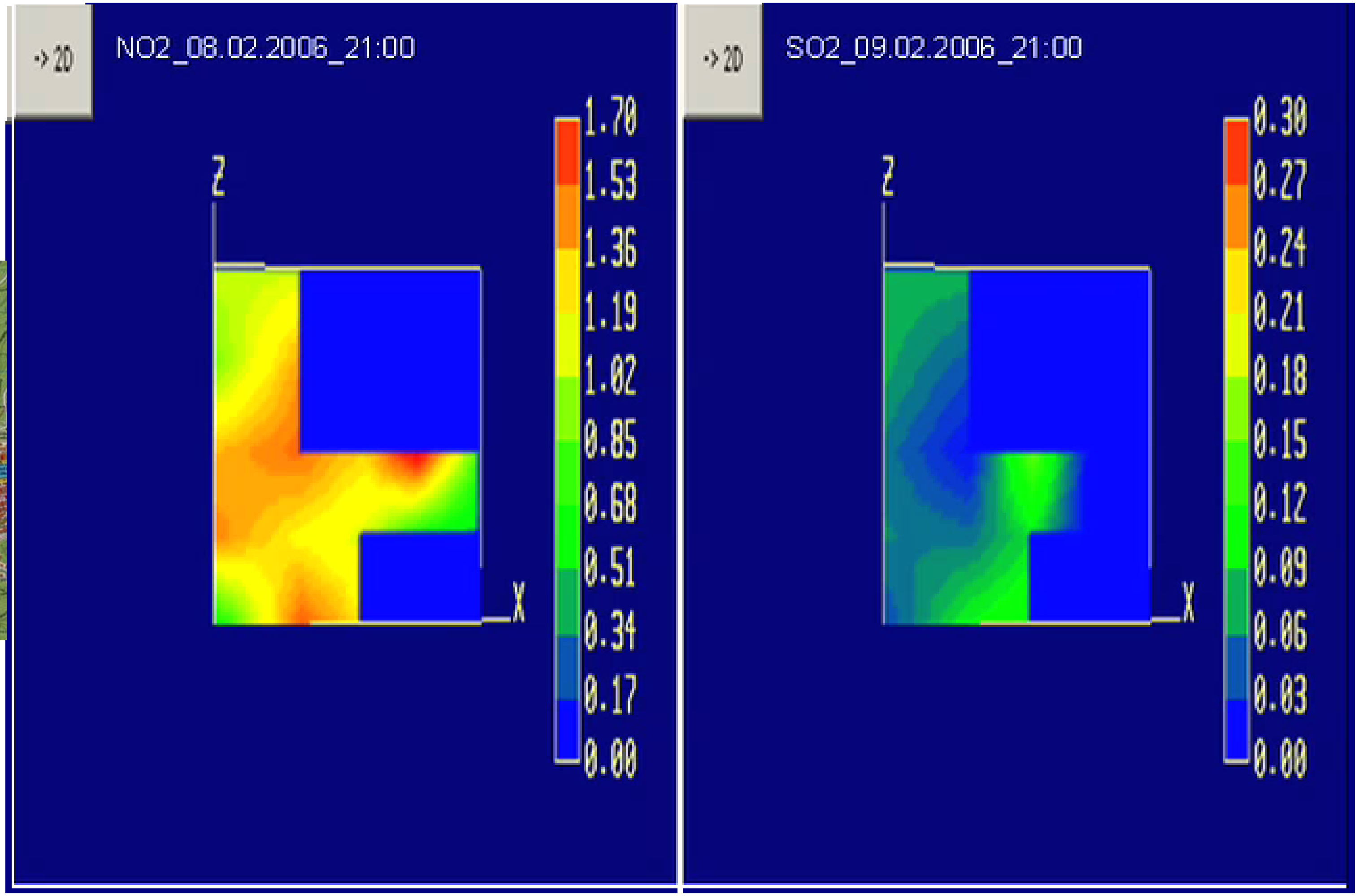






2D Reconstructions: Feb. 8 – Feb. 9, 2006; 3 hour Averages

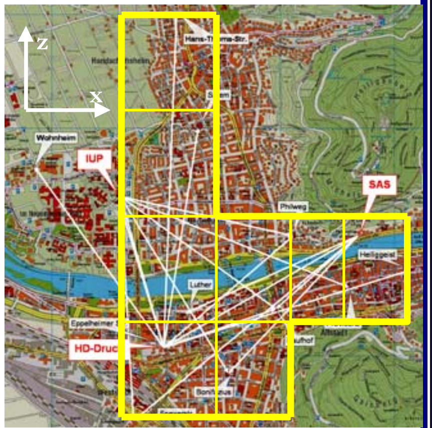
movie

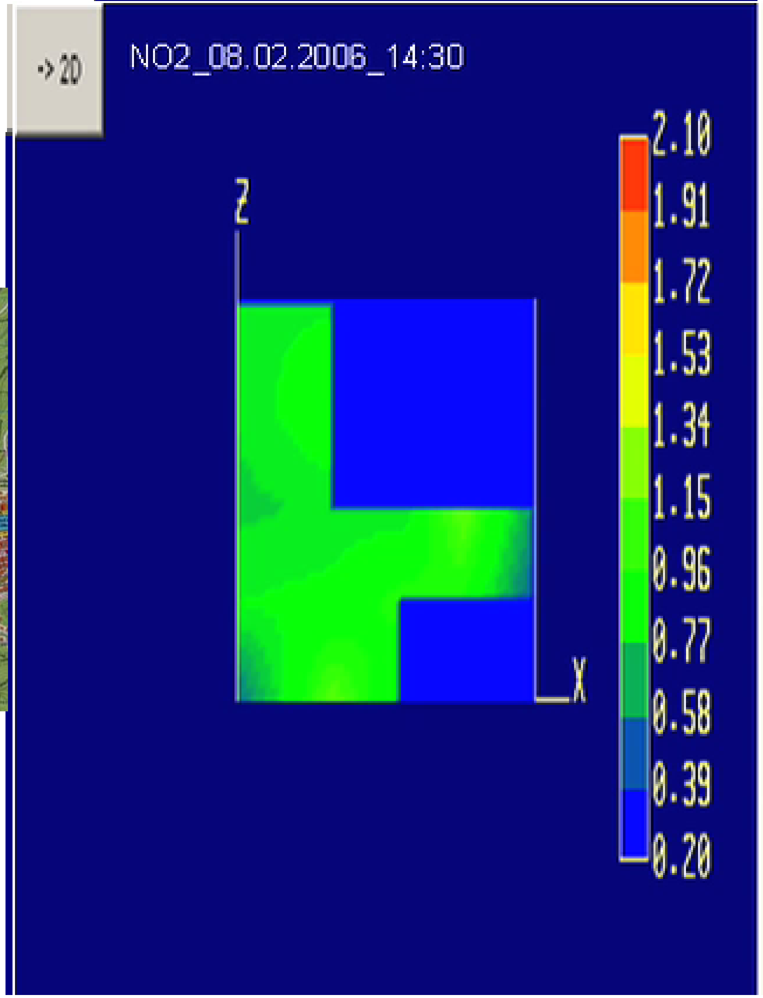


1 unit = $5 \cdot 10^{11}$ Molecules / $cm^3 \approx$ 19 ppbv

2D Reconstructions: Feb. 8 – Feb. 9, 2006; 30 min. Averages

movie

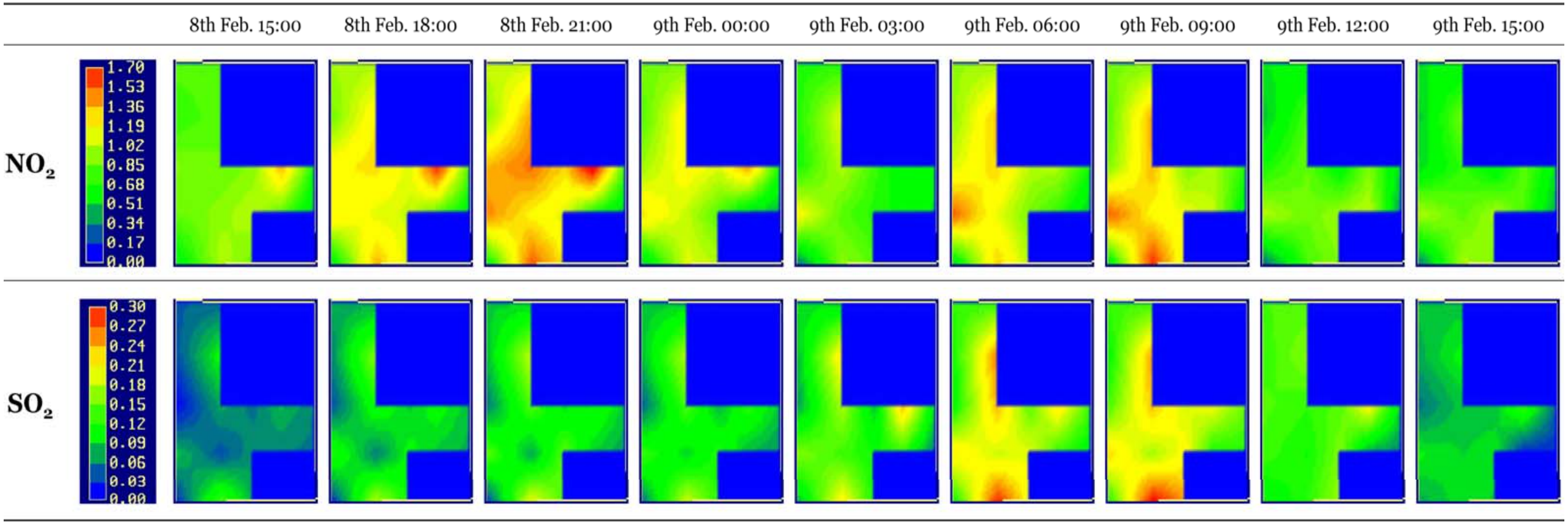


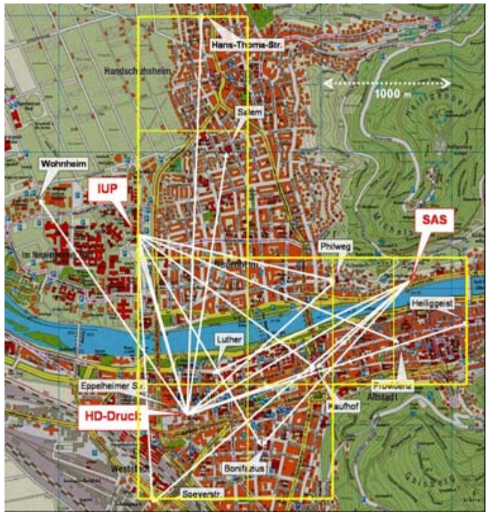


1 unit = $5 \cdot 10^{11}$ Molecules / $cm^3 \approx 19$ ppbv

Time Series (3 hour avg.) of Tomographic DOAS Measurements of NO_2 and SO_2 in Heidelberg, 2006

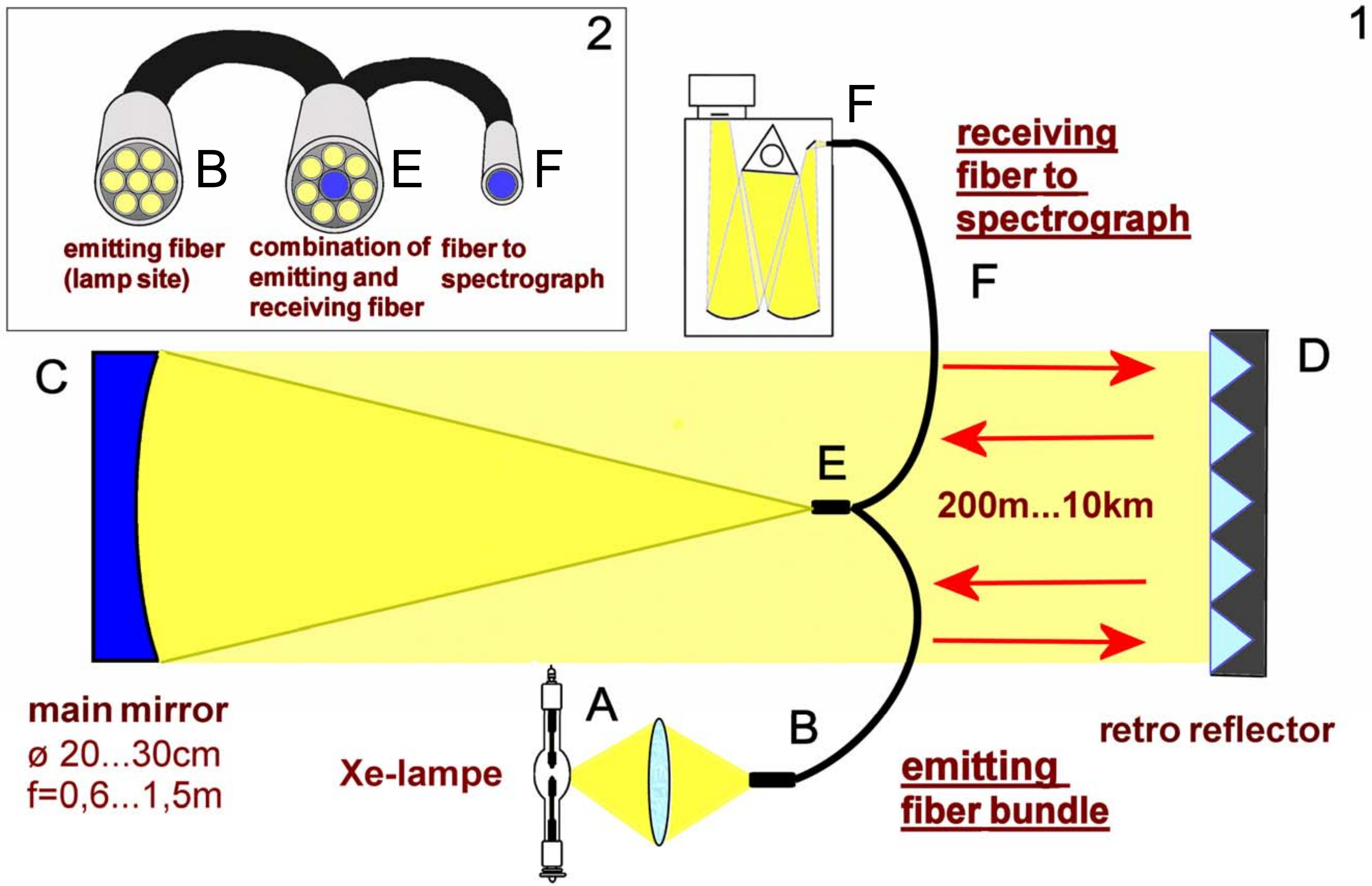
D. Pöhler, I. Pundt K.U. Mettendorf





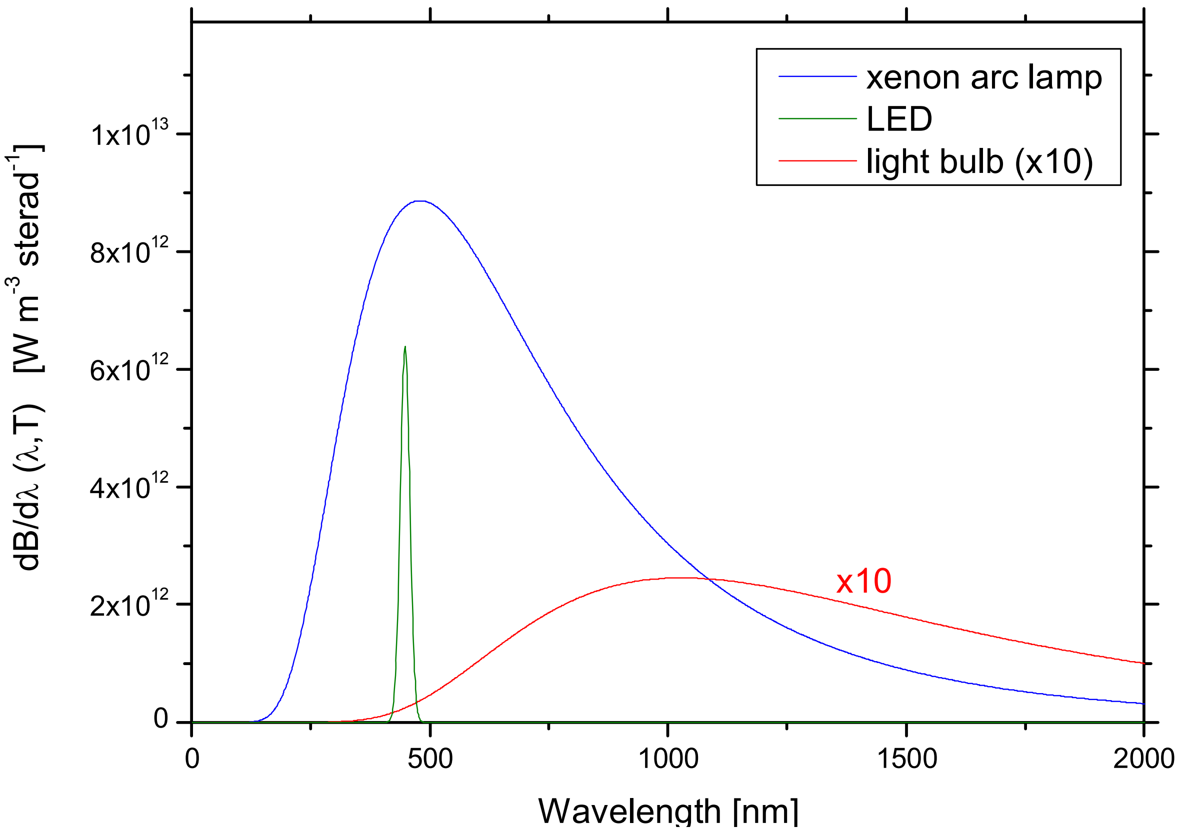
Institut für Umweltphysik

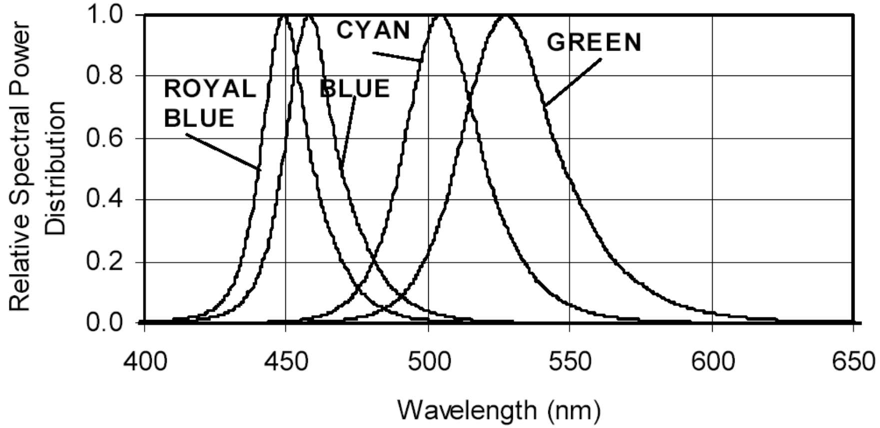
Modern Design of an Active DOAS Instrument



Tschritter 2007,
Merten 2008,
Merten et al. 2009

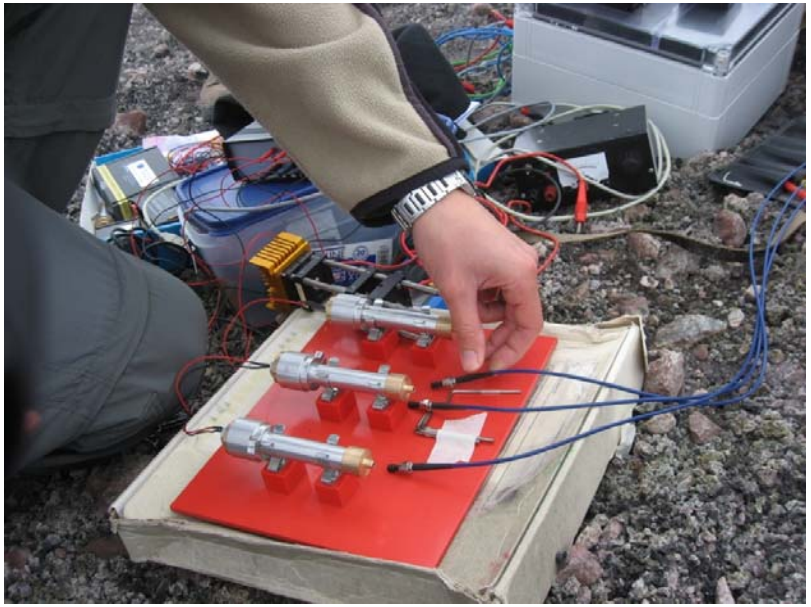
Different Light Sources for DOAS

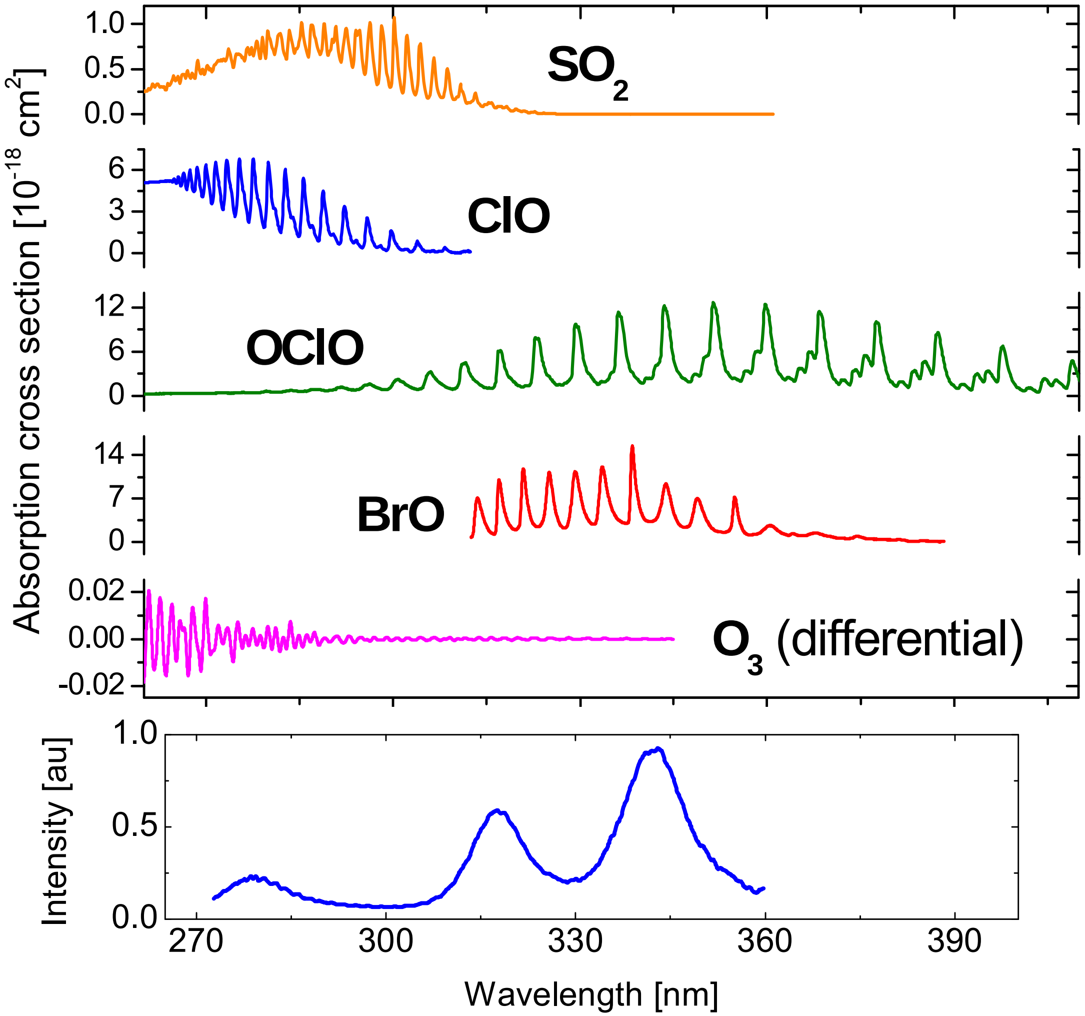




Christoph Kern

Light Emitting Diodes as Active DOAS Light Sources





LED 1 LED 2 LED 3

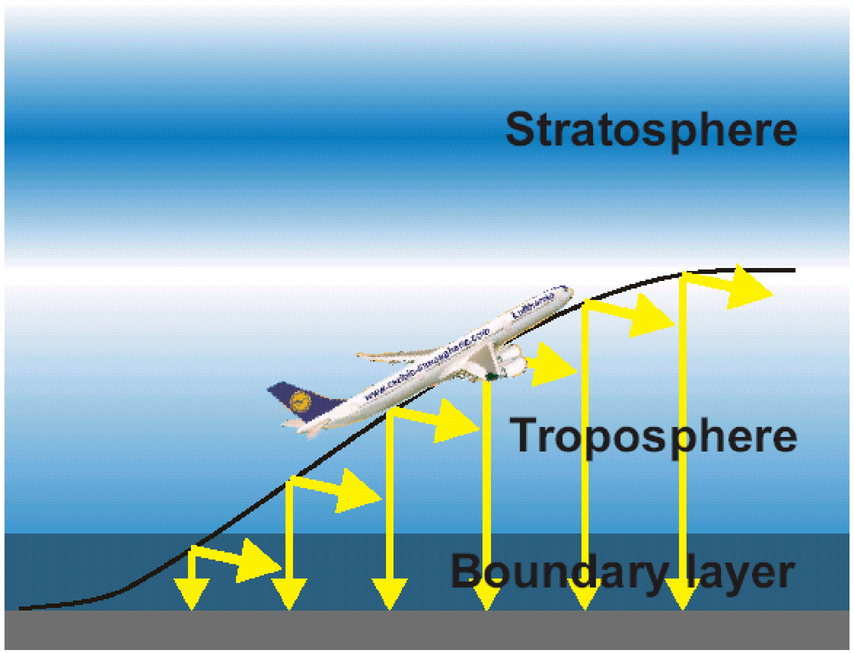
Muli-LED Set-up for simultaneous measurement of ClO, OClO, BrO, SO_2, O_3

Airborne Multi AXis DOAS (AMAX-DOAS)

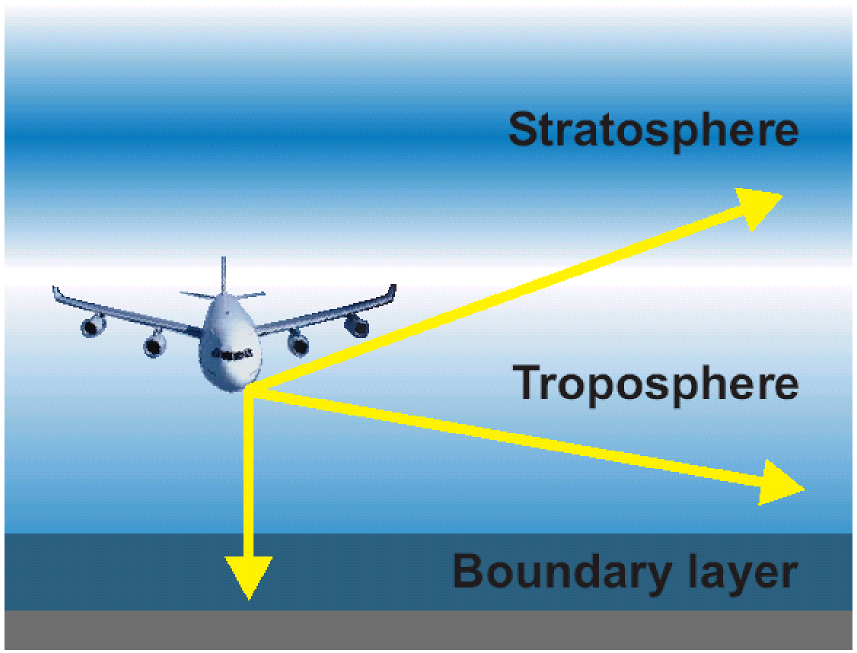
1) DLR Falcon: SCIAMACHY Validation, 10 viewing angles, 2 spectrometers (UV, vis.)

