Due applicazioni della fotometria solare allo studio della qualità dell'aria: determinazione del diossido di azoto e delle proprietà ottiche degli aerosol

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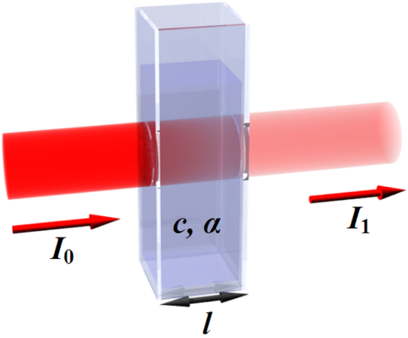
Introduction

Bouguer-Lambert-Beer law

$$dI = -K_{ext} I \rho ds \qquad (1)$$

$$[K_{ext}] = \frac{m^2}{kg} \qquad (2)$$



[Wikipedia]

Troposphere

- mostly produced from high temperature processes
- one of the most important precursors of tropospheric ozone
- controls the OH radical
- criteria pollutant (very reactive, dangerous for human health: highly oxidant and carcinogenic)
- related to acid rain (HNO_3 is very soluble in water)
- locally contributes to radiative forcing

Stratosphere

- catalyst of ozone destruction (25÷40 km, Crutzen)
  - ∼50% of ozone removal is due to NO_2
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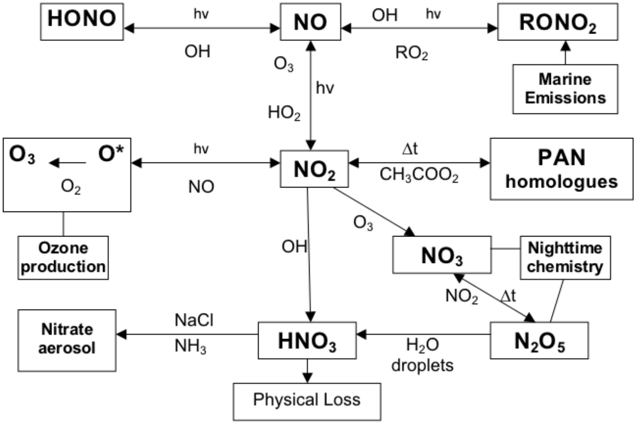
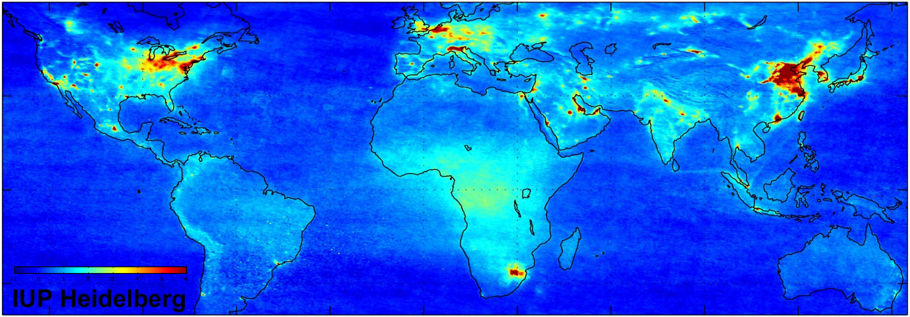
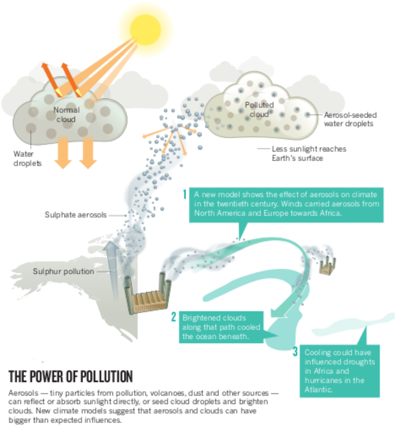
Introduction

NO_2 in the atmosphere





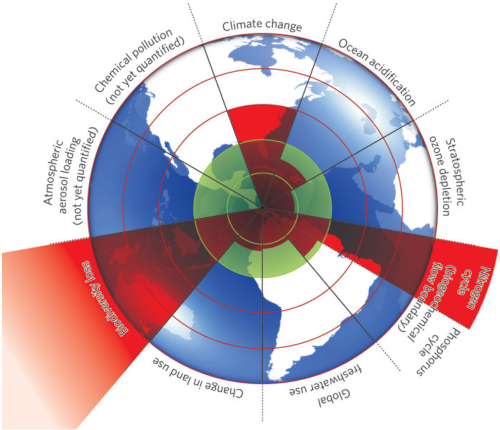
[SCIAMACHY]