2) Lufthansa Airbus A340-600, CARIBIC experiment 3 viewing angles, 3 spectrometers (UV), 2004 - 2014

Vertical profile measurements during ascent and descent



Measurement of stratospheric, free tropospheric and total tropospheric column at cruise altitude



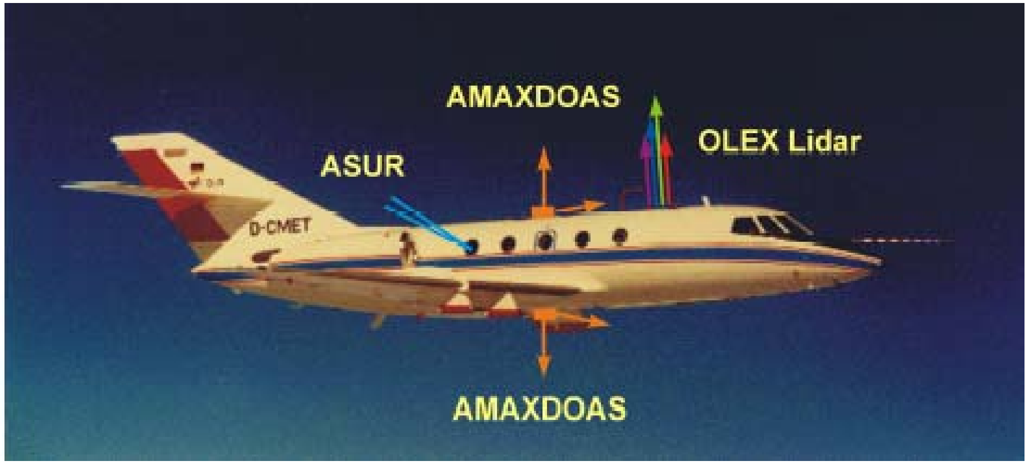
AMAX-DOAS Measurement of the NO_2 Distribution

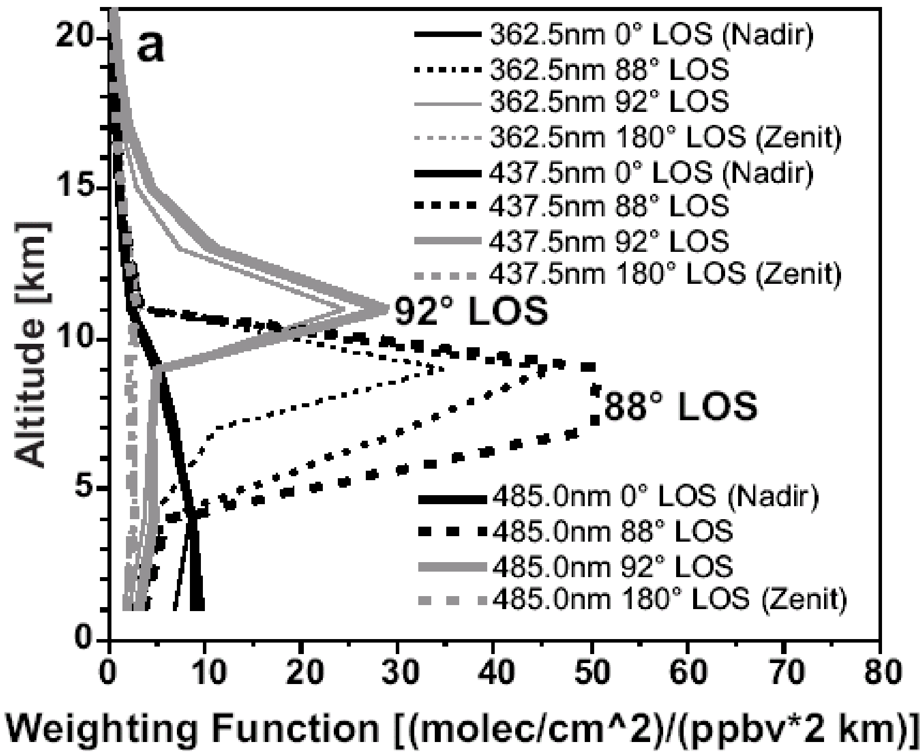
Bruns et al. ACP, 2005

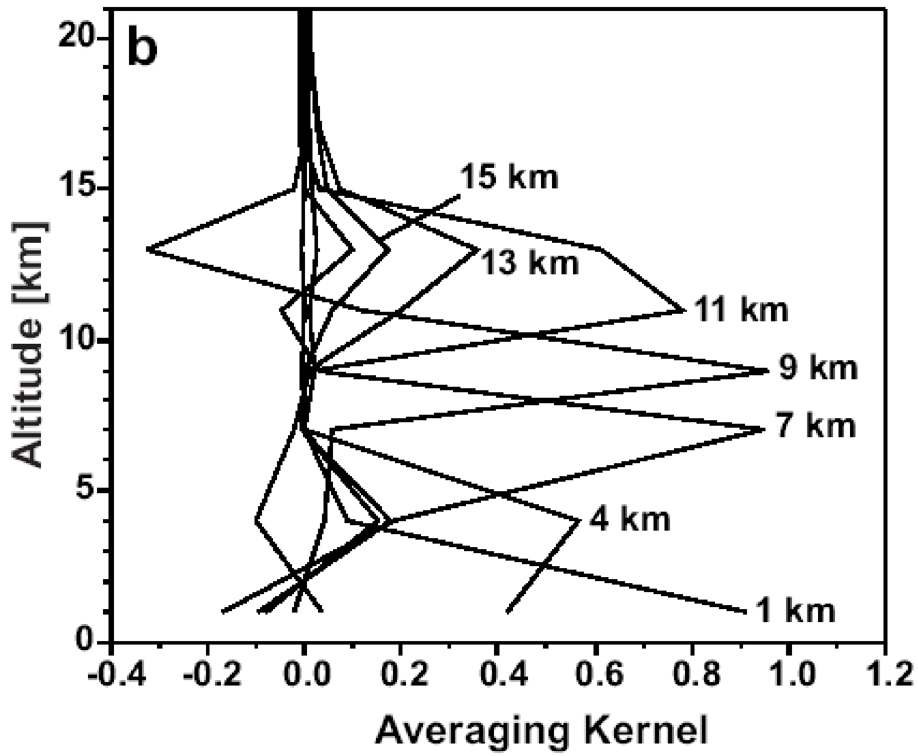
Falcon (DLR)

Total of 4 Observation directions:

0° (nadir)
88° forward, slightly up
92°,forward, slightly down,
180° zenith







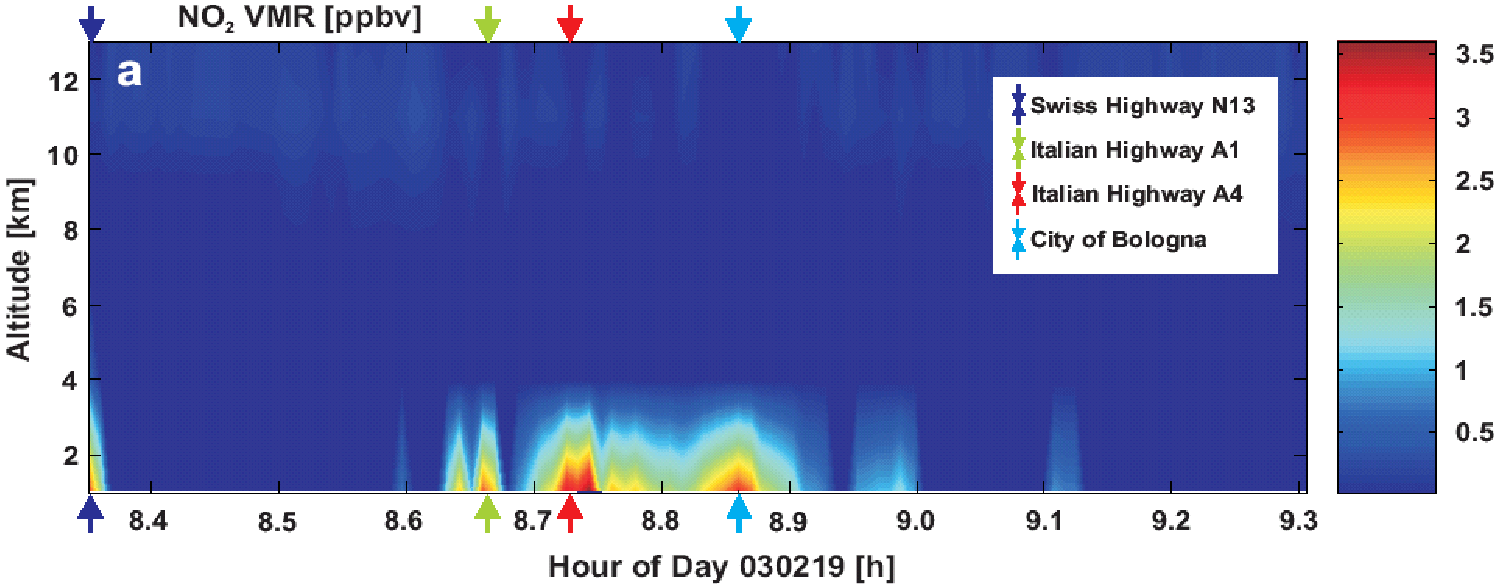
AMAX-DOAS Measurement of the NO_2 Distribution

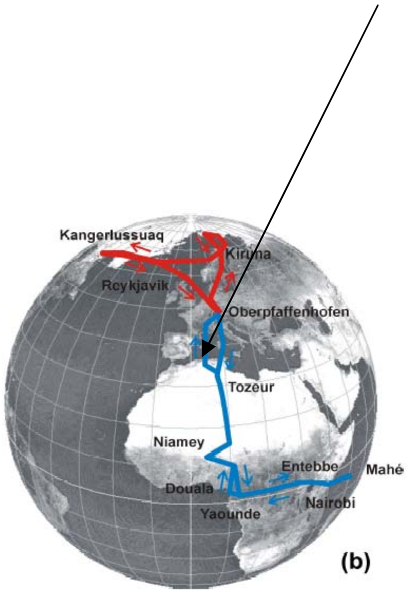
Feb. 19, 2003, Basel, Switzerland – Tozeur, Tunesia

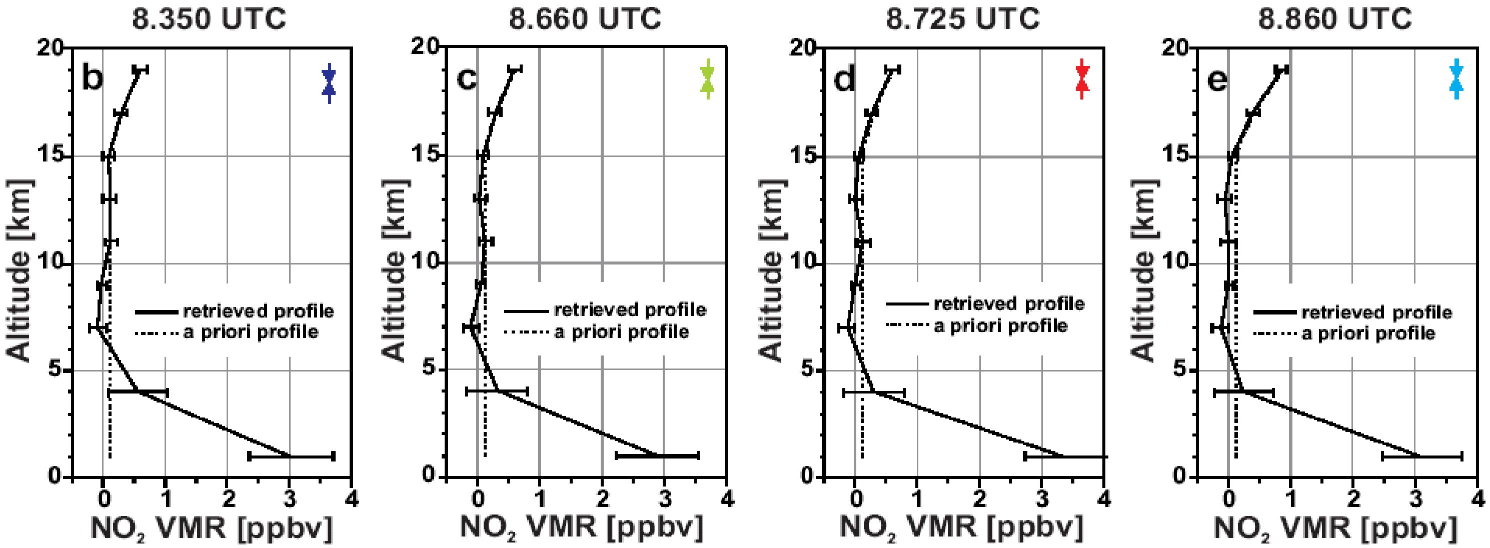
Bruns et al. ACP
6, 3049, 2006

Heue et al. ACP
5, 1039, 2005

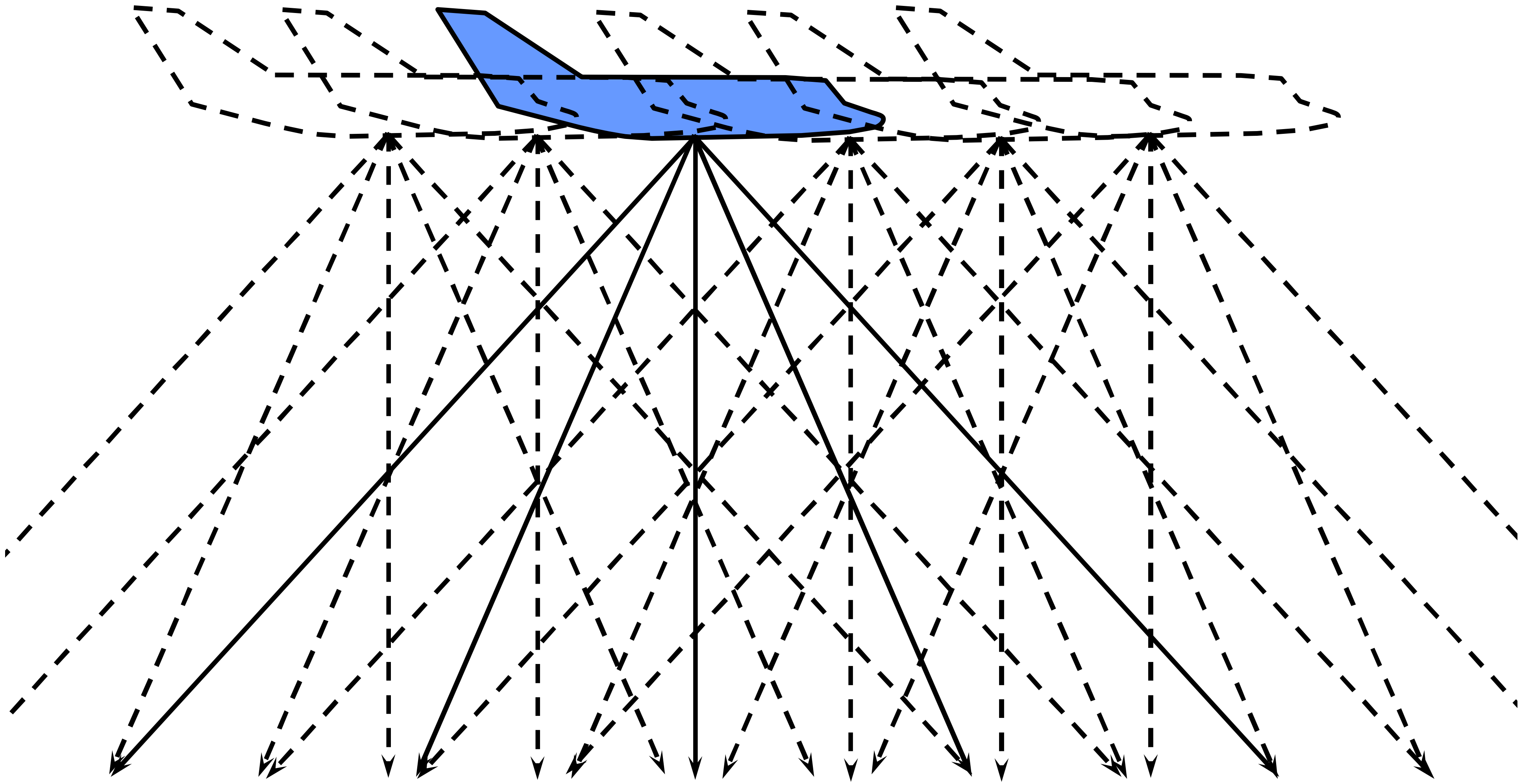
Wang et al. ACP
5, 337, 2005



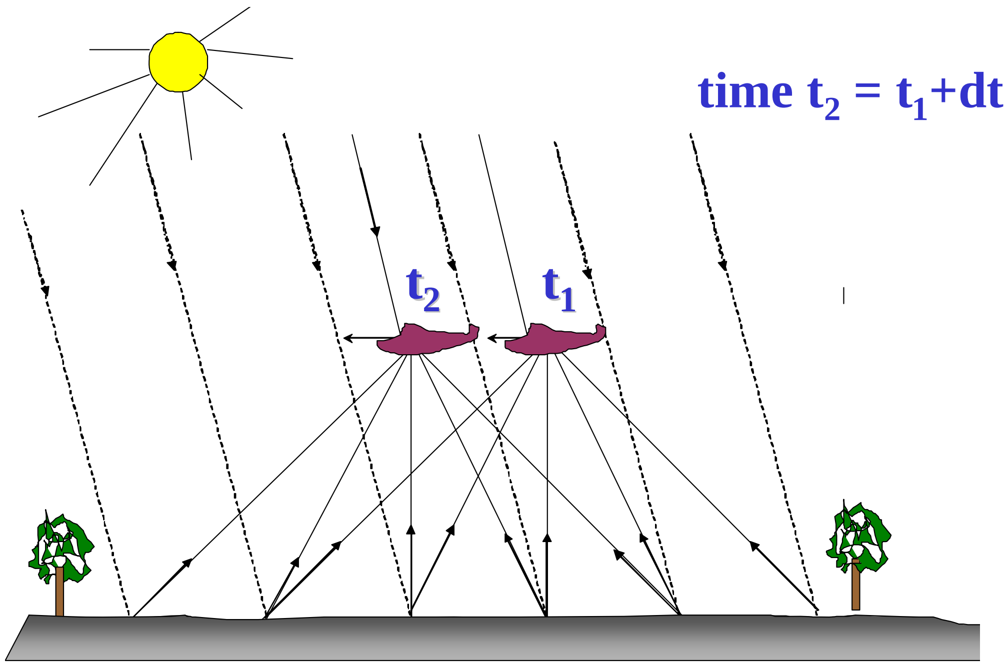




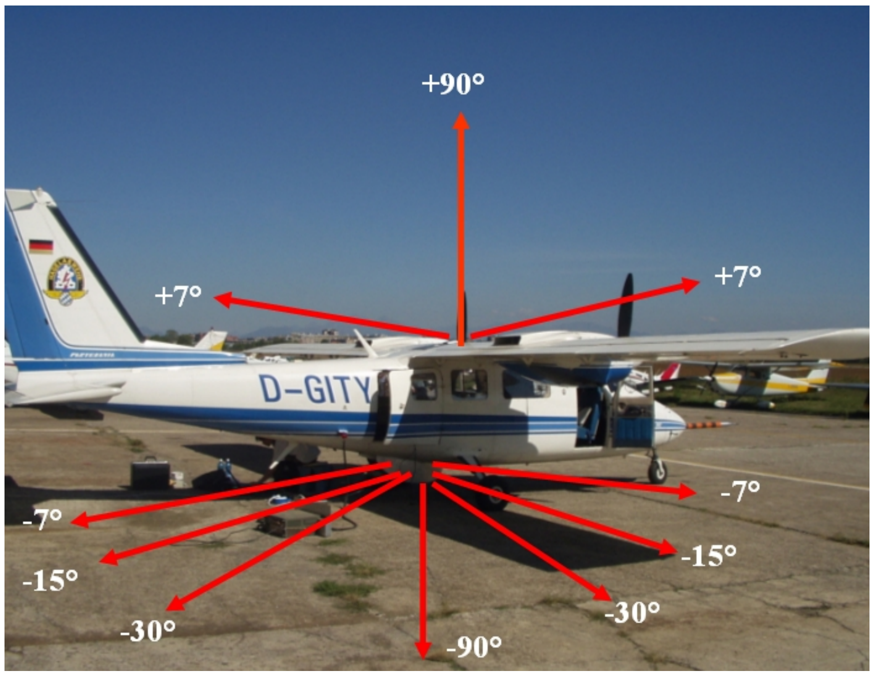
2D – Tomography with AMAX - DOAS

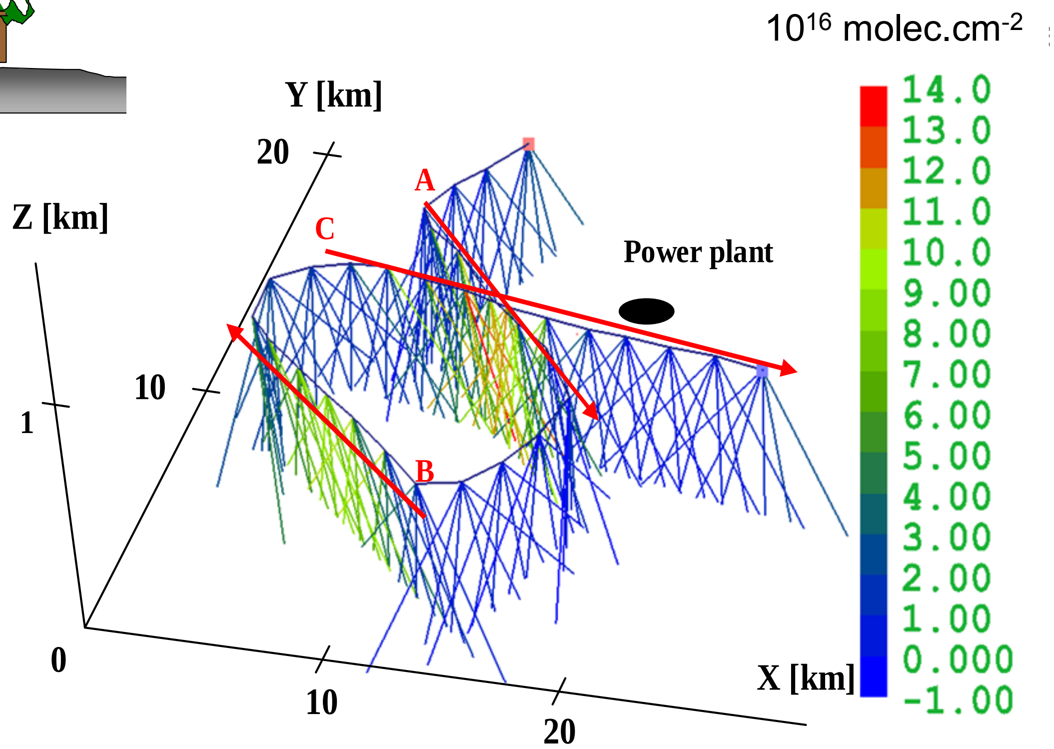


Tomographic AMAX-DOAS Measurement of Trace-Gas Distributions

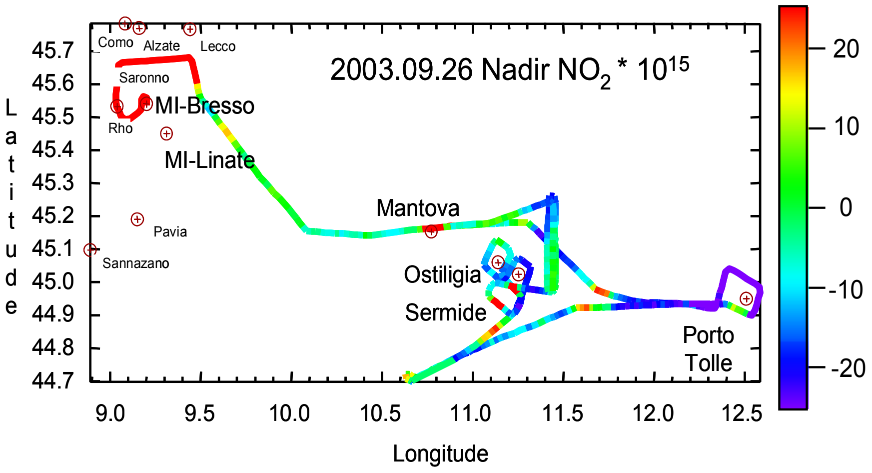


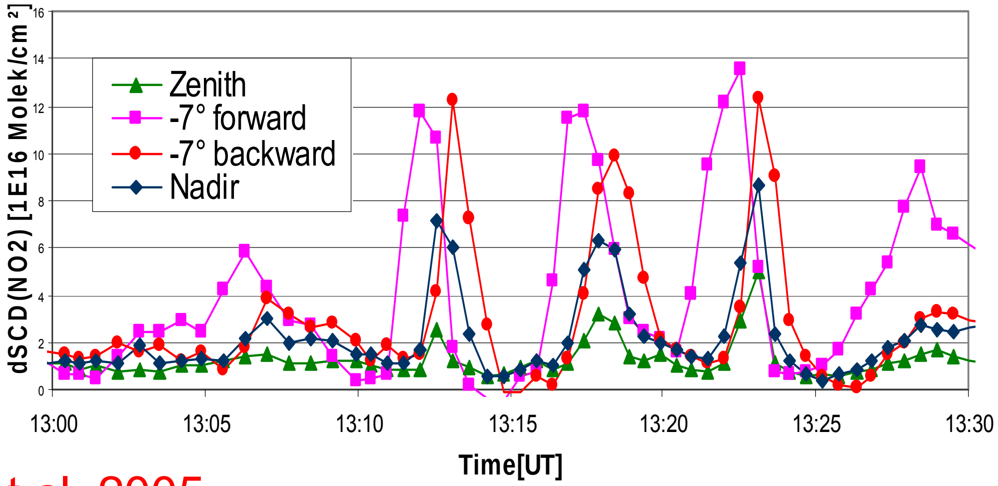
Example: NO_2 at Sermide Power Plant (Milano, Italy) 26. Sept. 2003,
Pundt et al. 2005





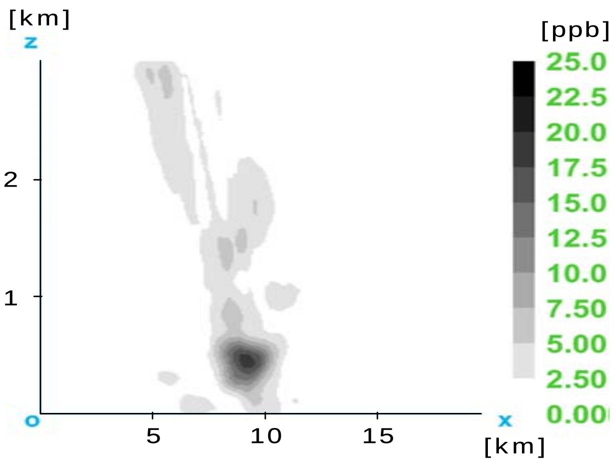
Tomographic AMAX-DOAS Measurement of NO_2 Distributions at Sermide Power Plant (Milano, Italy) 26. Sept. 2003



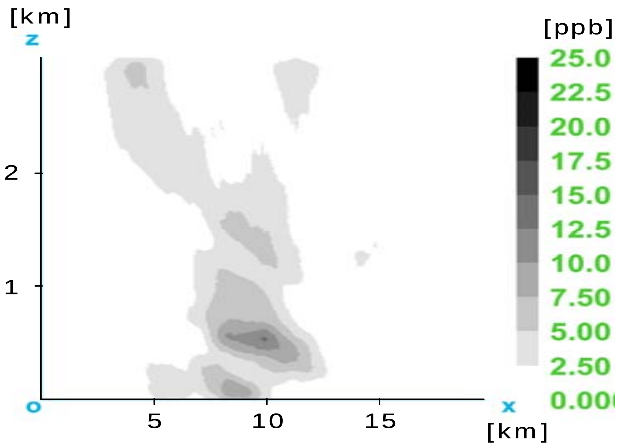


Pundt et al. 2005

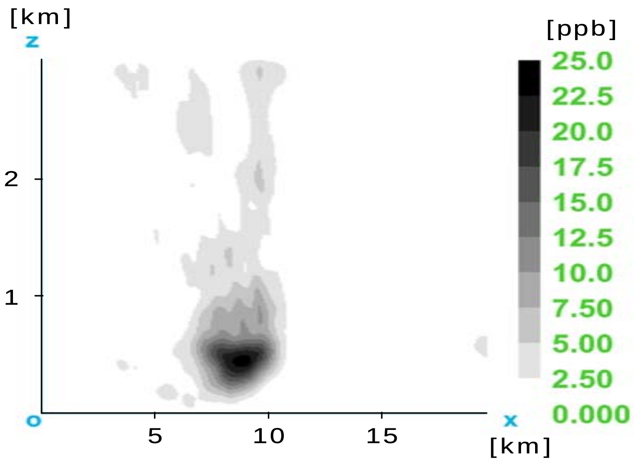
1st overflight



2nd overflight

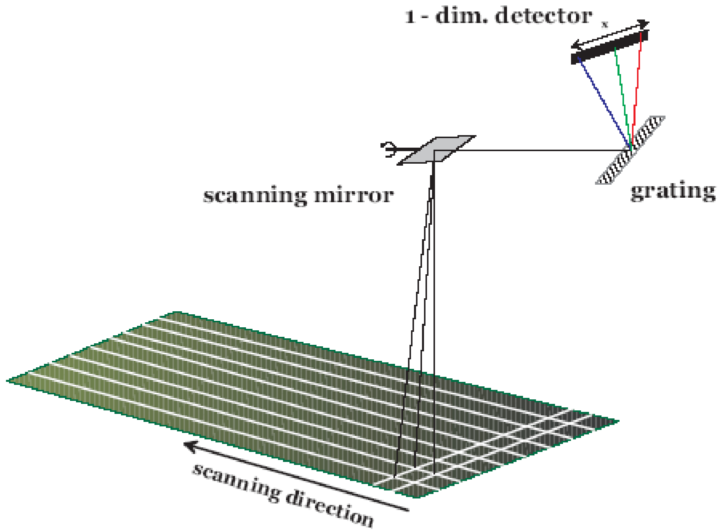


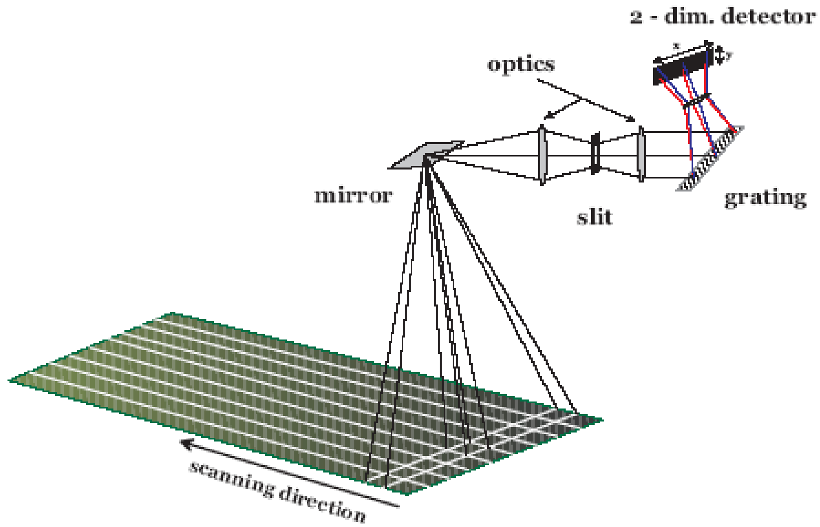
3rd overflight



3) (Passive) Imaging Spectroscopy

1) Scanning: Whiskbroom (one pixel at a time) ↔ 2) Pushbroom techniques (column of pixels at once)

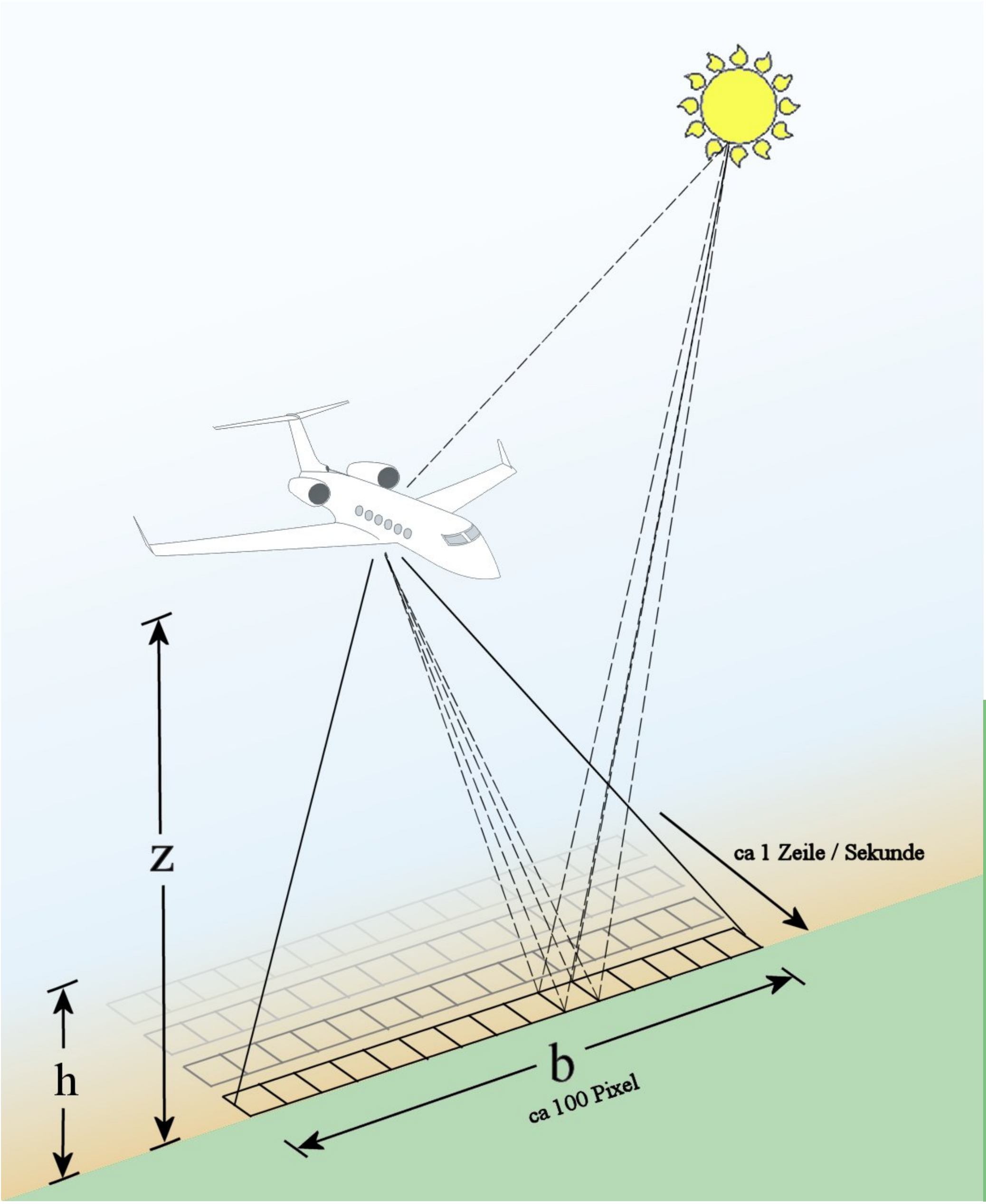




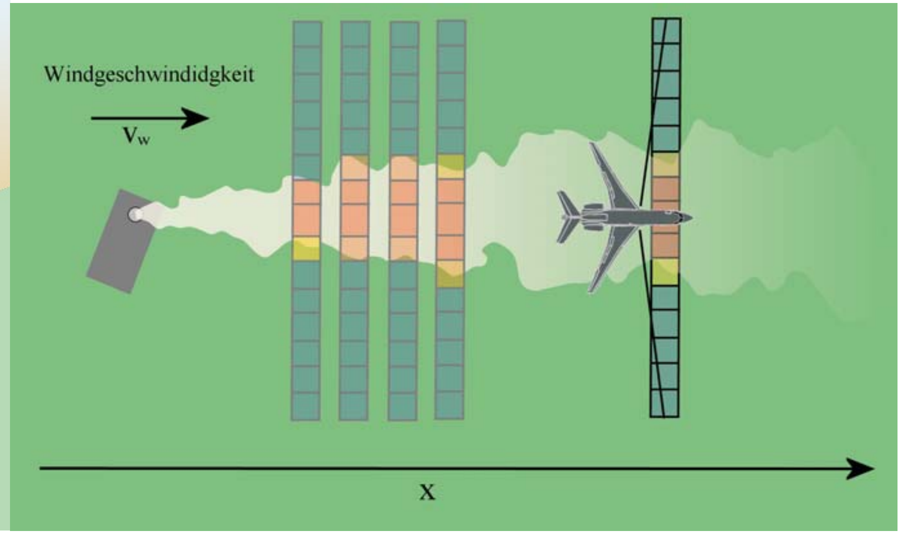
3) Full 2D Techniques (whole image at once):

- Imaging Fourier-Transformation Spectroscopy
- Gas Correlation

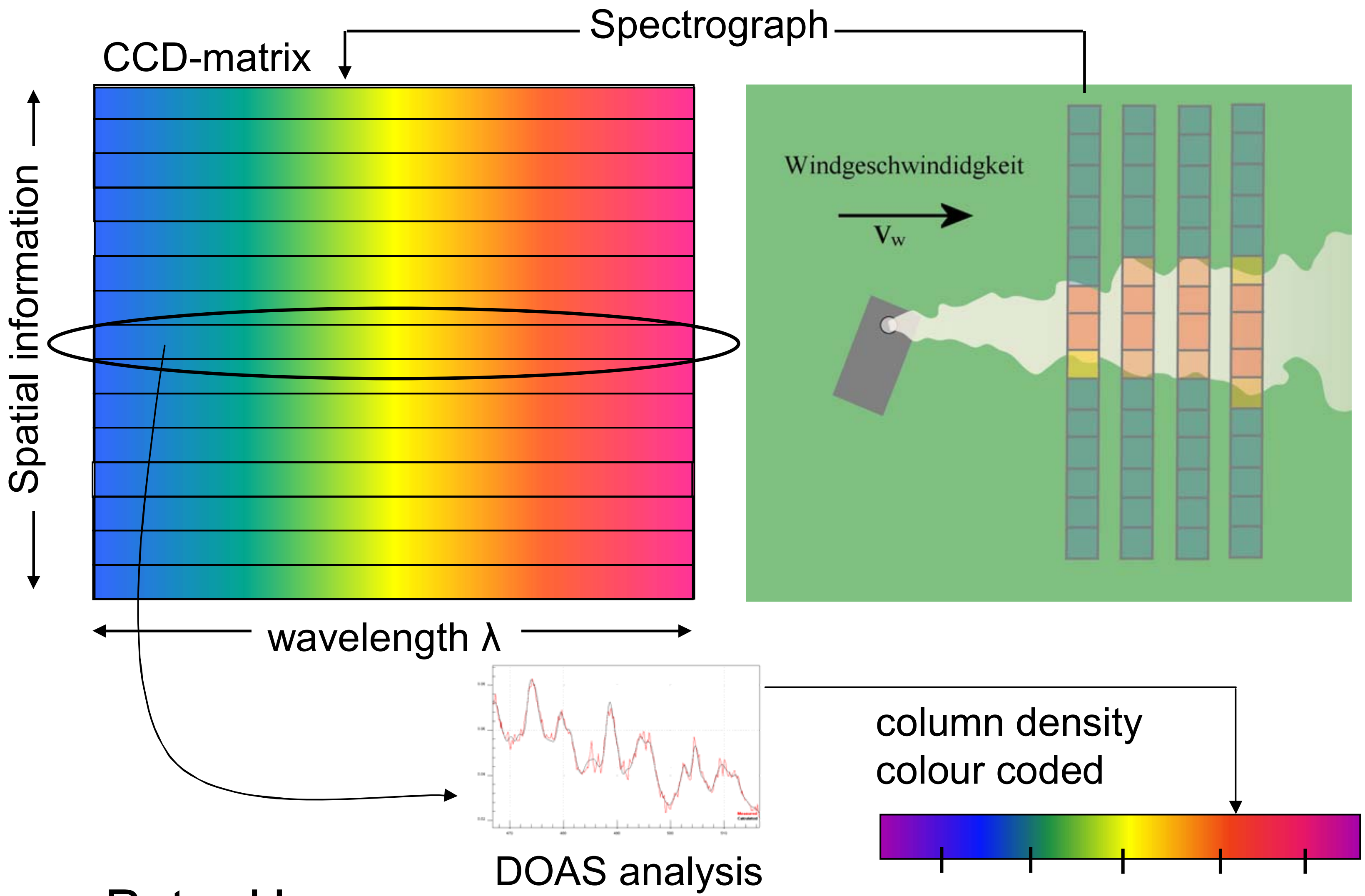
Aircraft-Based Imaging DOAS



Determine 2D distributions of trace gas (e.g. NO_2, SO_2, CH_2O) column densities along „stripes“ (≈10km width) along the flight track.



Aircraft-Based Imaging DOAS

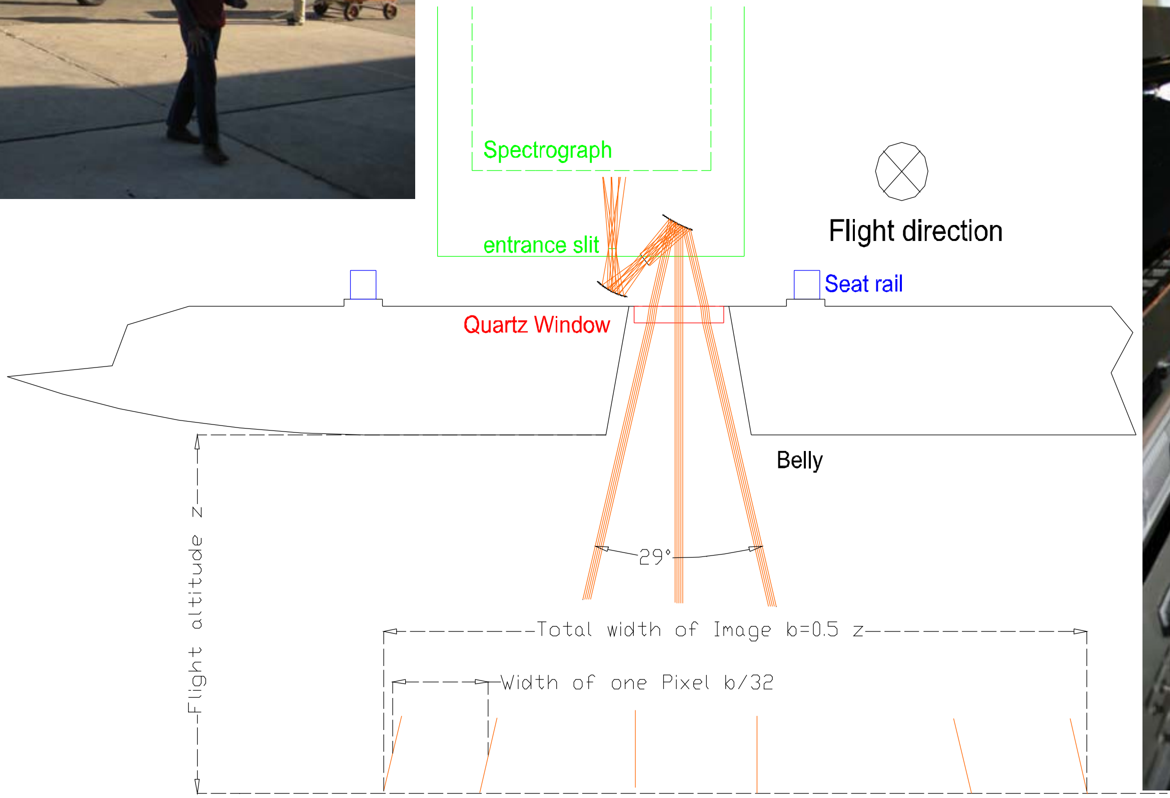


Klaus-Peter Heue

Airborne Imaging-DOAS, Instrumental Setup

Rockwell 690A Aircommander operated by the South African Weather Service (ZS-JRA)

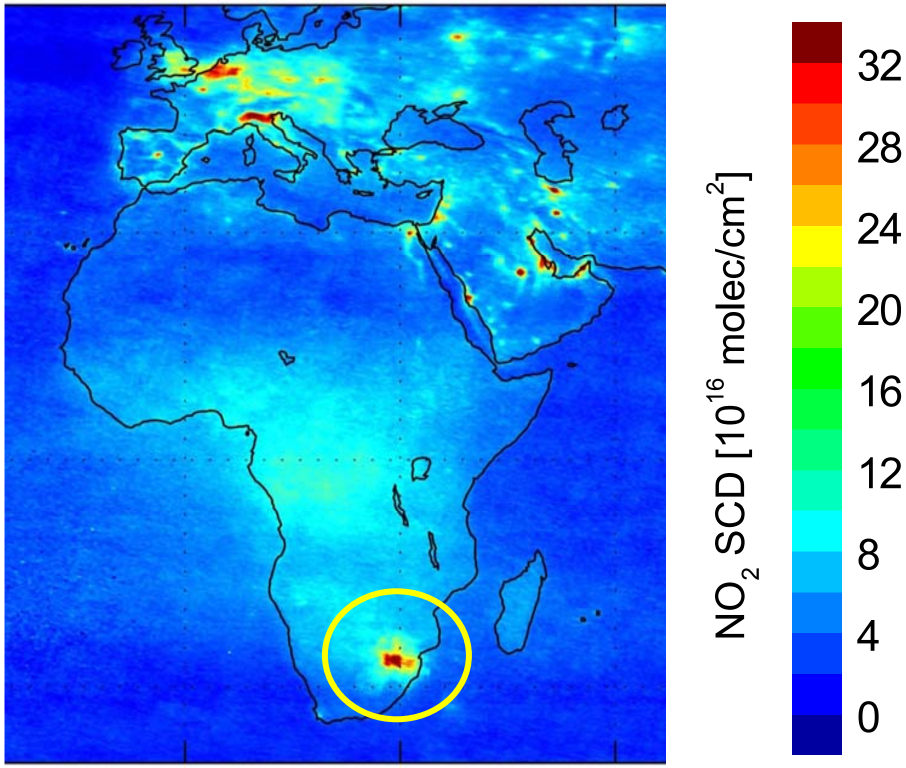
Klaus-Peter Heue et al. 2007

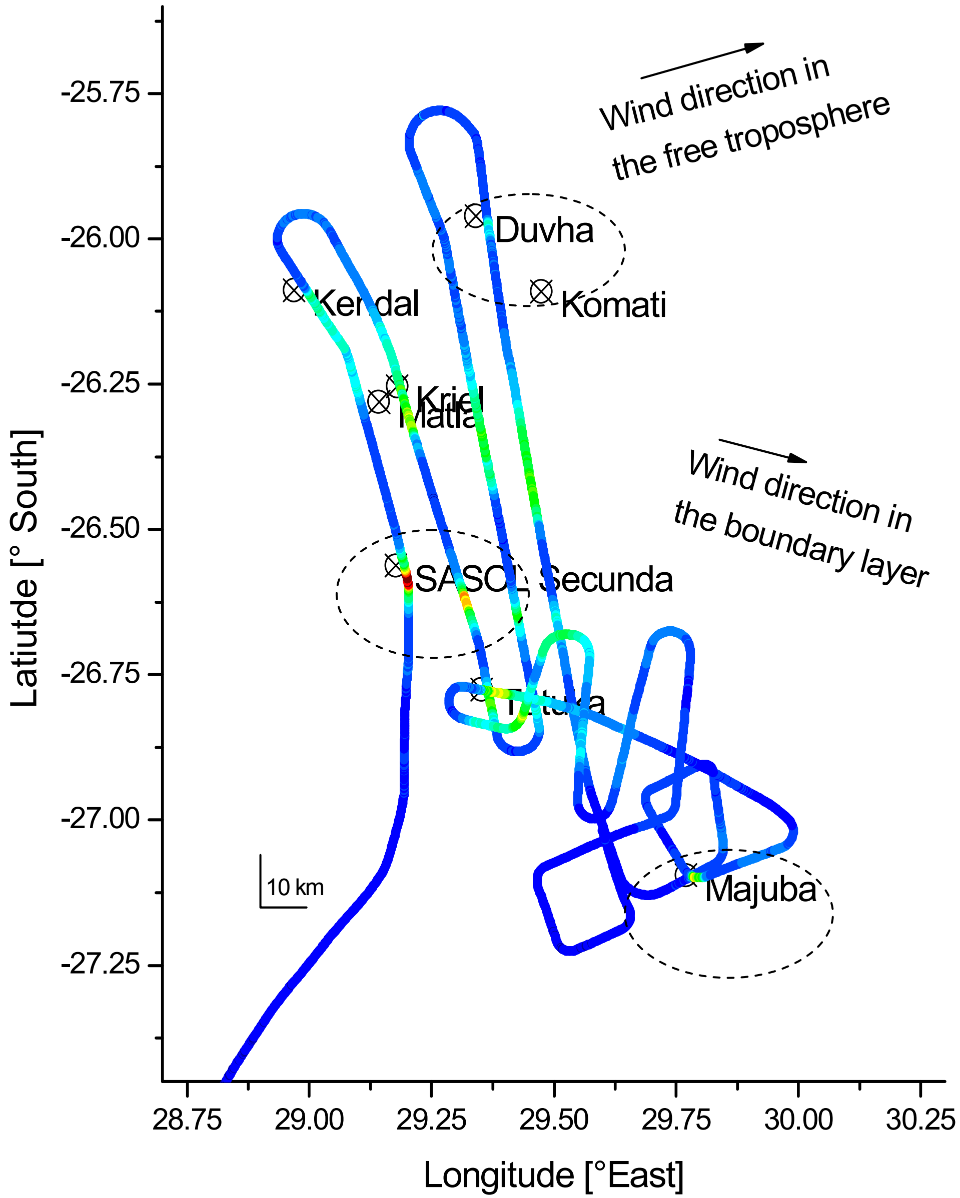


- Acton 300i spectrograph (f = 300mm), Andor CCD detector (1024 x 512 pixel)
- Mirror entrance optics (f_1=-51.5mm and f_2=25.6mm) total focal length f_{tot}=13.7mm
- 29° field of view theoretically; 24.5° in reality due to obstructions