Normal cloud
Water droplets
Polluted cloud
Aerosol-seeded water droplets
Less sunlight reaches Earth's surface
Sulphate aerosols
Sulphur pollution
1 A new model shows the effect of aerosols on climate in the twentieth century. Winds carried aerosols from North America and Europe towards Africa.
2 Brightened clouds along that path cooled the ocean beneath.
3 Cooling could have influenced droughts in Africa and hurricanes in the Atlantic.
THE POWER OF POLLUTION
Aerosols — tiny particles from pollution, volcanoes, dust and other sources — can reflect or absorb sunlight directly, or seed cloud droplets and brighten clouds. New climate models suggest that aerosols and clouds can have bigger than expected influences.

[Nature]

Introduction

Aerosols



[Nature]

Introduction

Solar photometry represents a valuable, alternative approach to air quality monitoring!

[ARPA VdA]

Nitrogen dioxide

Aim of present research

- employ a Brewer MKIV spectrophotometer to accurately measure total NO_2 content (and other species as well?) in the visible range
  - accurately characterize Brewer #066
  - improve/redesign the retrieval algorithm (new cross-sections, better techniques, ...)
  - calibrate Brewer #066 ←no calibrated standard MKIV for NO_2 measurements is available worldwide
  - compare the results of ZS and DS techniques using MKIV
  - satellite and ground-based instruments intercomparisons?

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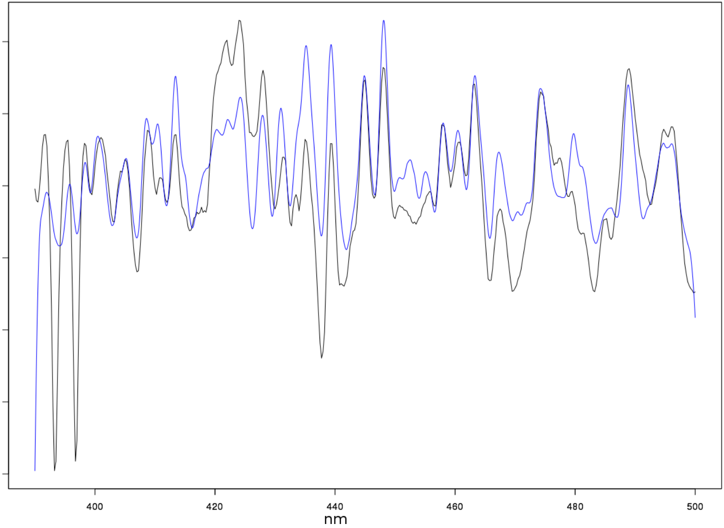
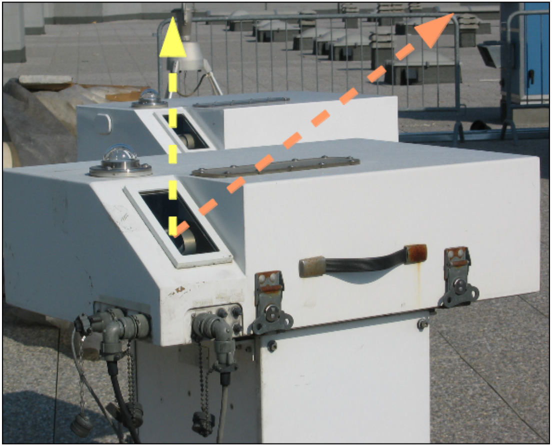
Nitrogen dioxide

Preliminary analysis on solar spectra (Varimax PCA)



Nitrogen dioxide

The Brewer spectrophotometer



Mostly used for ozone measurements (UV)