Overview of one Highveld flight

2nd flight on October 5th

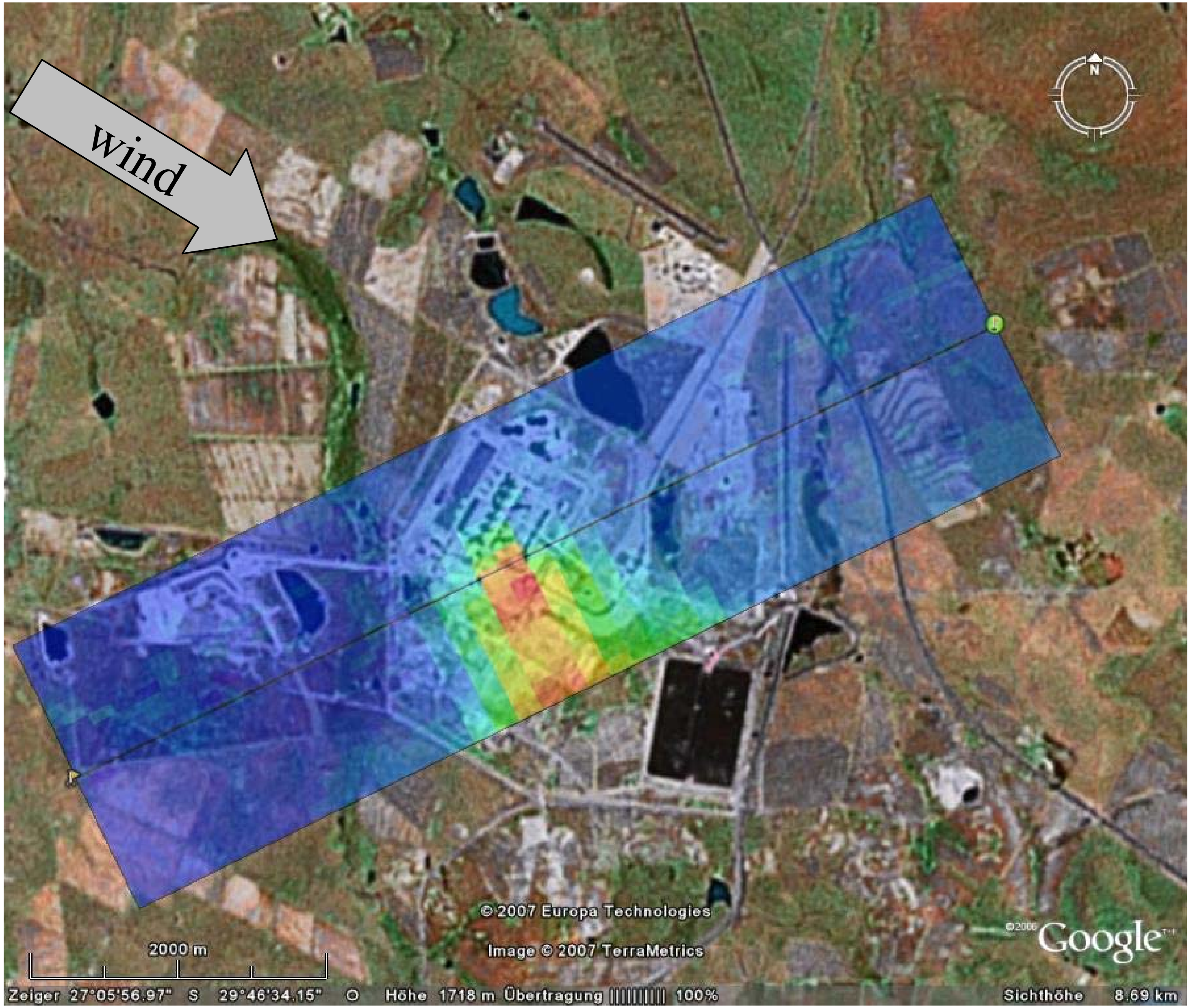




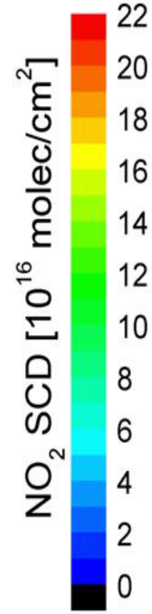
Flights in the Highveld area: SA, three in October 2006,
Seven in August 2007 - data analysis is in progress
4400m above ground, 1900m swath width, 70m x 75m resolution

Klaus-Peter Heue et al. 2007

Airborne I-DOAS Measurements at Majuba Power Station (SA), 4500 m Above Ground, Oct. 5, 2006

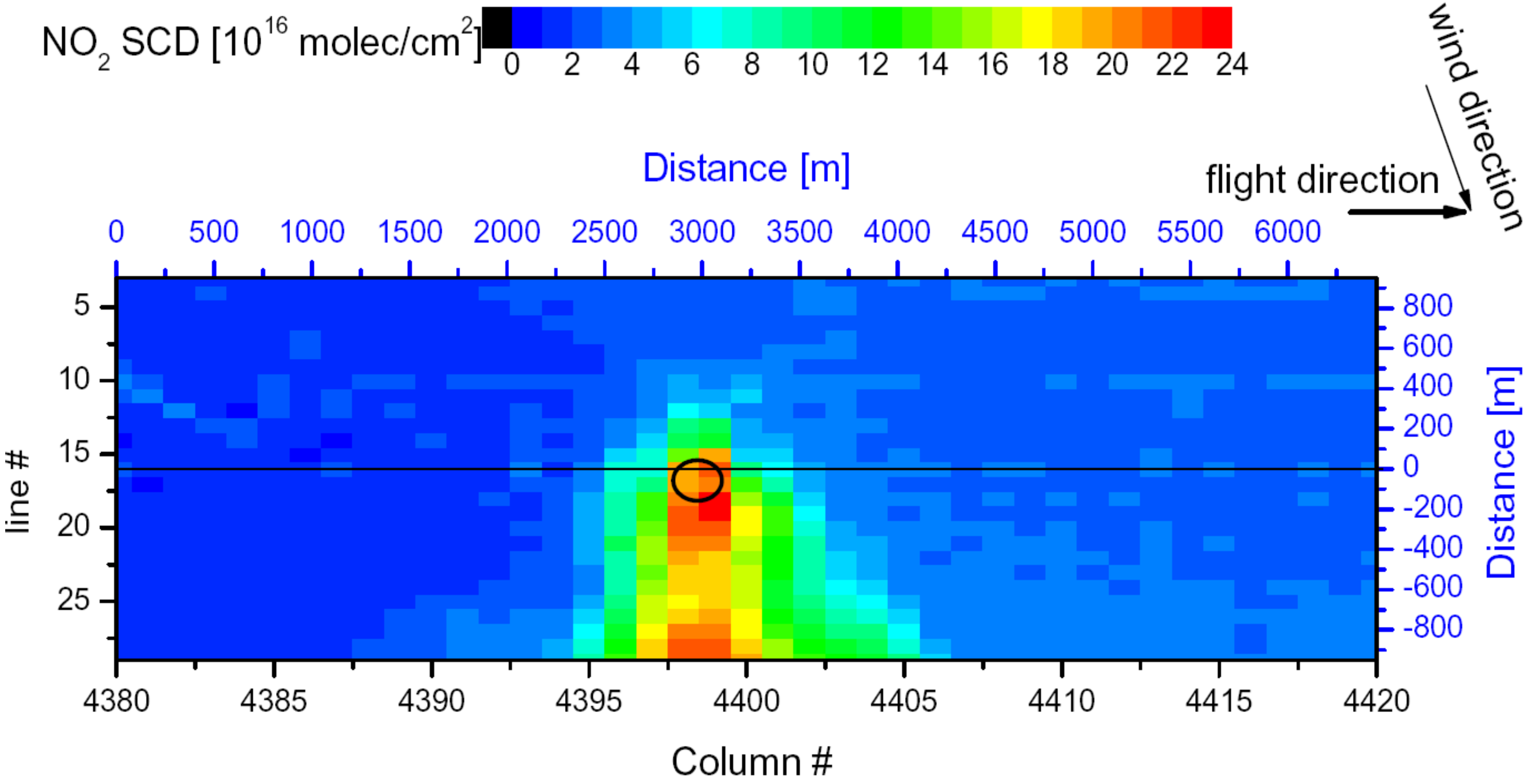


- NO_2 dSCD close to Majuba powerplant
- Swath width 1.9 km length 6.6 km
- Resolution 70m x 75m



Klaus-Peter Heue et al. 2007

Airborne I-DOAS Measurements at Majuba Power Station (SA)
4500 m Above Ground, Oct. 5, 2006



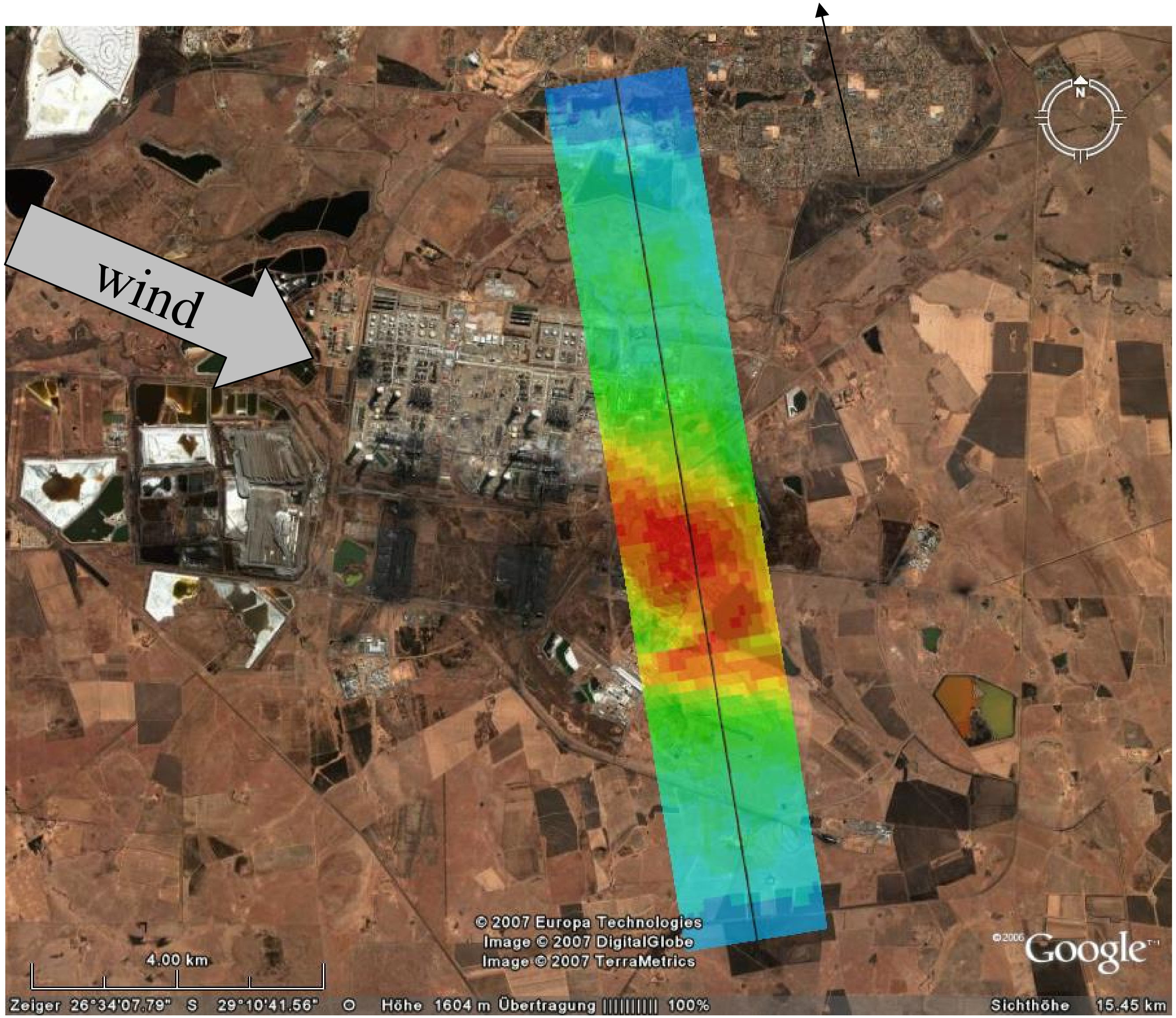
K.-P. Heue, T. Wagner,
S.P. Broccardo,
S.J. Piketh, K.E. Ross and
U. Platt, ACP, 2007

Airborne I-DOAS Measurements at Majuba Power Station (SA) Oct. 5, 2006 Comparison to a SCIAMACHY Ground-Pixel

SCIAMACHY single geound pixel, October 4, 2006

Klaus-Peter Heue et al. 2007

Secunda (SASOL) Power Station (SA), 4500 m above ground

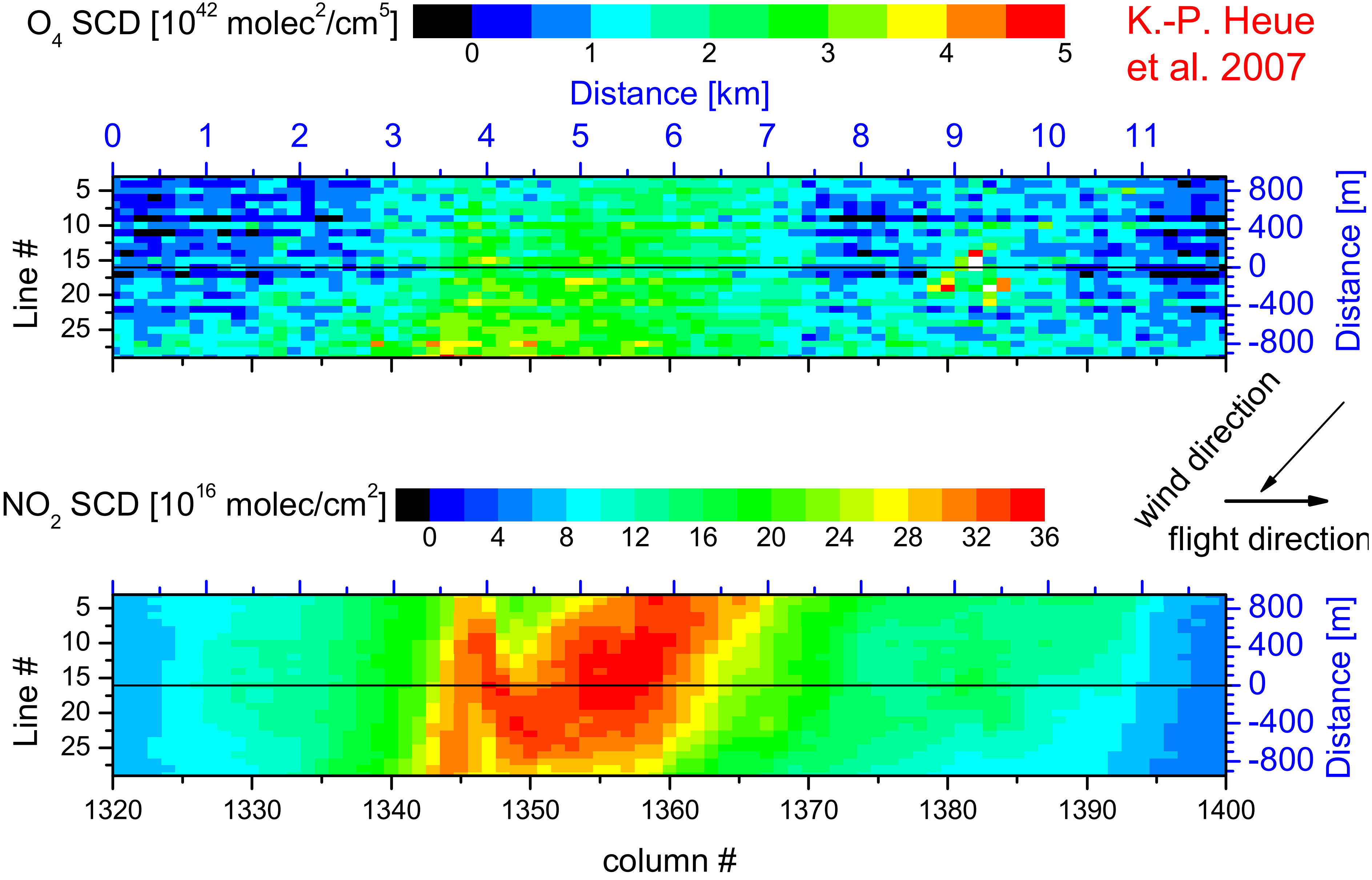


Total distance 11.9km
Swath width 1.9 km
27 pixels,
each 70 m wide

K.-P. Heue, T. Wagner, S.P. Broccardo, S.J. Piketh, K.E. Ross and U. Platt, in prep., 2007

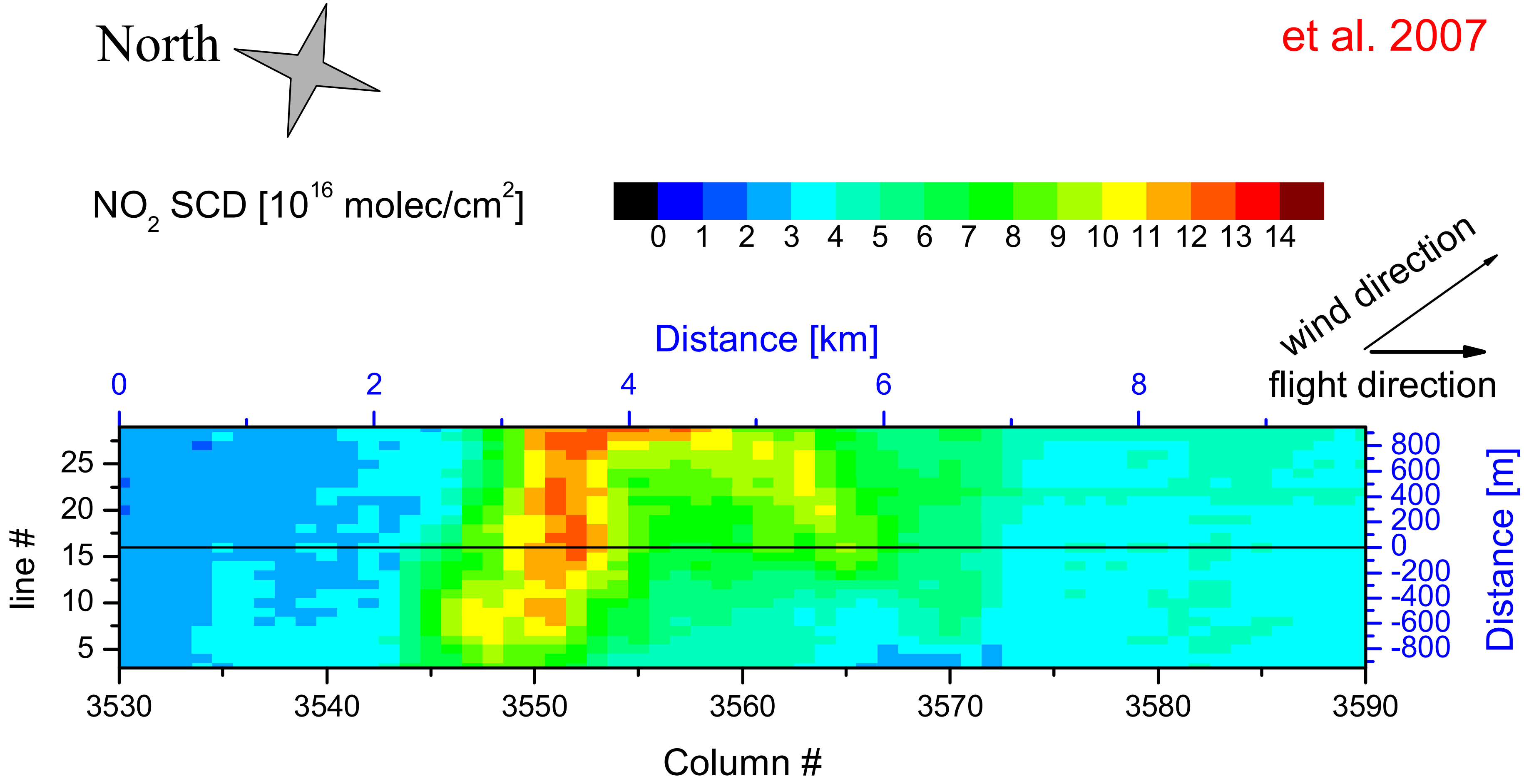
Secunda (SASOL) NO_2 and O_4

K.-P. Heue et al. 2007

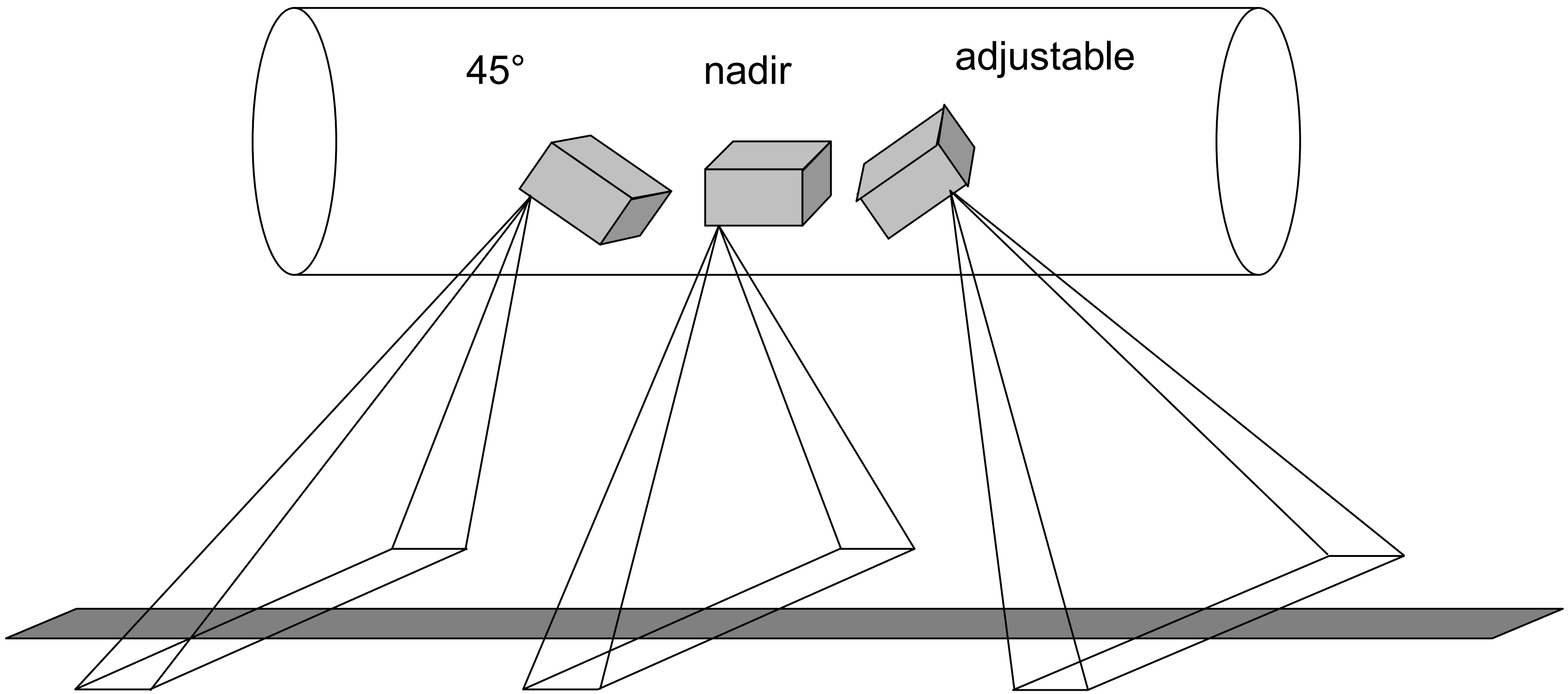


Duvha Power Station (SA)

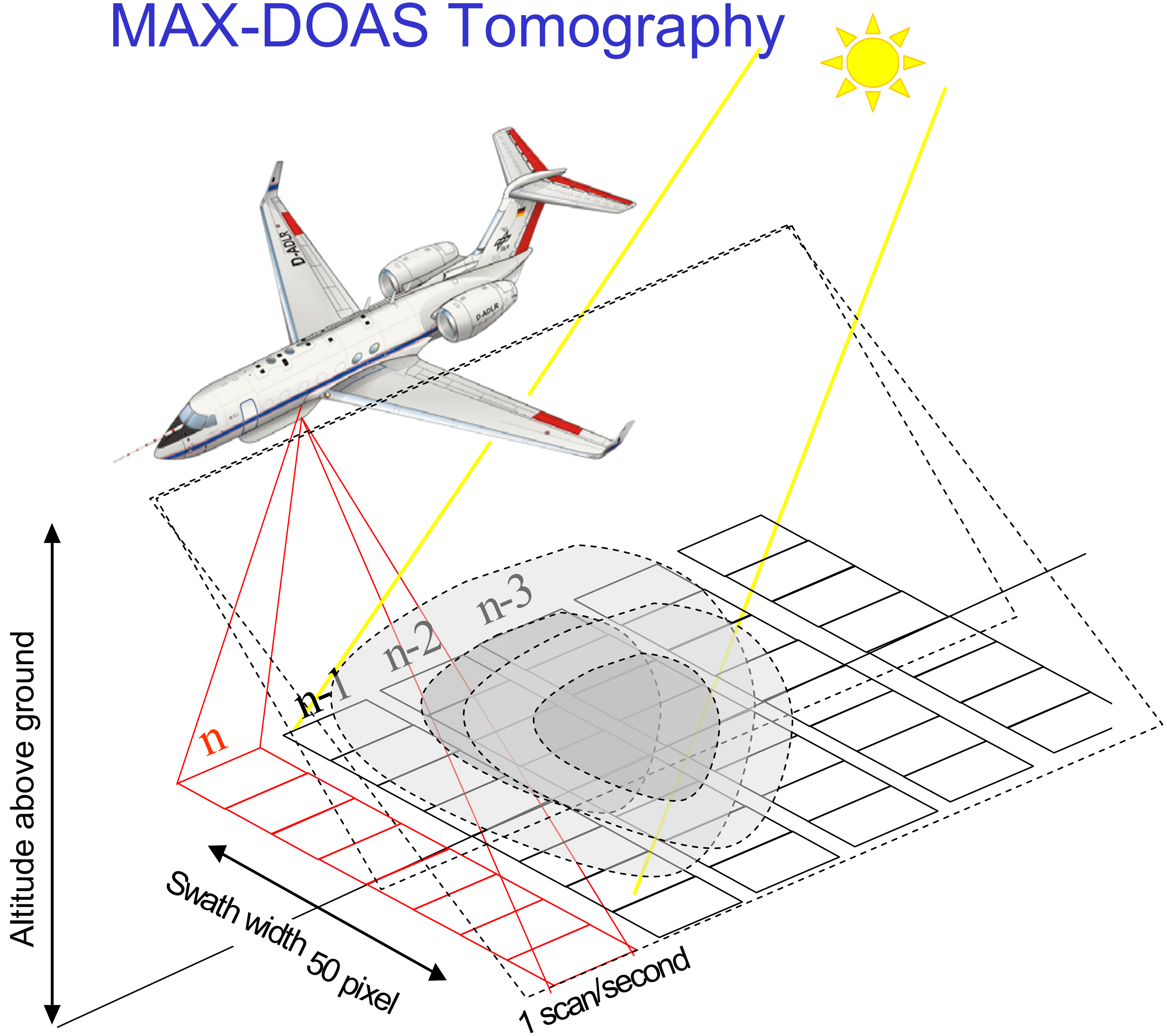
K.-P. Heue
et al. 2007



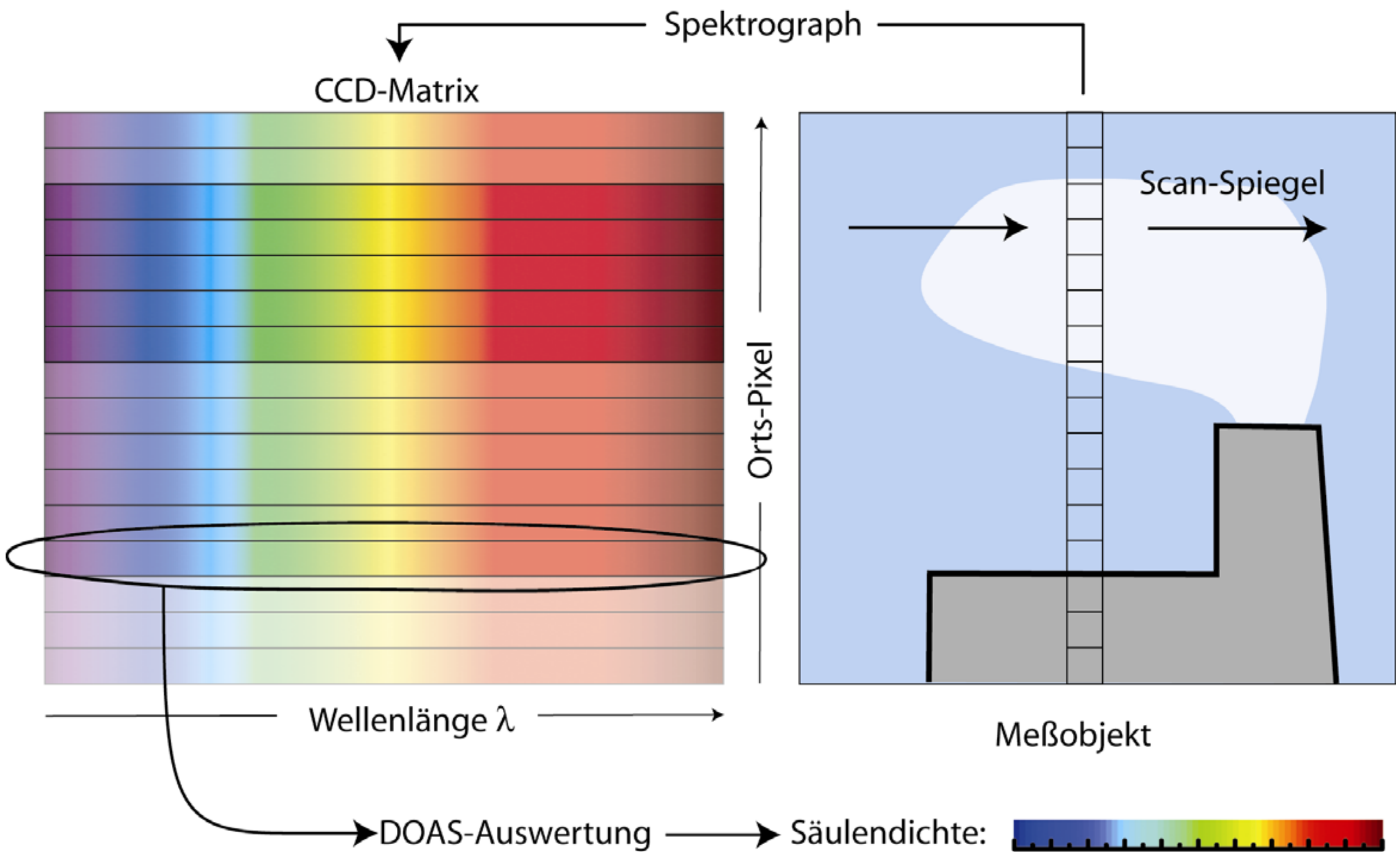
New Instrument for HALO (High Altitude LOng Range Aircraft: 3D – Measurements by combination of Push-Broom and Tomographic Measurements



Future: 3D by Combination of Imaging + MAX-DOAS Tomography



Ground-Based Imaging DOAS (I-DOAS), the Principle



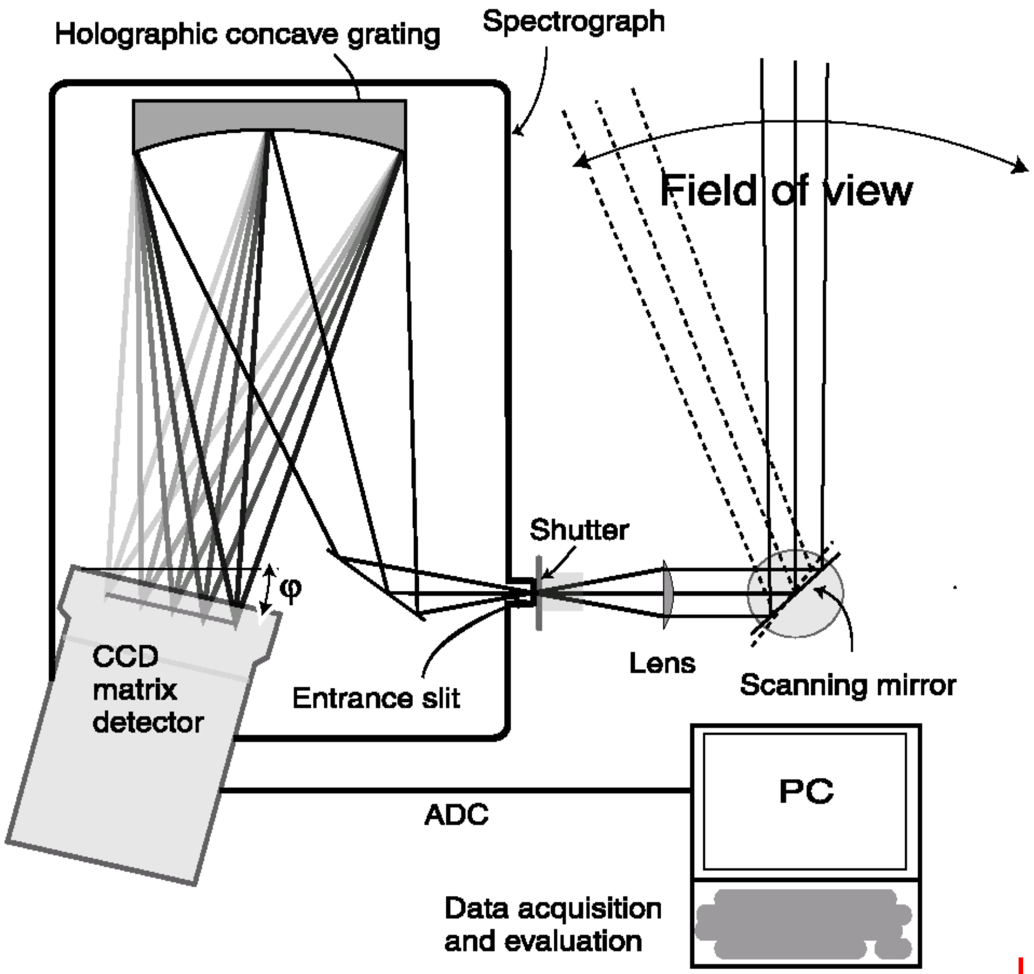
F. Lohberger

Diploma Thesis,

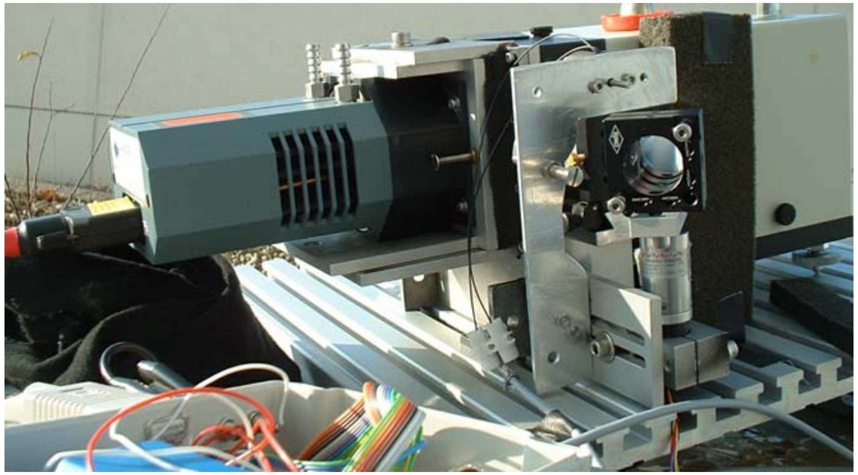
University of Heidelberg, 2003

- Simultaneous recording of spectra in a column of the image (100 - 500 pixels)
- Scanning of the entire image by rotating mirror (100 - 500 columns)
- DOAS-evaluation of Spectra yields column density for each pixel

Imaging DOAS (I-DOAS), Instrumental Setup



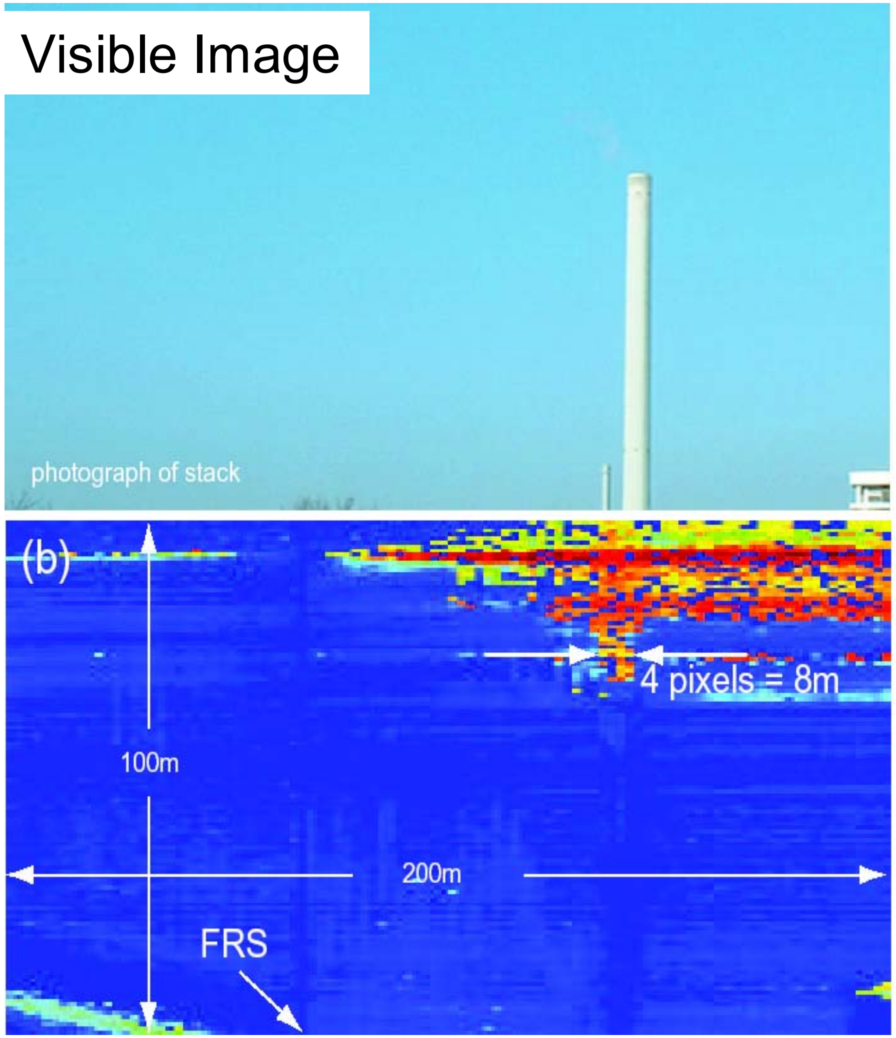
Size: ca. 50 x 50 x 20 cm^3 plus PC



Lohberger et al., Applied Optics 2004

Imaging DOAS Towards the "Trace Gas Goggle"

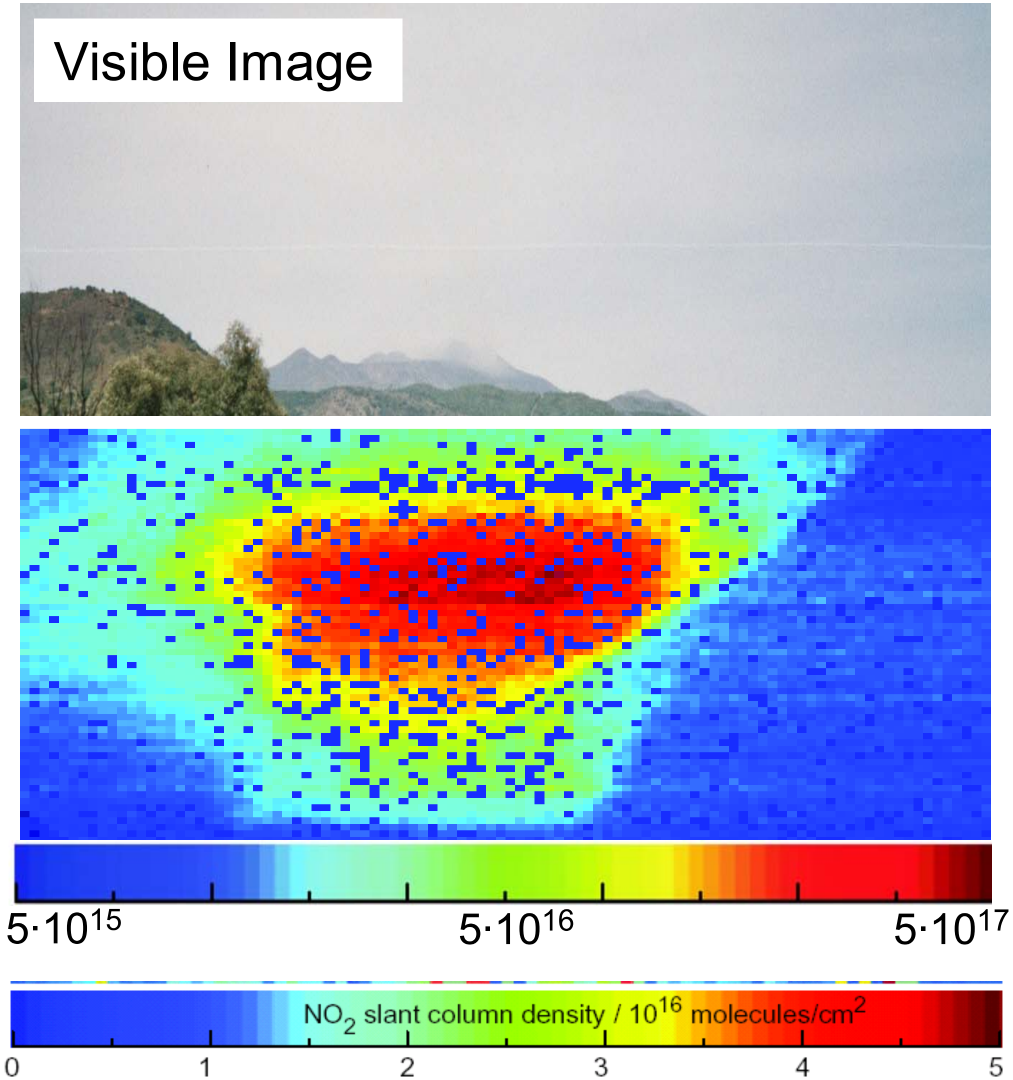
NO_2 in the Plume of University of Heidelberg Heating Plant, 450 m Distance



Lohberger et al., Applied Optics 2004

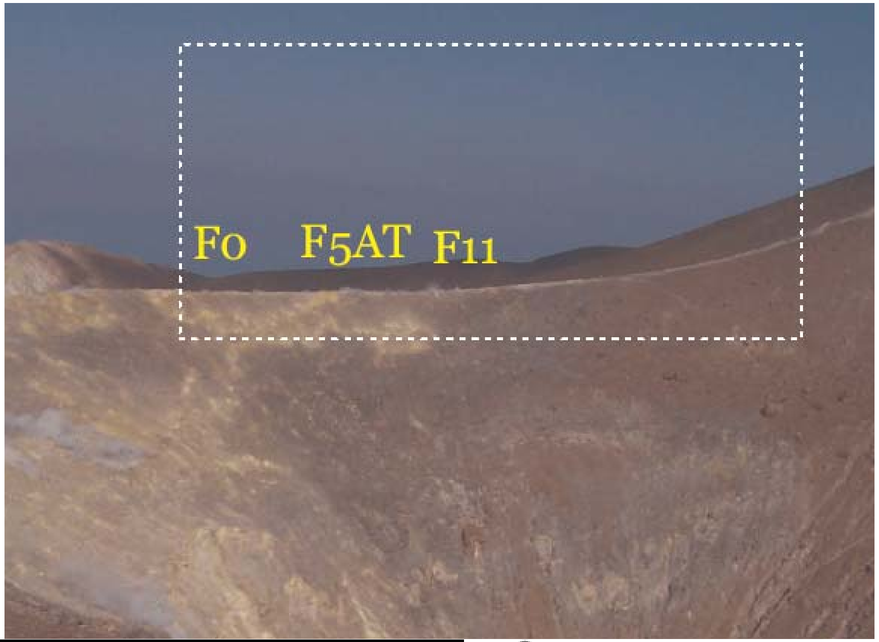
N. Bobrowski, I. Louban, 2005

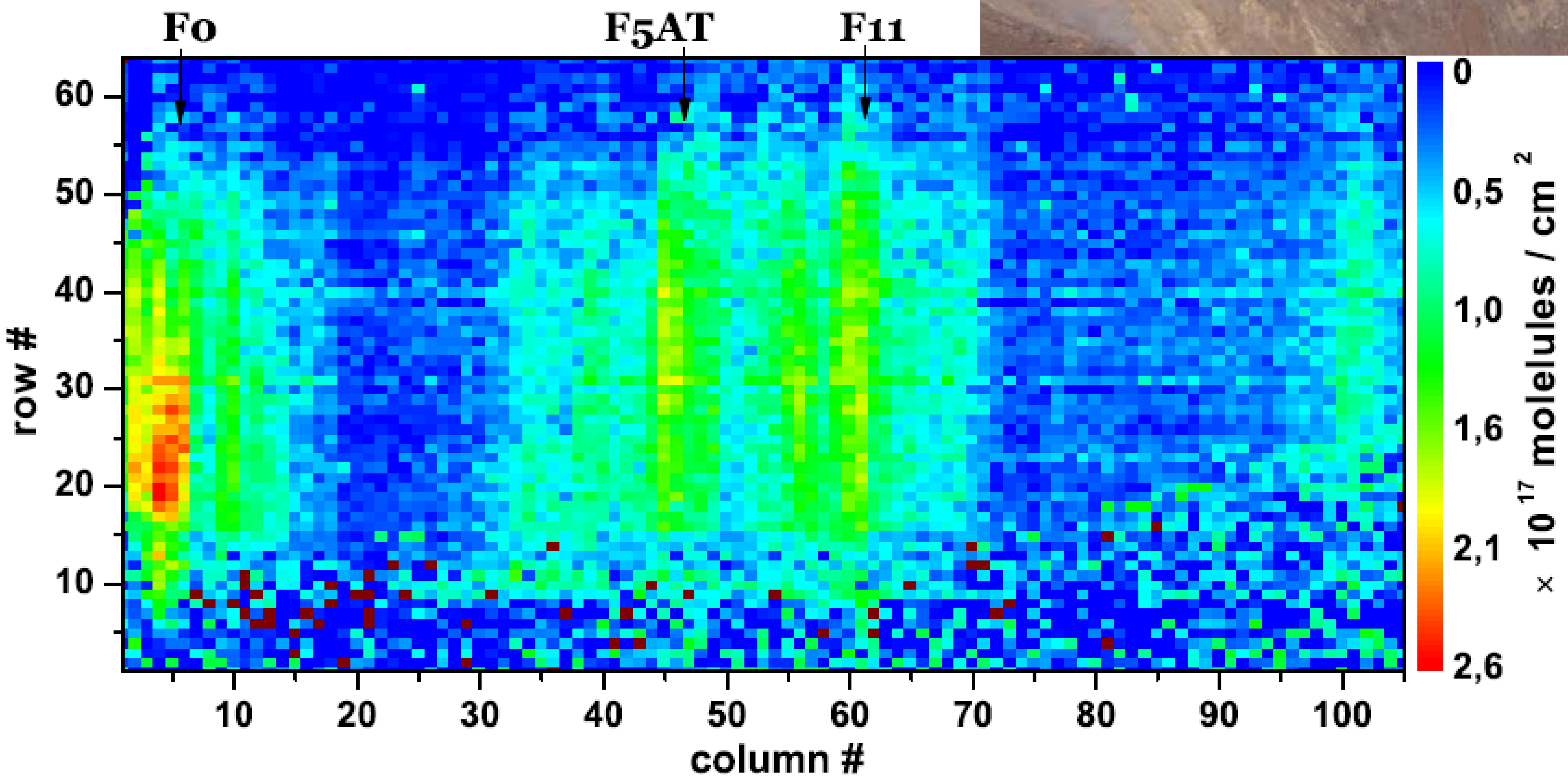
SO_2 in the Plume of Etna, Oct. 2003



Imaging DOAS

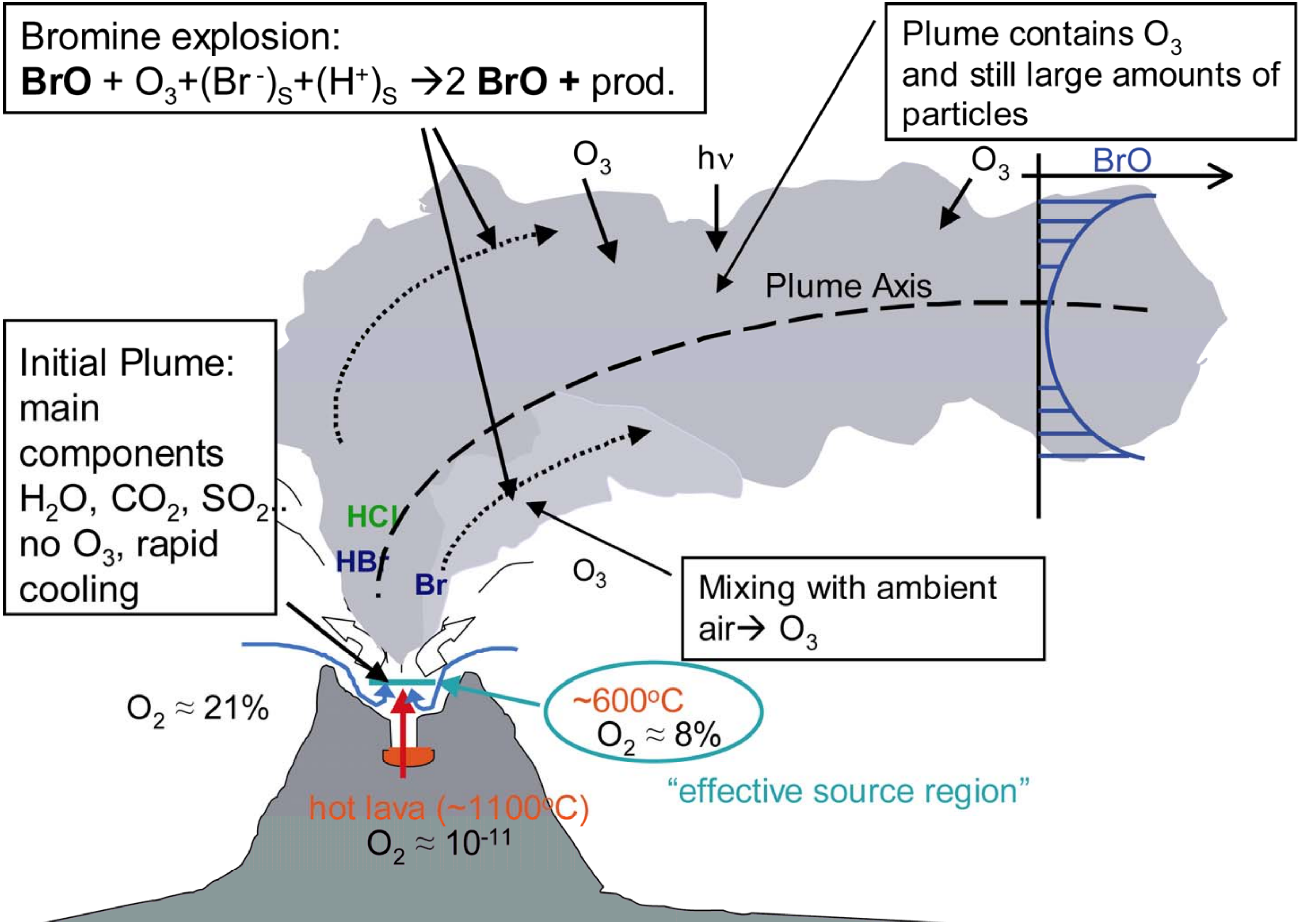
Volcano Island, Italy
Oct. 6, 2004
Ilia Louban