Nitrogen dioxide

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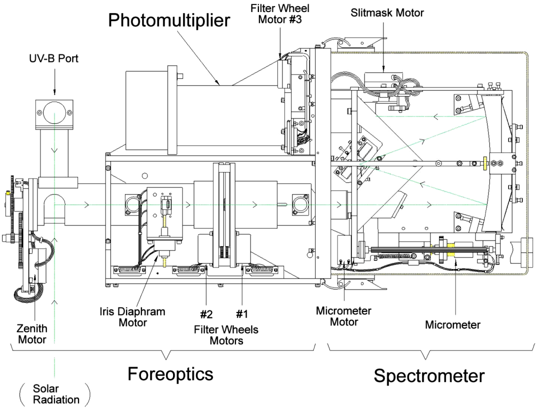
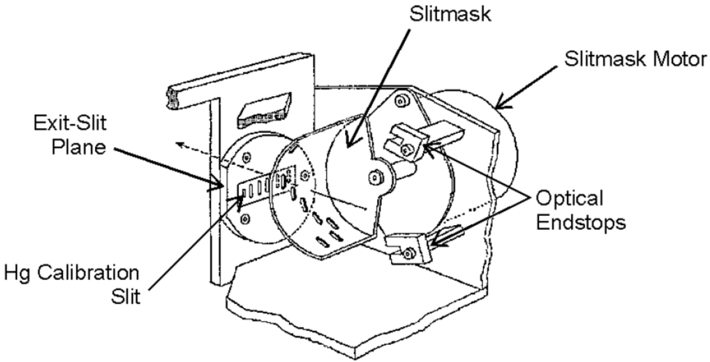


[Kipp&Zonen]

Nitrogen dioxide

The Brewer spectrophotometer



[Kipp&Zonen]

Characterization

- Focus in the visible range
- Wavelength-steps dispersion function
- Filter transmission in the visible
- Internal polarization
- Straylight
- Temperature dependence

New routines were developed

Brewer #066 at Plateau Rosa (3500 m asl), July 2011

$$
\begin{aligned}
F_{corr}(\lambda_i) =& ETC(\lambda_i) - [K_{NO_2}(\lambda_i)\mu_{NO_2}X_{NO_2} \\
&+ K_{O_3}(\lambda_i)\mu_{O_3}X_{O_3} \\
&+ \delta_{aer}(\lambda_i)\mu_{aer}]
\end{aligned} \tag{3}
$$

- the contribution of other atmospheric species is assumed to be negligible
- F_{corr} takes into account the attenuation of the filters and Rayleigh scattering

Nitrogen dioxide

The classical Brewer algorithm

$$\Sigma\gamma_i F_i = \Sigma\gamma_i ETC_i - \mu_{NO_2} X_{NO_2}(\Sigma\gamma_i K_i) \tag{4}$$

$$MS_9 = NB_1 + M_2 MS_{11} NA_1 \tag{5}$$

- only NO_2 contribution remains if weighting coefficients are correctly calculated
- the retrieved NO_2 content depends on the NO_2 X-secs
- weighting coefficients depend on the X-secs used for species different from NO_2
- effective X-secs strongly depends on operational wavelengths and shape of the transmission function

Nitrogen dioxide

The classical Brewer algorithm

$$\begin{pmatrix} \sigma_{O_3}(\lambda_1) & \sigma_{O_3}(\lambda_2) & \sigma_{O_3}(\lambda_3) & \sigma_{O_3}(\lambda_4) & \sigma_{O_3}(\lambda_5) \\ \beta_{Ray}(\lambda_1) & \beta_{Ray}(\lambda_2) & \beta_{Ray}(\lambda_3) & \beta_{Ray}(\lambda_4) & \beta_{Ray}(\lambda_5) \\ \delta_{aer}(\lambda_1) & \delta_{aer}(\lambda_2) & \delta_{aer}(\lambda_3) & \delta_{aer}(\lambda_4) & \delta_{aer}(\lambda_5) \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \gamma_1 \\ \gamma_2 \\ \gamma_3 \\ \gamma_4 \\ \gamma_5 \end{pmatrix} = \mathbf{0}_{\mathbf{K}_{4,1}}$$

i.e.

$$\begin{cases} \vec{\gamma} \perp \vec{\sigma_{O_3}} \\ \vec{\gamma} \perp \vec{\beta_{Ray}} \\ \vec{\gamma} \perp \vec{\delta_{aer}} \\ \vec{\gamma} \cdot (1,1,1,1,1) = 0 \end{cases}$$

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$\vec{\gamma} \in \mathbf{ker}(\mathbf{A}) \rightarrow$ only 1 dimension left (normalization)