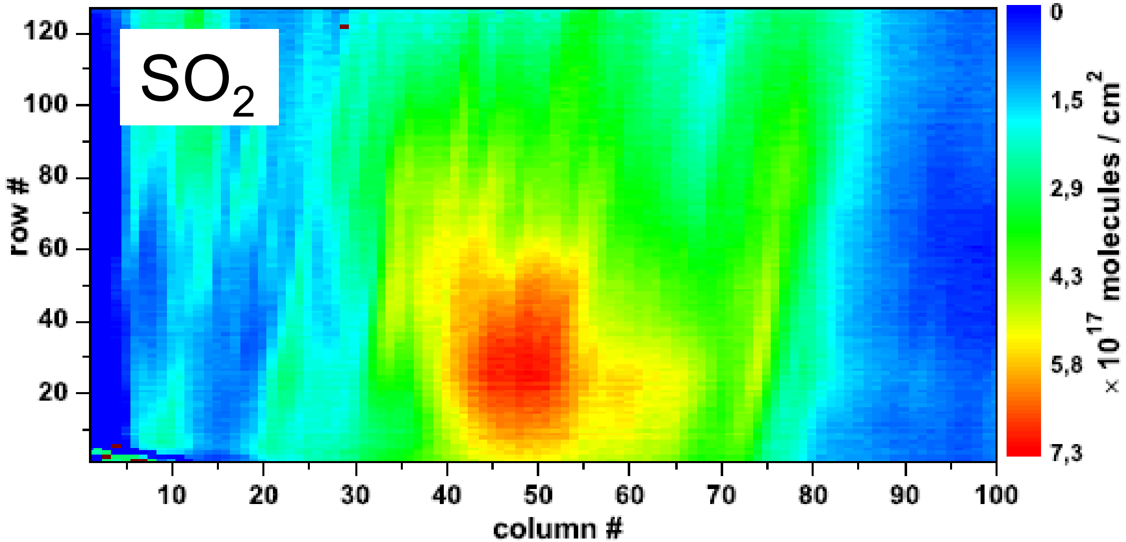
k

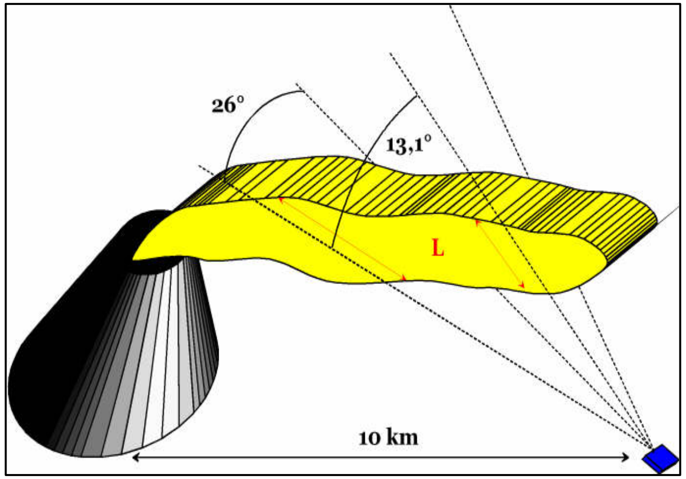
BrO Chemistry in Volcanic Plumes

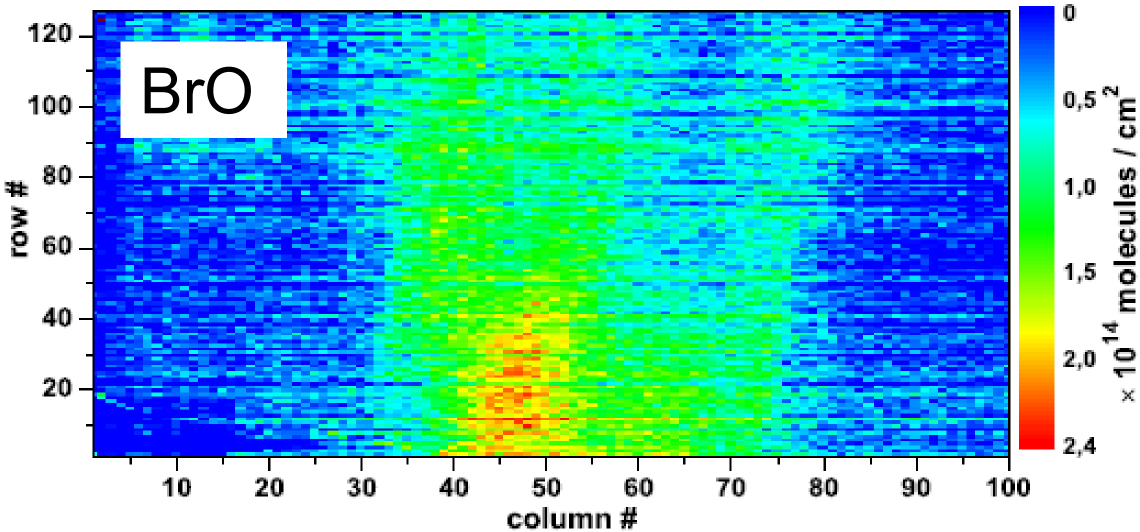


Imaging DOAS Cross-Sections of the Etna-Plume, May 10, 2005

Visible Image



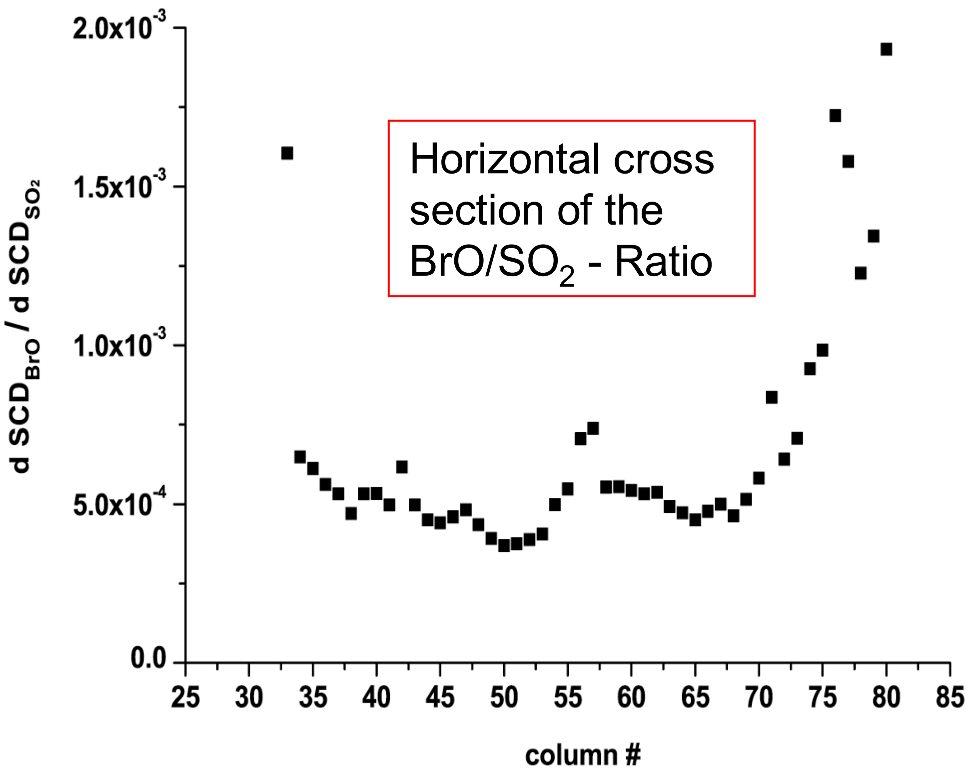


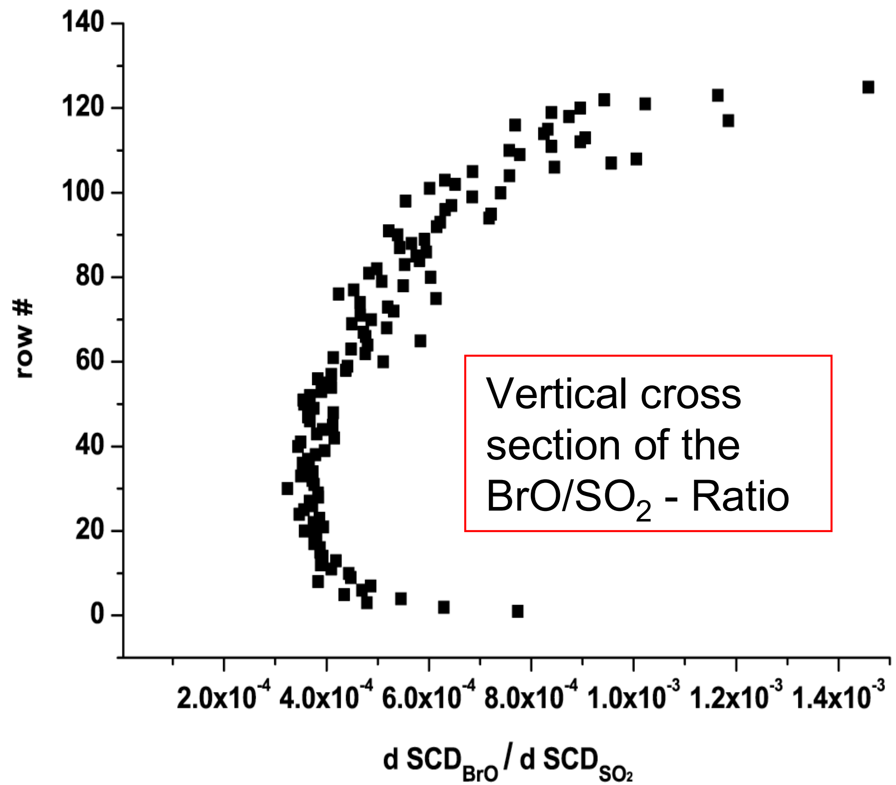


Louban et al. 2008,

Bobrowski et al. 2006

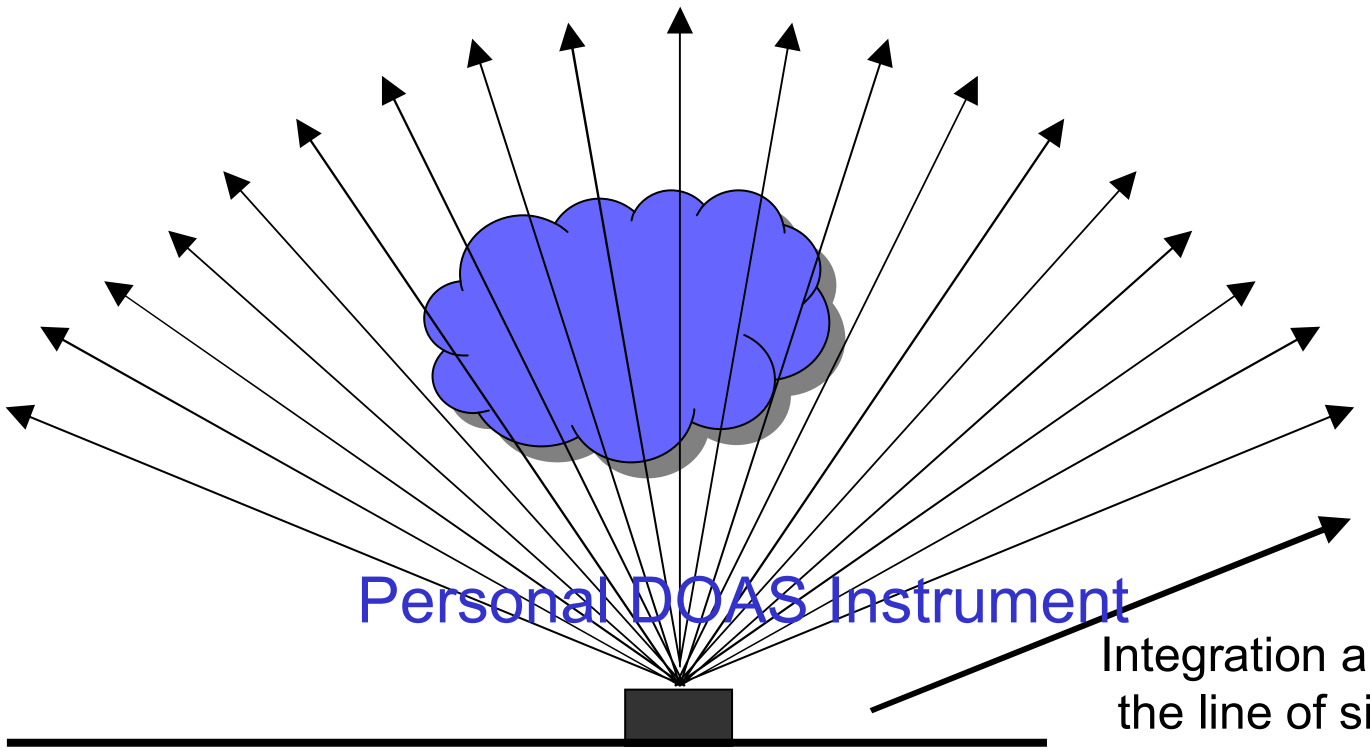
BrO/SO_2 ratio spatial distribution over the plume cross section as measued by Imaging DOAS (Louban et al. 2009)





→Supports the idea of BrO – formation by mixing-in of O_3 (and HO_2) from the edge of the plume.

2) Multi-Axis DOAS (MAX-DOAS) for Quantification of Plumes

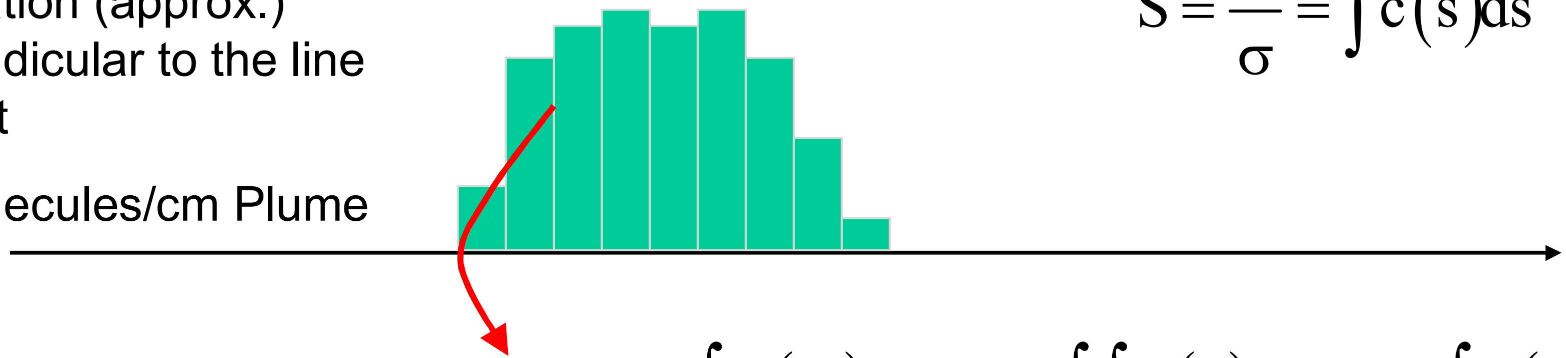


Integration along the line of sight

$$S = \frac{D}{\sigma} = \int c(s)\,ds$$

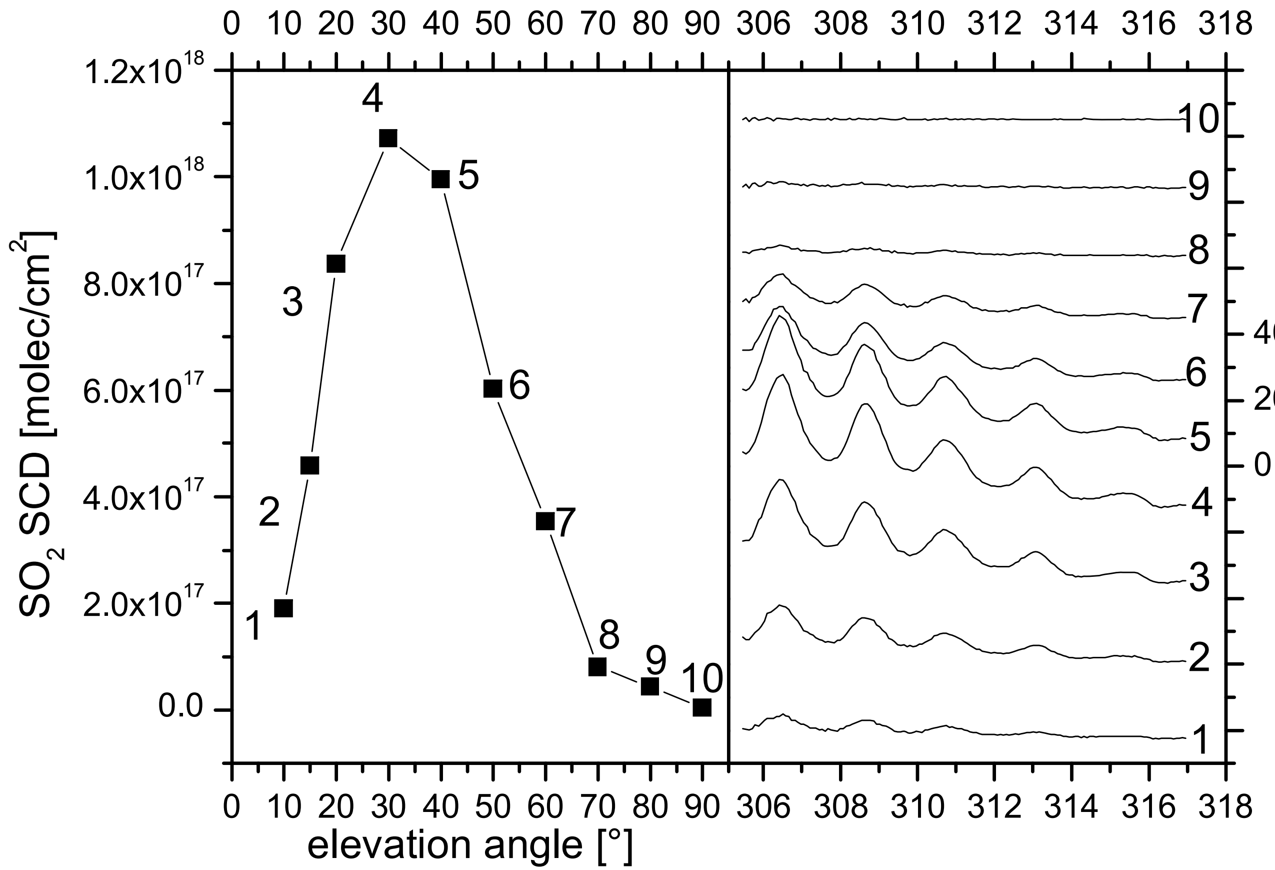
Integration (approx.) perpendicular to the line of sight

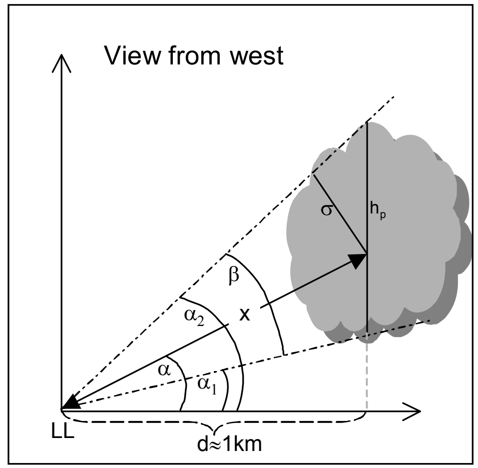
--> Molecules/cm Plume



$$Q = R\int S(\alpha)\,d\alpha \approx R\int\int c(s)\,ds\,d\alpha = \int_A c(\vec{x})\,dA'$$

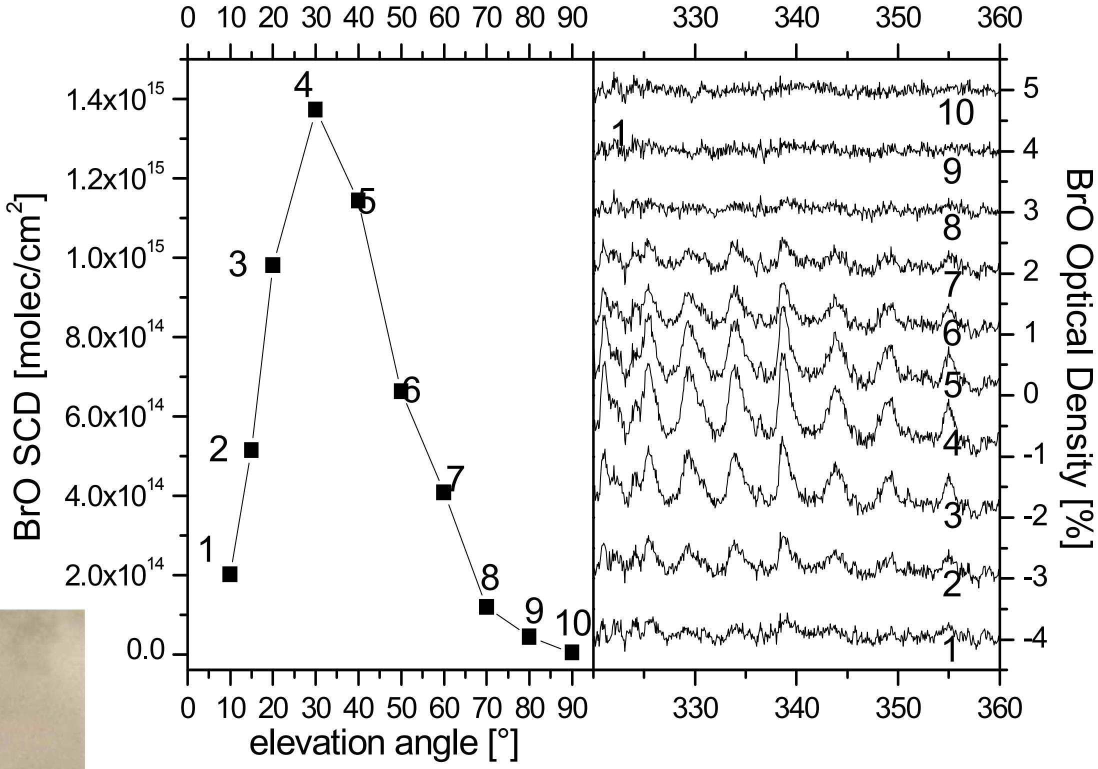
Example: Plume height Determination by Scanning MAX-DOAS





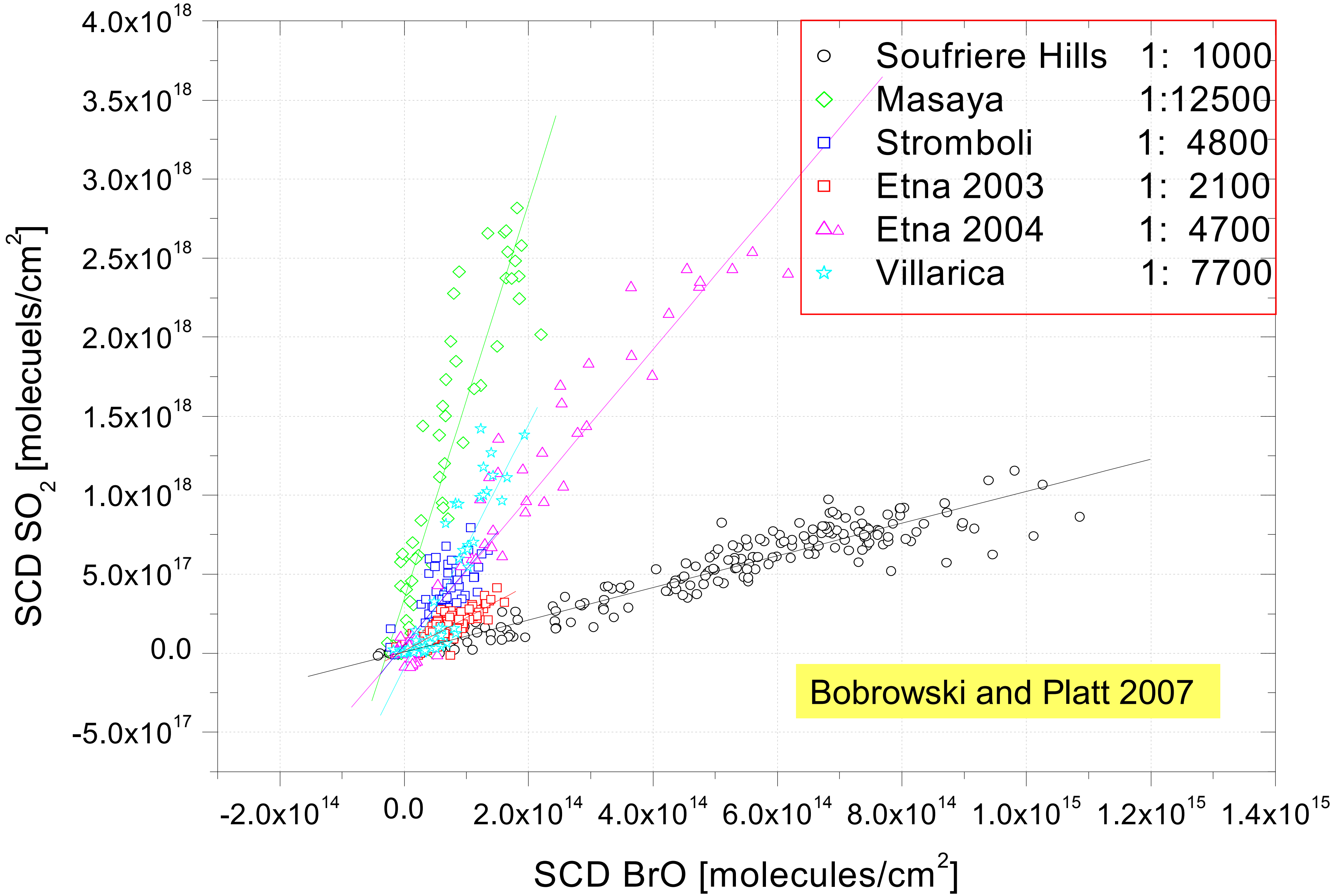
SO_2 from Soufriere Hills Volcano on Montserrat, Caribean, May 25, 2002, Bobrowski et al. 2002

MAX - DOAS BrO from Soufriere Hills Volcano on Montserrat, Caribean, May 25, 2002

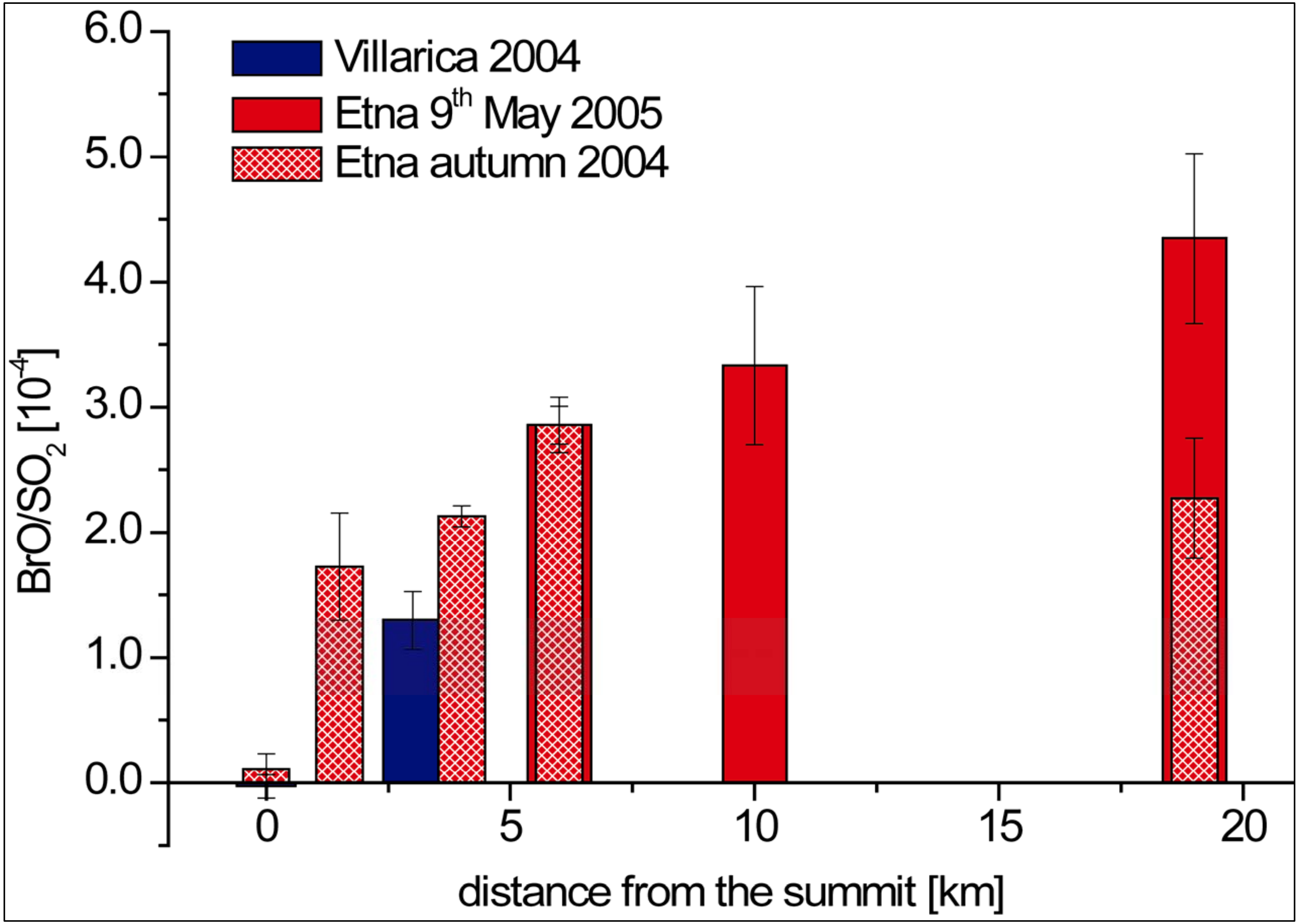


Bobrowski et al. 2002

BrO/SO_2 in Different Volcanic Plumes



Variation of the BrO/SO_2 Ratio with Distance from the Source



Bobrowski et al. 2006

2) Static Multi-Spectrometer DOAS System

Application: NOVAC Network for Observation of Volcanic and Atmospheric Change

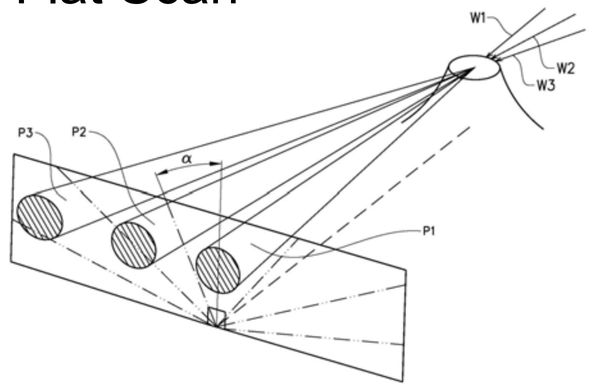
Coordinator: Bo Galle, Gothenburg

Setup of a static multi-spectrometer DOAS system for plume observation.

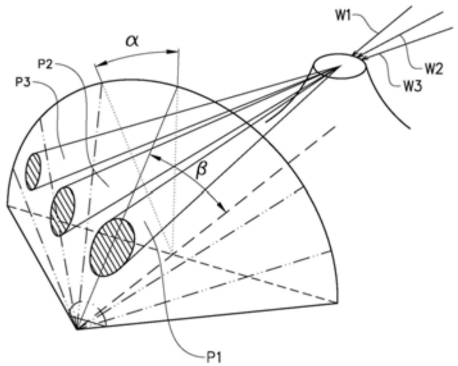
Present status:

>40 instruments at 16 volcanoes (Europe, Central America, Reunion)

Flat Scan



Conical Scan



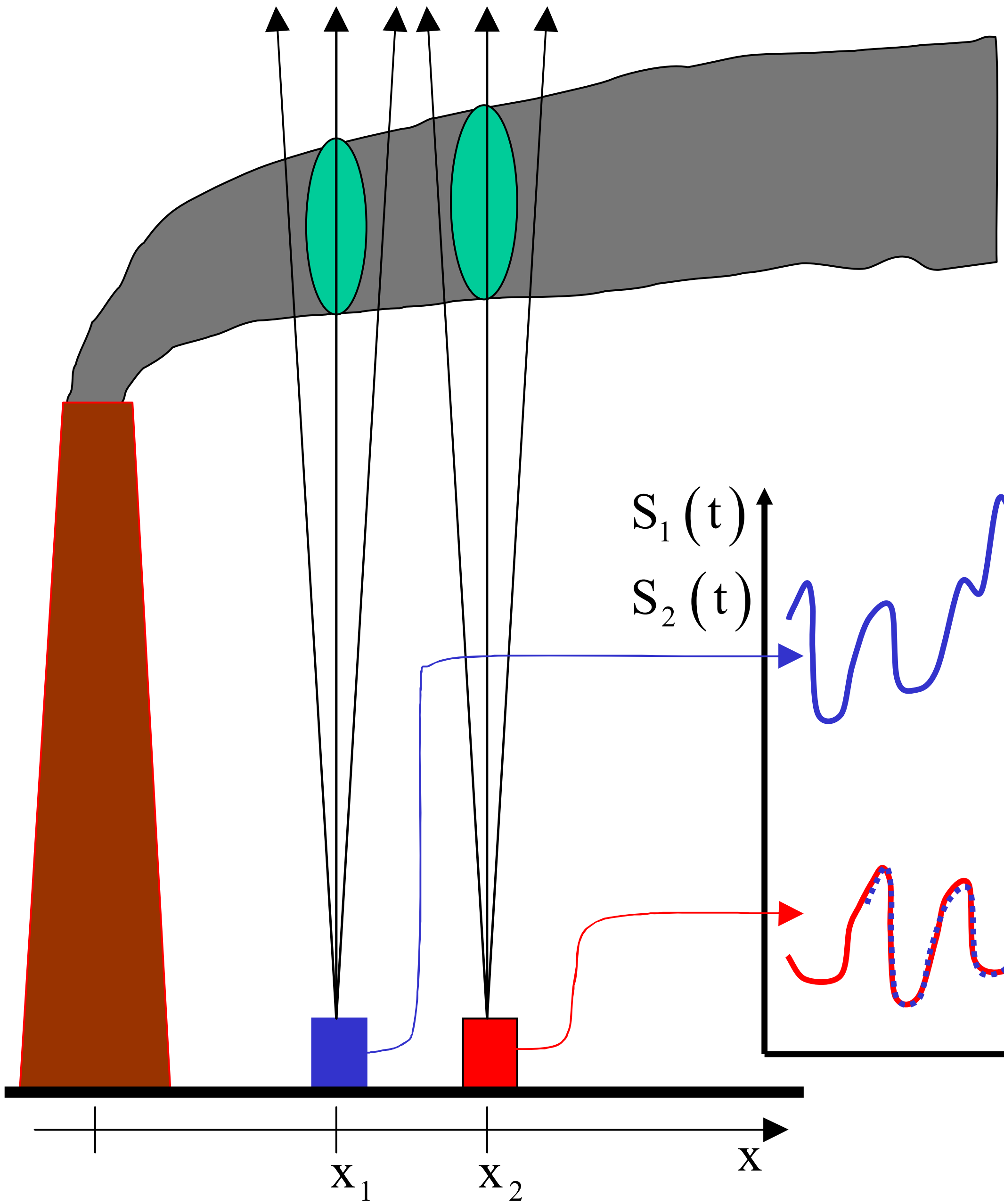
Flux Measurements

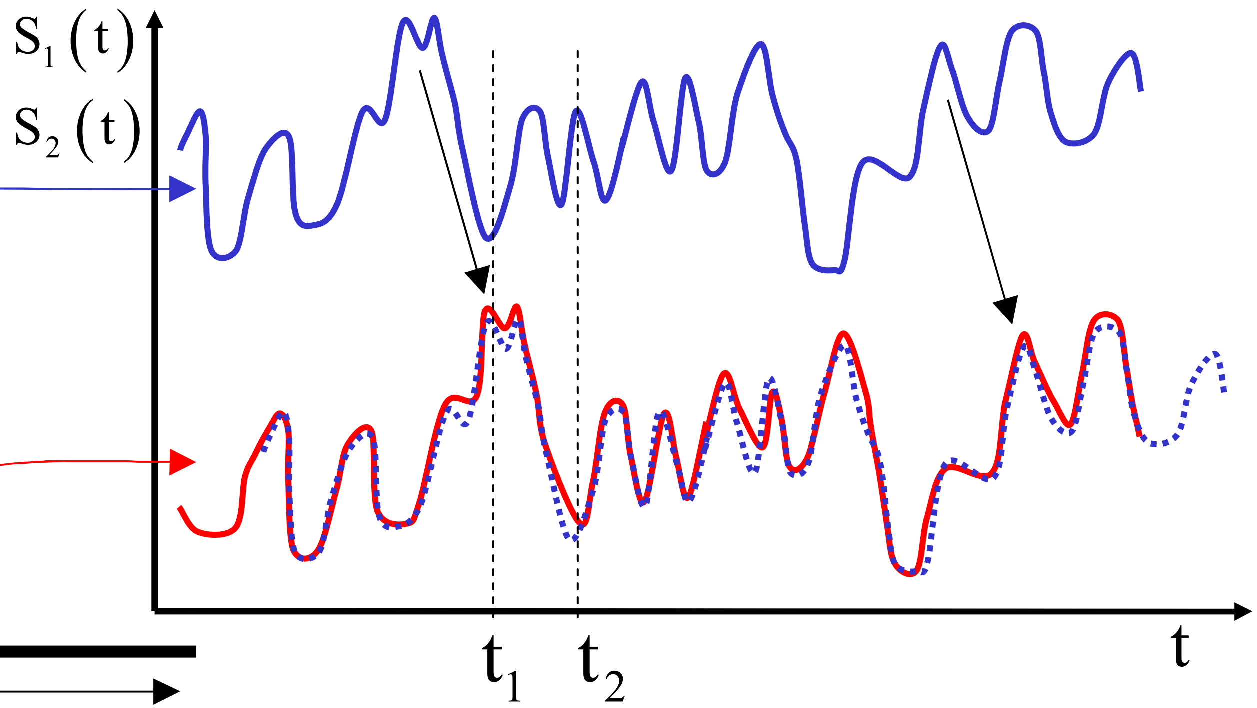
1) Measure fluctuations of column density at two different positions x_1, x_2 downwind of the source.

2) Determine time lag $\Delta t = t_2 - t_1$

3) Wind speed v_P and trace gas flux J in the pume are:

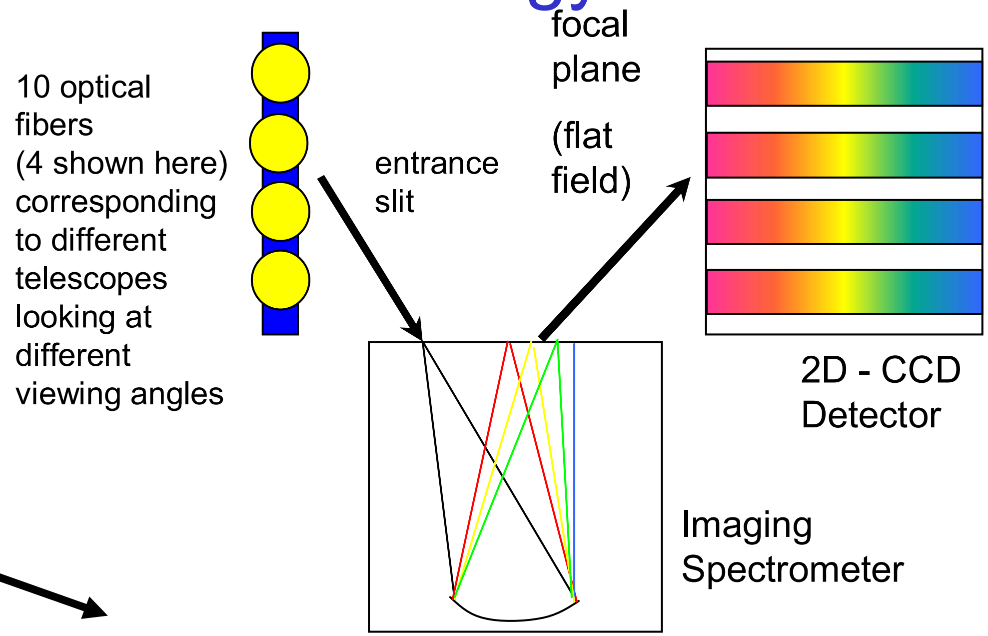
$$v_P = \frac{\Delta x}{\Delta t} = \frac{x_2 - x_1}{t_2 - t_1}, \quad J = Q \cdot v_P$$





MINI - MAX – DOAS Technology

Simultaneous observation of different elevation angles



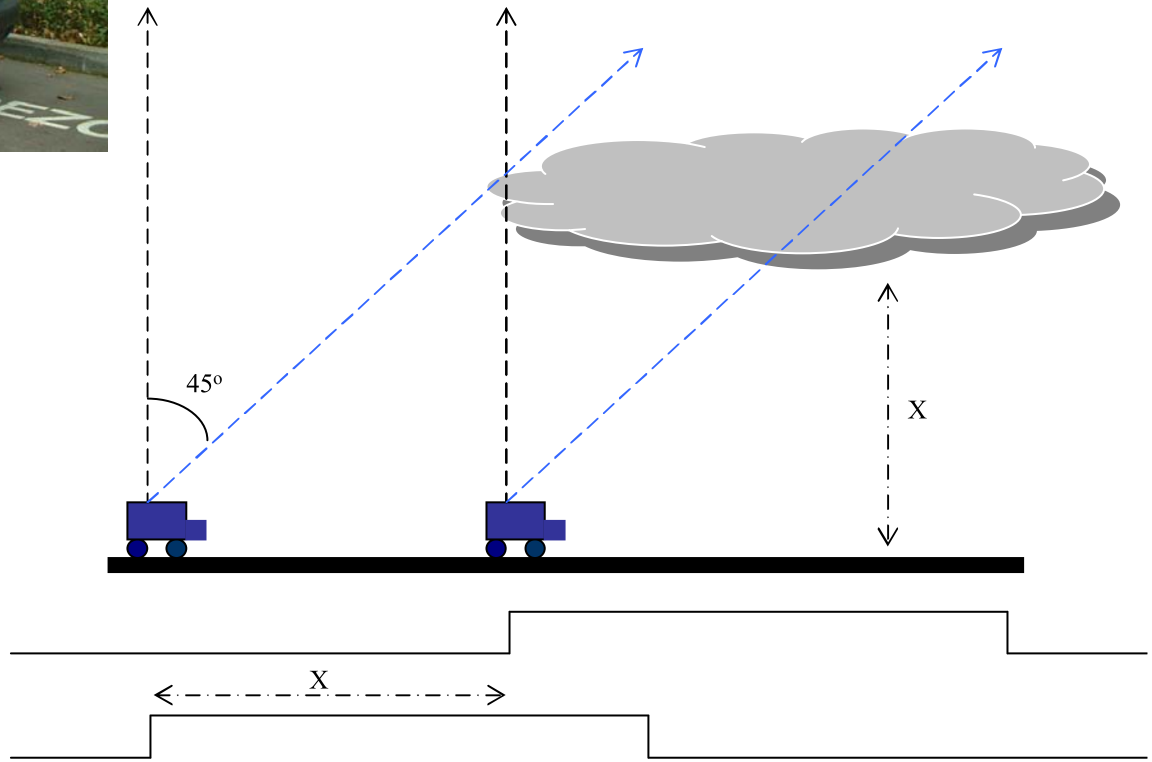
Scan (sequential observation) of different elevation angles

Personal DOAS Instrument

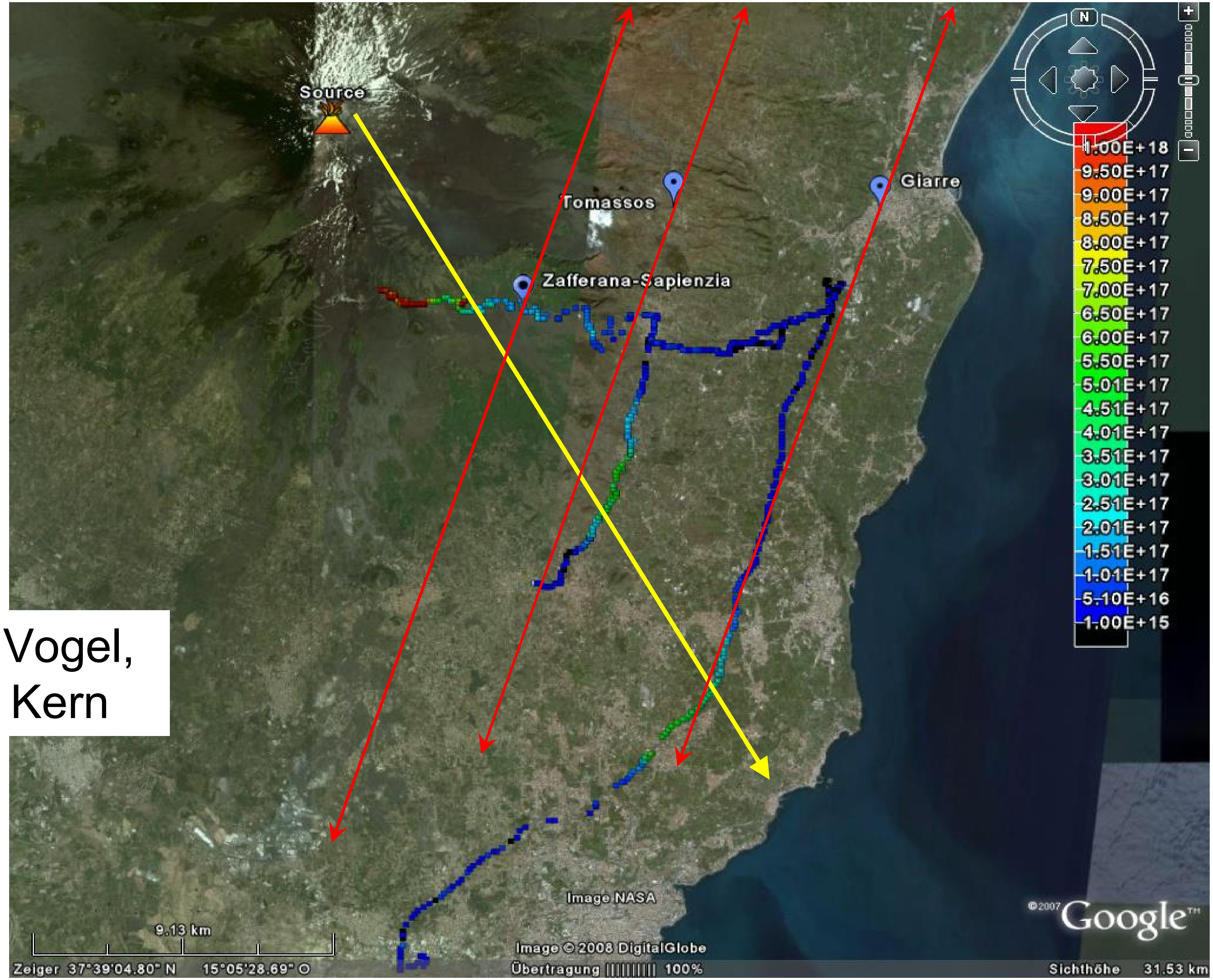
Plume Monitoring from Mobile Instruments

Ossama Ibrahim,
Torsten Stein
8 November 2005

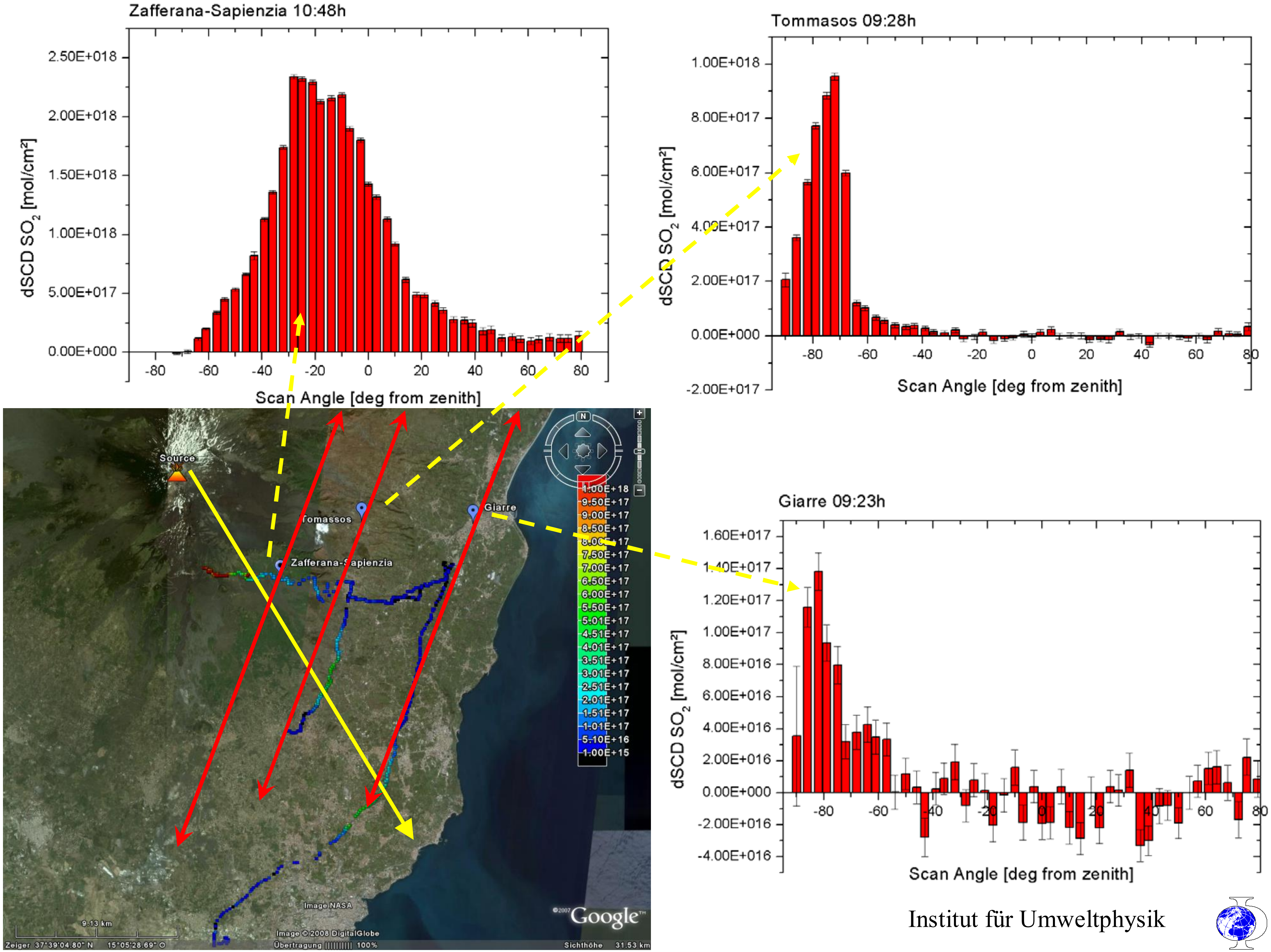
Determine plume height with dual spectrometer system:



Plume Scans and Traverses at Mt. Etna, Italy, July 16, 2008

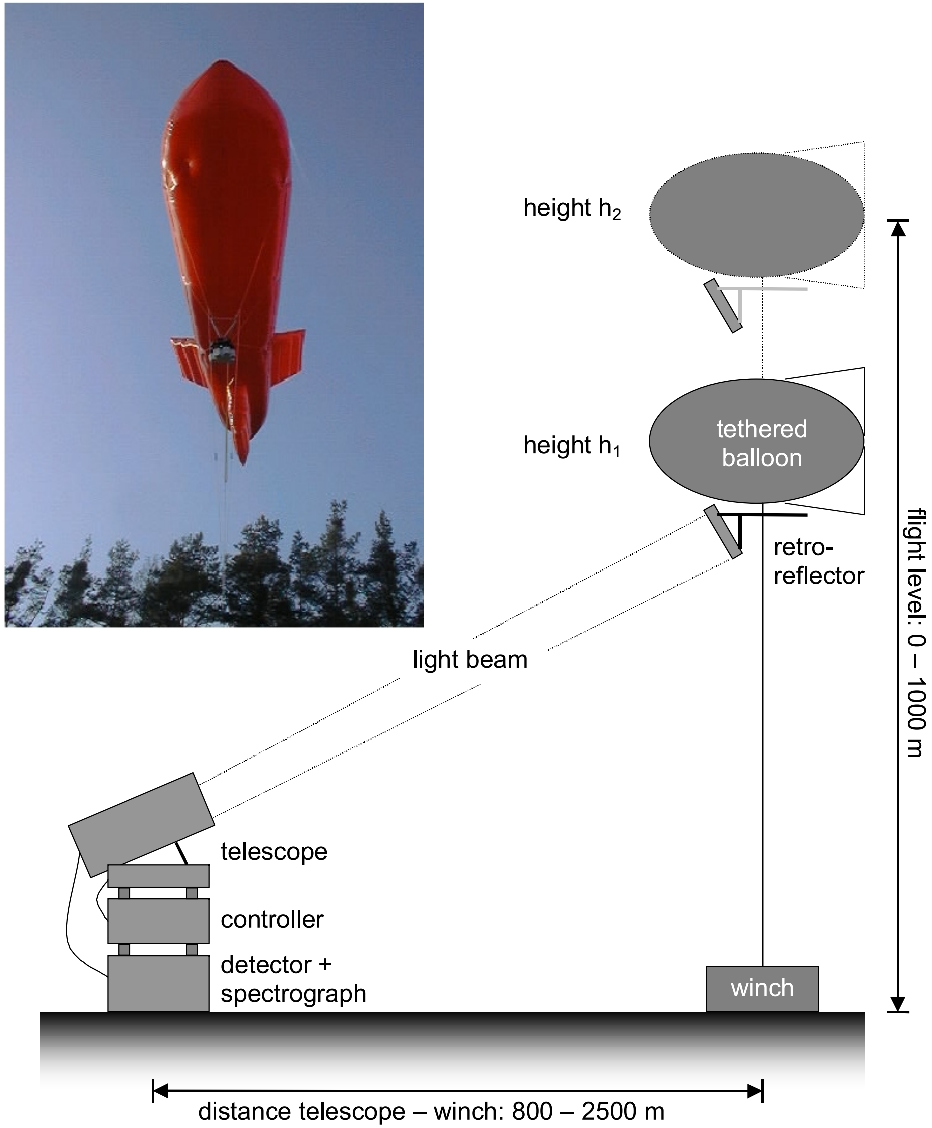


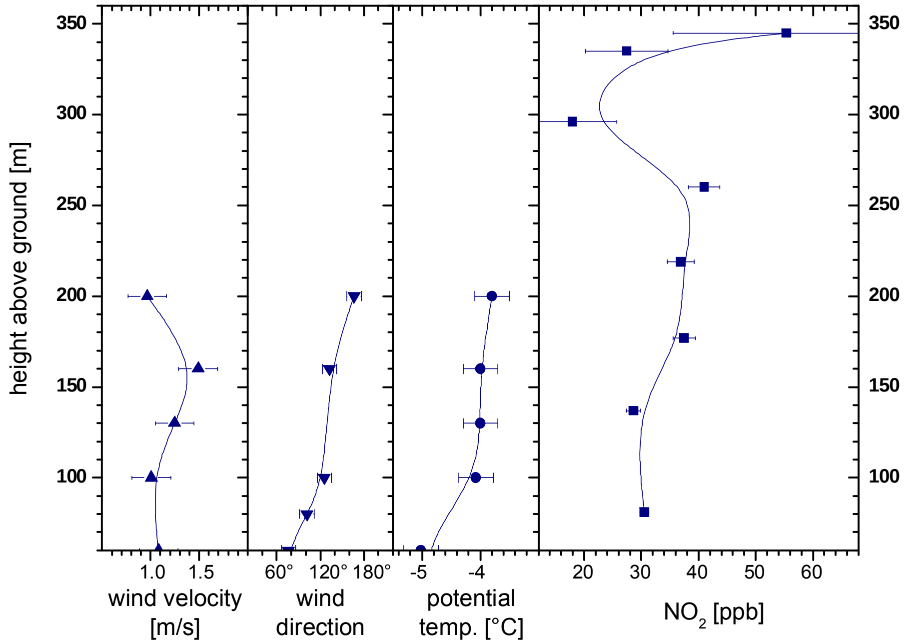
L. Vogel,
C. Kern



Zafferana-Sapienzia 10:48h
dSCD SO_2 [mol/cm²]
Scan Angle [deg from zenith]
Tommasos 09:28h
dSCD SO_2 [mol/cm²]
Scan Angle [deg from zenith]
Giarre 09:23h
dSCD SO_2 [mol/cm²]
Scan Angle [deg from zenith]
Source
Tommasos
Zafferana-Sapienzia
Giarre
Image NASA
Image © 2008 DigitalGlobe
©2007 Google