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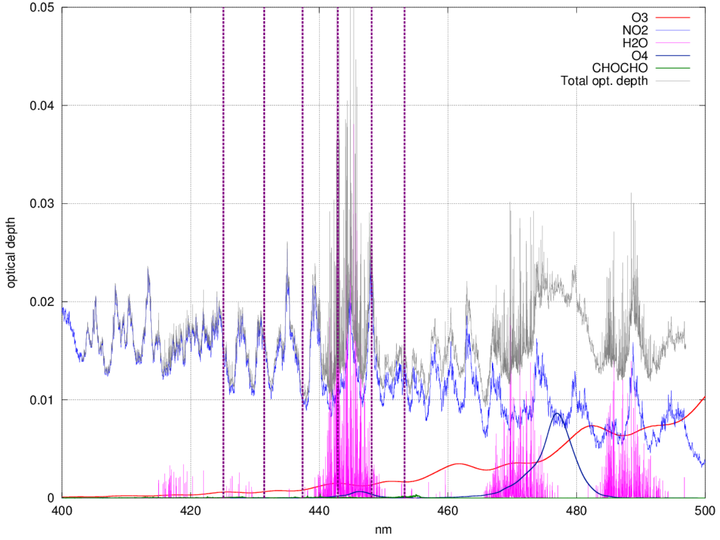

Nitrogen dioxide

Algorithm improvements

We need additional degrees of freedom to remove influence of all absorbers

- add 1 slit and search for $\vec{\gamma}$ so that $|\vec{\gamma} \cdot \sigma_{\vec{NO_2}}| = max$
- **or** add 1 slit and search for $\vec{\gamma}$ so that $\vec{\gamma} \perp \sigma_{\vec{O_4}}$
- **or** add 1 slit and search for $\vec{\gamma}$ so that $\vec{\gamma} \perp \sigma_{\vec{H_2}O}$
- search for a new operating step of micrometer $\rightarrow$ new set of wavelengths (all past data are lost)

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Alternative approach: **jump scans** $\rightarrow$ increase the number of equations and determine more unknowns:

- NO_2
- O_3
- O_4
- H_2O
- Rayleigh
- aerosol optical depth (AOD)
- Ring effect
- effective NO_2 temperature
- wavelength misalignments

Best if overconstrained system $\rightarrow$ SVD / least squares solution

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Best if overconstrained system $\rightarrow$ SVD / least squares solution

- calibration of Brewer #066 (Langley plot)
- determination of air mass factors (AMFs) for direct sun (DS) and zenith sky (ZS) measurements
- $\rightarrow$ need of photochemical models?
- comparison between the two viewing geometries

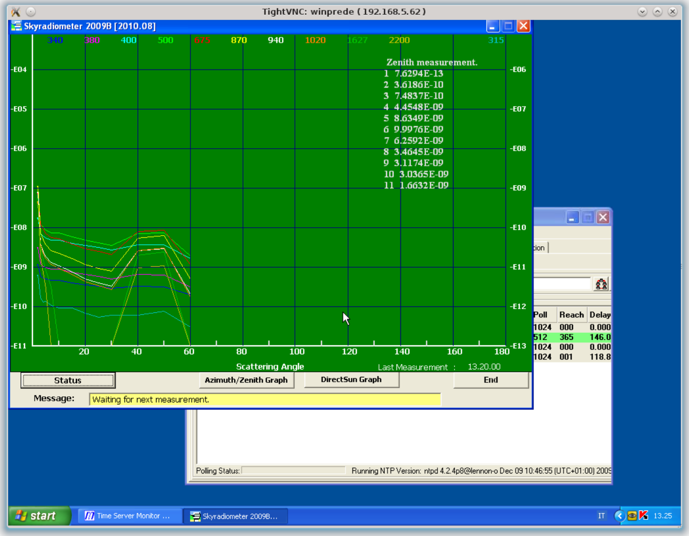
Aerosol properties
POM02 photometer

Aerosol properties

- supported by Euroskyrad network (NRT processing, quality control, comparison to other sites, etc.)
- several wavelengths (315, 340, 380, 400, 500, 675, 870, 940, 1020, 1627 and 2200 nm);
- two different collimators, but same detector;
- it is possible to retrieve many aerosol properties (which can also be useful for radiative transfer issues)
  - aerosol optical depth (AOD);
  - single scattering albedo;
  - real and imaginary refractive index;
  - Angstrom exponent;
  - distribution size
  - phase function