Vertical Profiles with Balloon - Borne Reflectors





17. Jan 2001, Karlsruhe

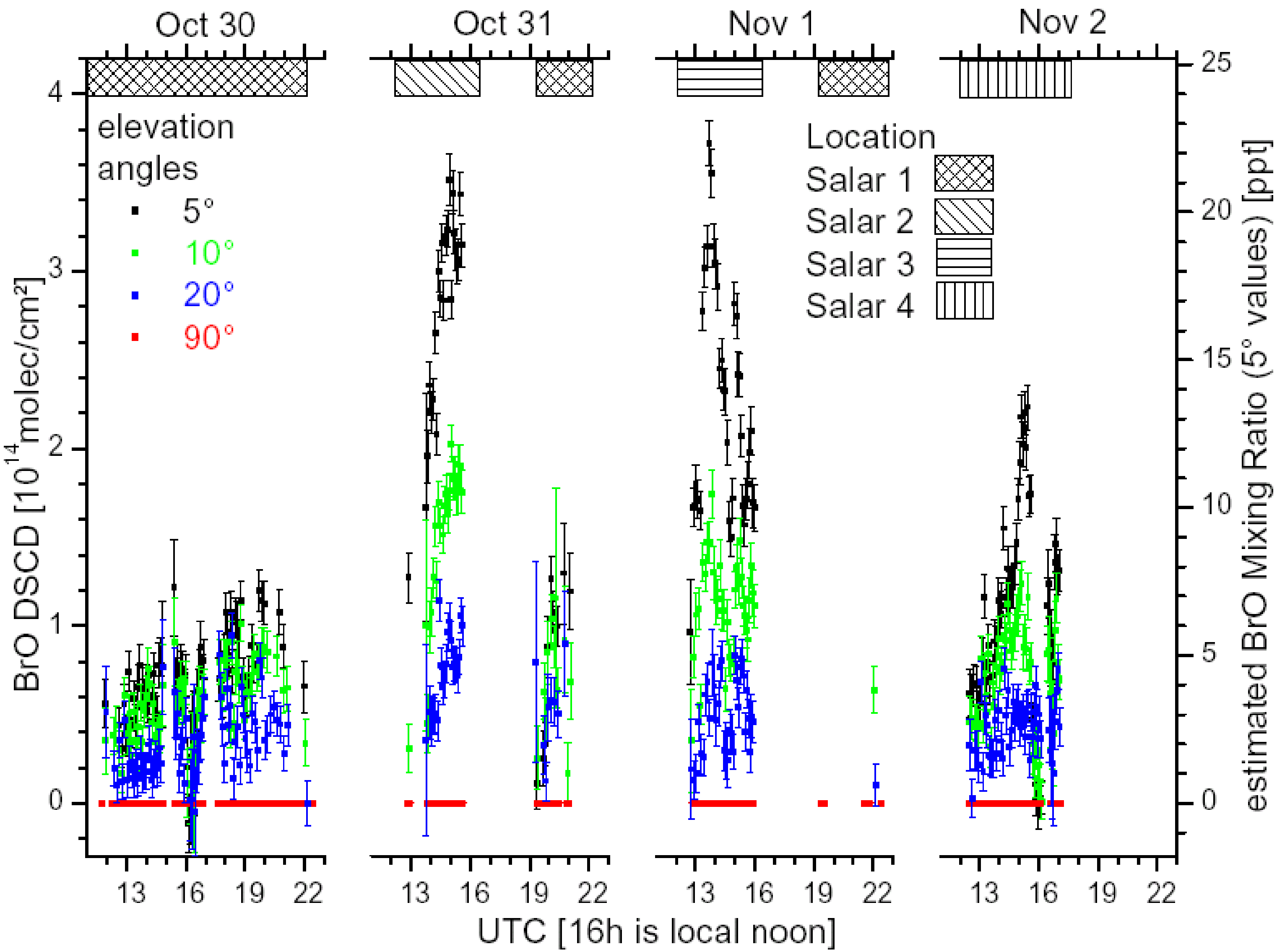
H.J. Veitel, Ph.D. thesis

Mini - MAX-DOAS Instrument at the Salar de Uyuni (Bolivia), Nov. 2002 (N. Bobrowski, G. Hönninger)

Salar de Uyuni (Bolivia), Oct./Nov. 2002

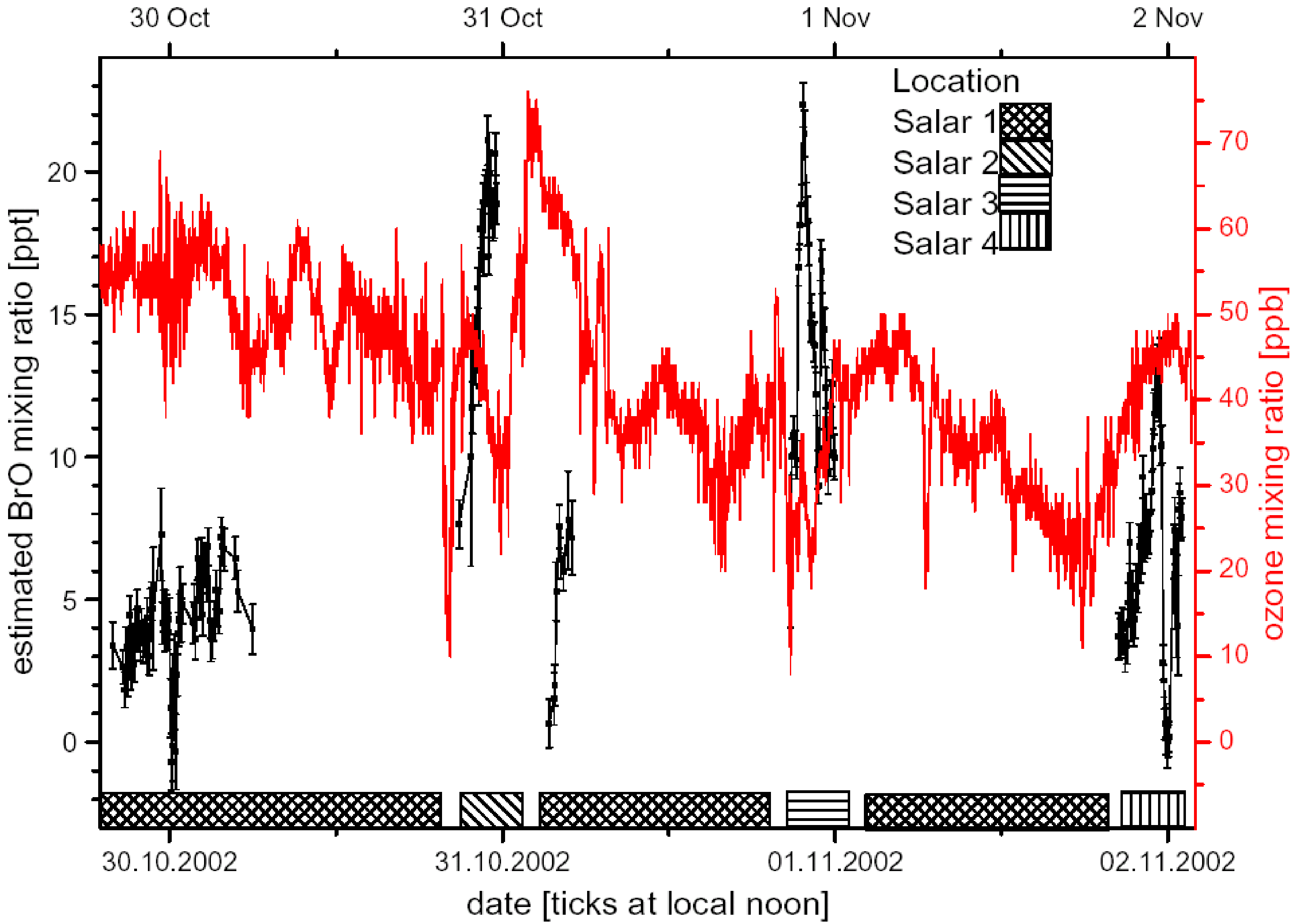
(N. Bobrowski, G. Hönninger)

BrO Measurements at the Salar de Uyuni (Bolivia), Oct./Nov. 2002 (N. Bobrowski, G. Hönninger)



Hönninger et al., GRL 31, L04101, 2004, doi:10.1029/2003GL018818.

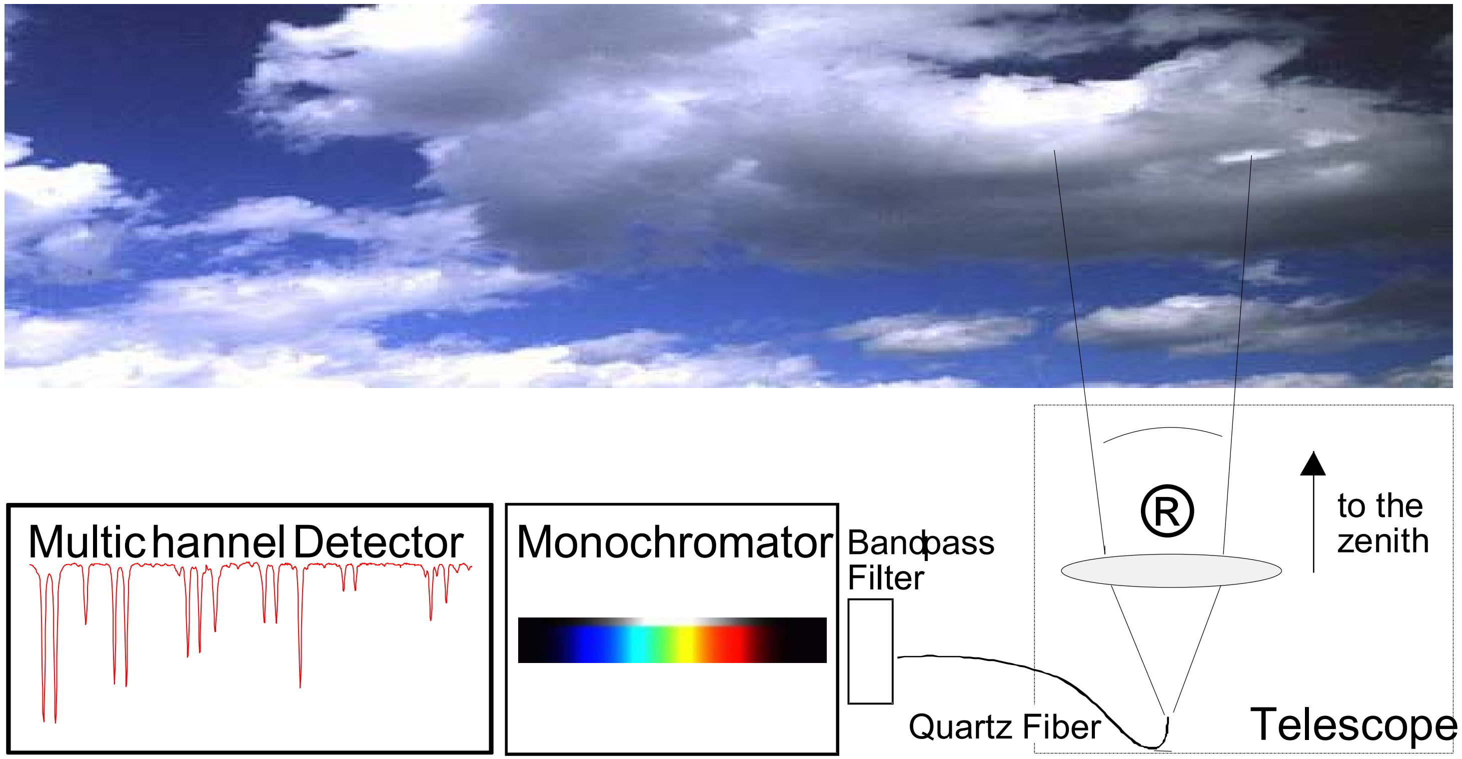
Estimated BrO Mixing Ratios and O_3 at the Salar de Uyuni (Bolivia), Oct./Nov. 2002 (N. Bobrowski, G. Hönninger)



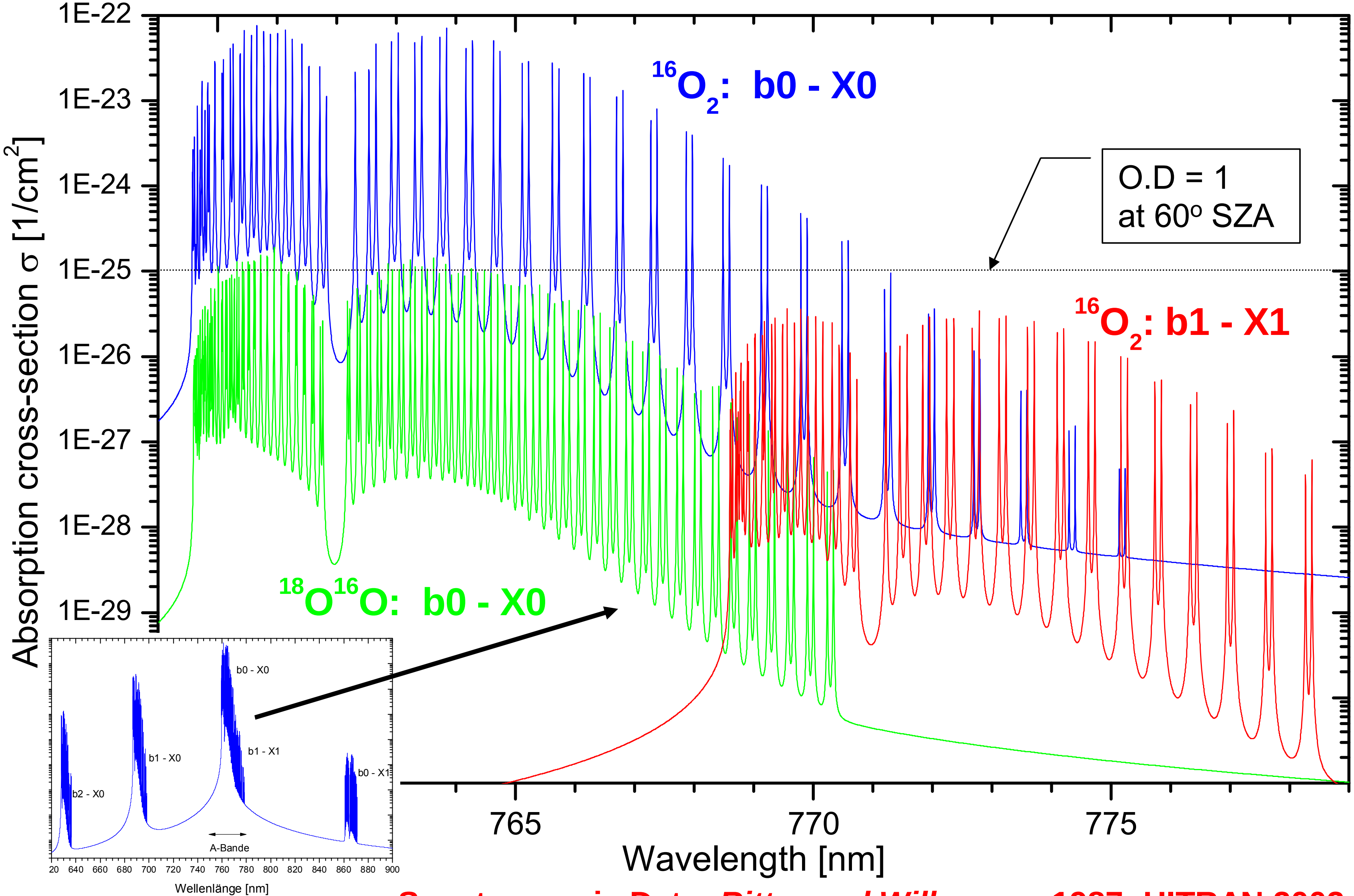
Hönninger et al., GRL 31, L04101, 2004, doi:10.1029/2003GL018818.

Photon Path Length Distribution (PDF) Inferred from High Resolution Oxygen A-Band Spectrometry

Idea: Reverse DOAS
Usually: Unknown Concentration - Known Pathlength
Here: Known Concentration - Unknown Pathlength
The Solar photon path length (distribution) in the atmosphere is inferred from DOAS measurements of an atmospheric absorber of known conc. (O_2, O_4, O_3)

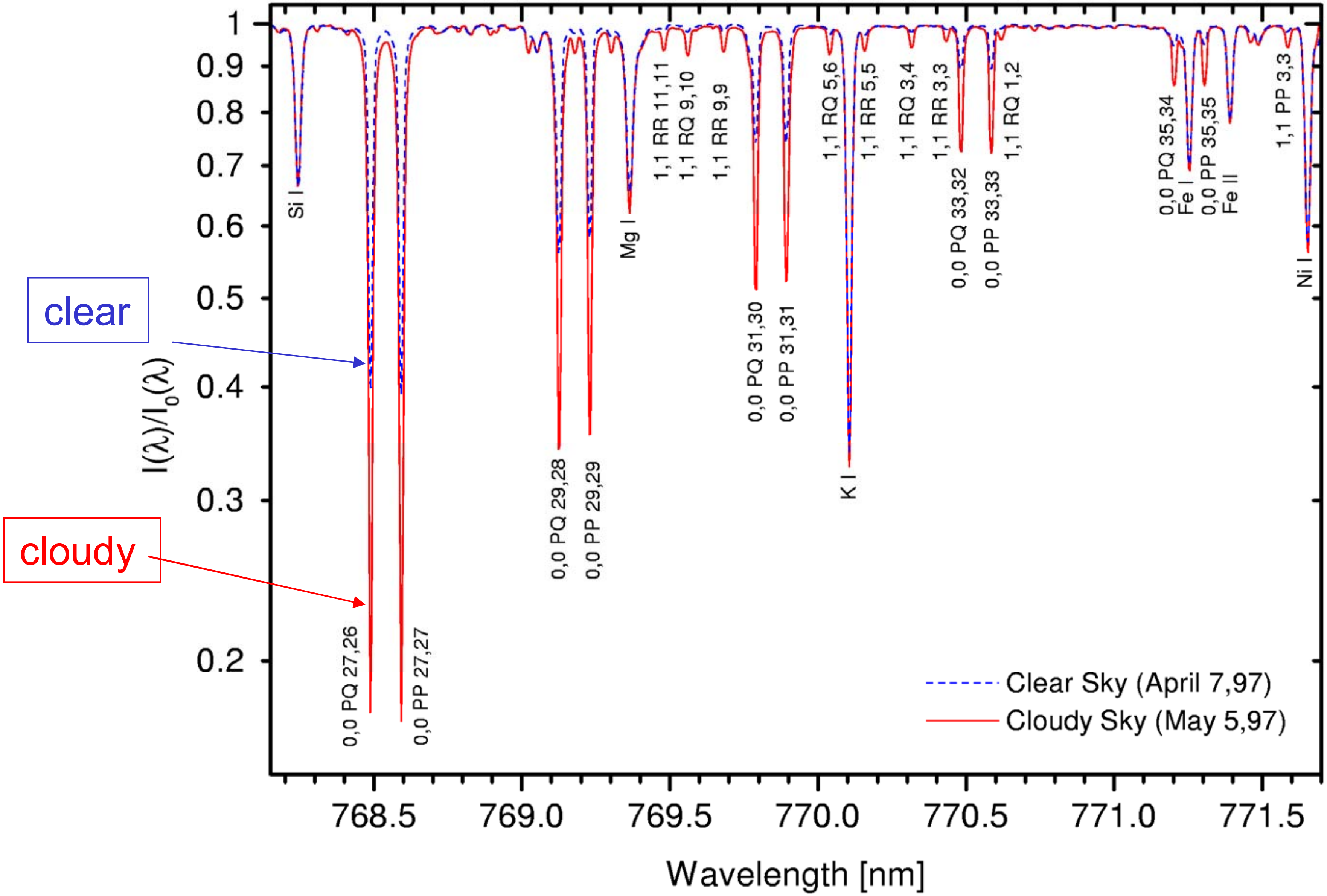


The Oxygen A-Band ($^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$)



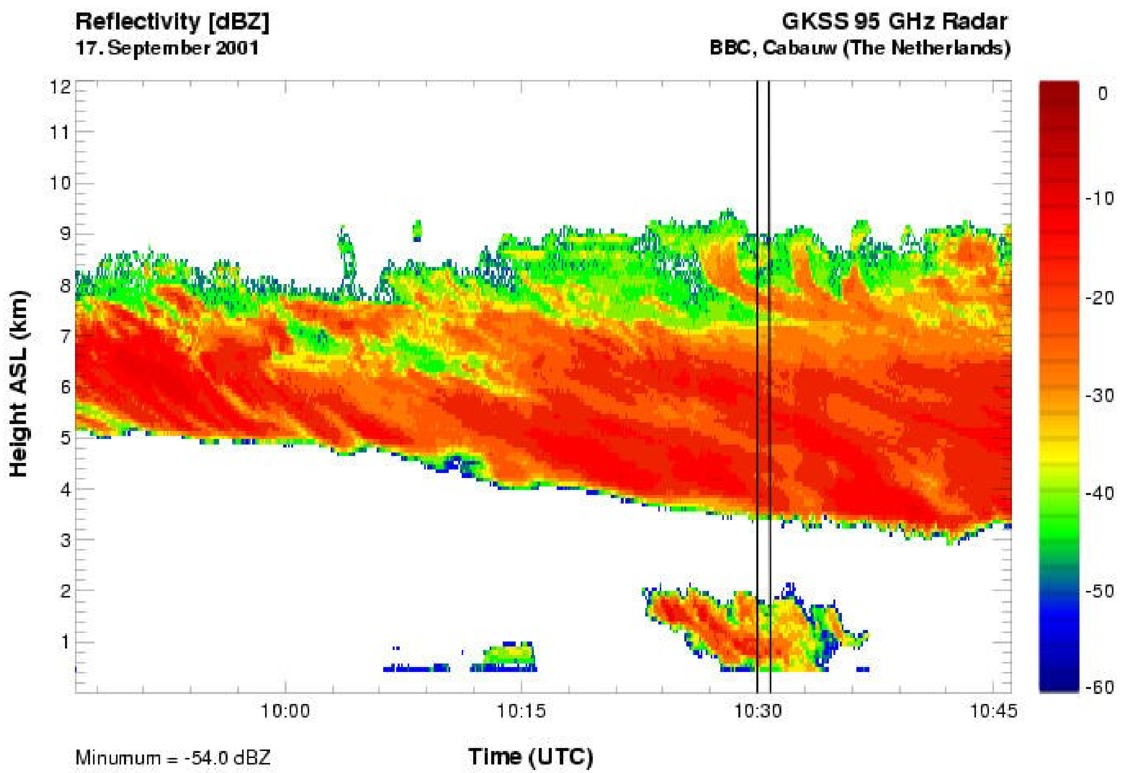
Spectroscopic Data: *Ritter and Wilkerson*, 1987; HITRAN 2002

Clear and Cloudy Sky Measurement of the O_2 A-Band

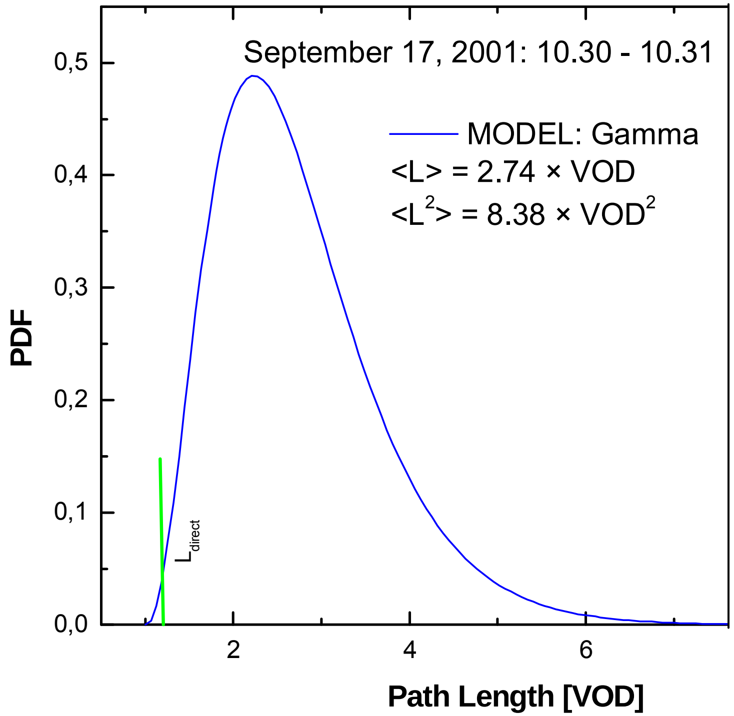


The Cloud Cover and Inferred Photon Path Distr. Fu.

(Sept. 17, 2001, UT 9:45 - 10:45)



K. Pfeilsticker, Th. Scholl



Cloud structure (backscattering ratio measured by the 95 GHz GKSS Radar) on Sept. 17, 2001, UT 9:45 - 10:45.

Inferred PDF assuming a Γ-type PDF distribution. The inferred PDF moments are given in units of vertical atmospheres

Specia thanks to:

Steffen Beirle
Nicole Bobrowski (not on foto)
Klaus-Peter Heue (not on foto)
Ilia Louban (not on foto)
Christoph Kern
Dennis Pöhler
Roman Sinreich
Thomas Wagner (not on foto)

Summary

- Spatially resolved DOAS techniques are rapidly developing.
- In particular new technologies like I-DOAS and ToTaL-DOAS will allow spatially resolved measurements at relatively little effort.
- Advances in technology like LED-DOAS will make active Tomographic DOAS – measurements possible.
- While retaining the traditional advantages of DOAS:
  - inherent calibration
  - simplicity
  - real time capability
  - non contact measurements

Further Information ...

U. Platt, University of Heidelberg, Germany
J. Stutz, University of California, USA

Differential Optical Absorption Spectroscopy

Principles and Applications

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Also:

http://troposat.iup.uni-heidelberg.de/index.html