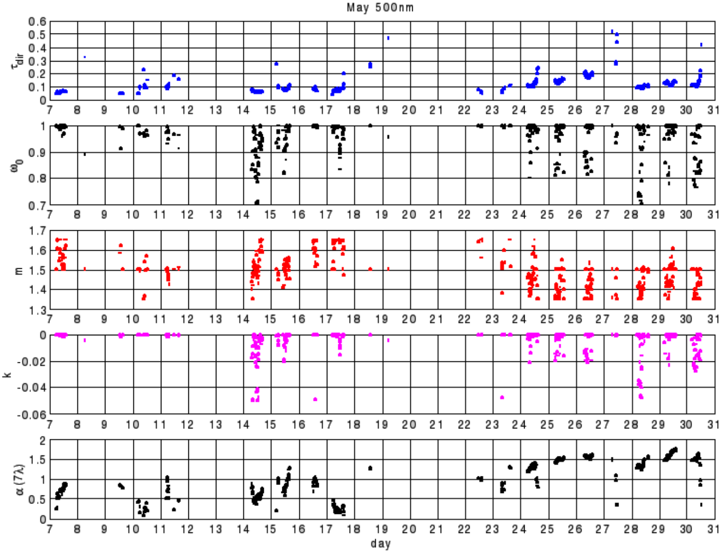
Aerosol properties

POM02 photometer



Aerosol properties

First results (Brewer)



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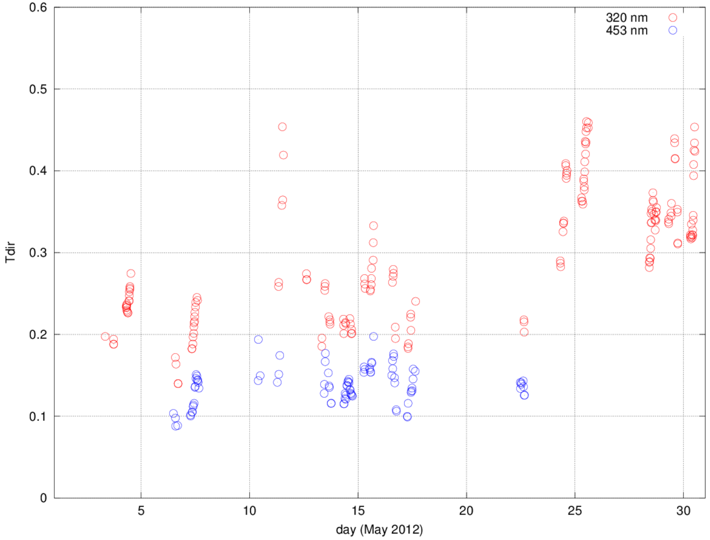

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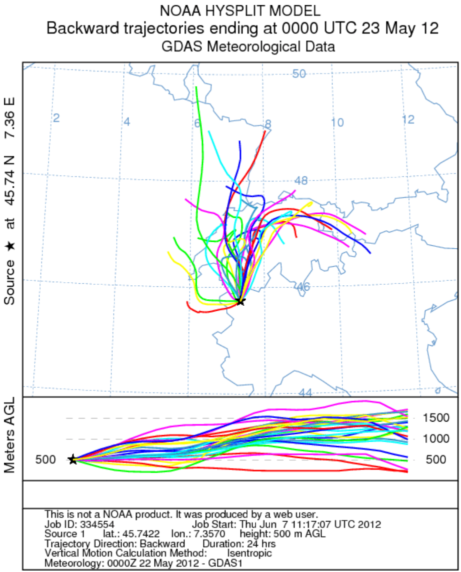

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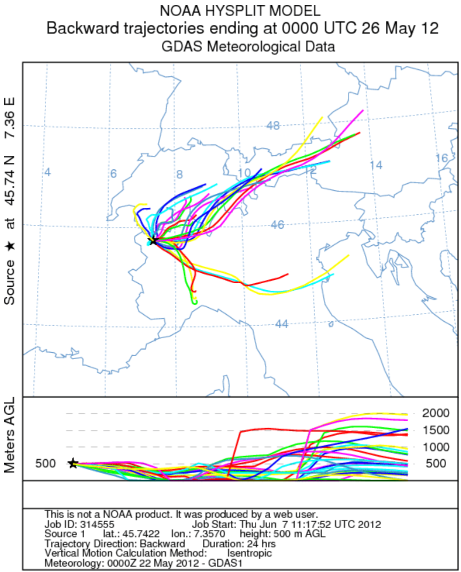

Conclusions

- photometric techniques cannot replace local measurements;
- i.e. they does not work with cloudy sky;
- however, they represent a complementary approach to air/climate monitoring;
- photometric measurements are representative of a wide area;
- solar monitoring has great importance!