Remote Sensing of Atmospheric Trace Gases

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Remote Sensing of Atmospheric Trace Gases: Outline

- **Ground-Based Differential Optical Absorption Spectroscopy (DOAS):**
  - The Beer-Lambert Law
  - Multi-Axis DOAS
  - Inverse modelling: Retrieval of trace gas and aerosol vertical profiles from MAX-DOAS
  - Longpath-DOAS
  - Cavity-Enhanced DOAS
Why measuring Atmospheric Trace Gases from the Ground?

**Satellite Observations**

- provide global distribution of atmospheric trace gases
- only very limited information on the vertical distribution of trace gases
- only one (or very few) measurement(s) per day, always at (nearly) the same time

**Ground-Based MAX-DOAS Observations**

- provide vertical distribution of trace gases in the planetary boundary layer
- high temporal resolution (~15 min.)
- measurements only at a single location
Absorption in the Earth’s atmosphere

Radiation Transmitted by the Atmosphere

- Downgoing Solar Radiation: 70-75% Transmitted
- Upgoing Thermal Radiation: 15-30% Transmitted

Total Absorption and Scattering

Major Components:
- Water Vapor
- Carbon Dioxide
- Oxygen and Ozone
- Methane
- Nitrous Oxide
- Rayleigh Scattering

DOAS
Absorption spectra of trace gases in the UV/Vis

Wavelength [nm]

Absorption spectra of trace gases in the UV/Vis
Absorption of light by gases

The absorption strength (optical density) depends on

- the concentration of the gas
- the length of the light path
- the ability of each molecule to absorb light of a specific wavelength (absorption cross section)

The amount of gases along a light path can be determined using their individual absorption structure.
Differential Optical Absorption Spectroscopy - DOAS -

Assume a light beam traversing an infinitesimally small air parcel containing a mixture of $N$ gases with concentrations $\rho_i$ ($i=1..N$)

The extinction of light is described by the Beer-Lambert law:

$$I(\lambda, L) = I_0(\lambda) \cdot \exp\left\{-\int_0^L \sum_i \sigma_i(\lambda, T, p) \cdot \rho_i(s) + \left(\sigma_{Rayl}(\lambda) + \sigma_{Mie}(\lambda)\right) \cdot \rho_{air}(s) \right\} \cdot ds$$

- $I_0, I$: Incident and transmitted light intensity
- $\sigma_k$: Wavelength, pressure and temperature dependent absorption cross section of the $k^{th}$ absorber
- $\sigma_{Rayl}$: Rayleigh cross section
- $\sigma_{Mie}$: Mie cross section (scattering on particles with $r \gg \lambda$)
Remote sensing of atmospheric trace gases: **Differential Optical Absorption Spectroscopy** (DOAS)

When sampling the light intensity on a discrete wavelength grid $\lambda_k$ (and neglecting the pressure and temperature dependence of the absorption cross section), the Beer-Lambert law can be solved numerically by minimising

$$
\chi^2 \equiv \sum_k \left[ \ln I(\lambda_k) - \ln I_0(\lambda_k) + \sum_i \sigma_i(\lambda_k) \cdot S_i + \sum_n c_n \cdot \lambda_k^n \right]
$$

to determine the integrated concentrations along the light path (Differential Slant Column Density, dSCD):

$$
dS_i = \int_0^L \rho_i(s) \cdot ds - S_{ref}
$$

The Optical Density is defined as $\tau(\lambda) \equiv \sigma(\lambda) \cdot S = -\ln \left( \frac{I(\lambda)}{I_0(\lambda)} \right)$

The polynomial $\sum c_n \lambda_k^n$ removes the broad-banded spectral structure caused by Rayleigh- and Mie-scattering. Thus only compounds with high frequent absorption features can be detected. The high frequent parts of $\sigma$ and $\tau$ are referred to as the differential absorption cross section and optical density $\sigma'$ and $\tau'$.
DOAS Analysis

- Simultaneous detection of several trace gases
- Retrieval algorithm based on non-linear least squares algorithm
- Optical densities of less than $5 \times 10^{-4}$ can be detected
- Detection limit depends on
  - residual noise
  - light path length
  - absorption cross section
  - possible interference with other species
Multi-AXis Differential Optical Absorption Spectroscopy (MAX-DOAS)

- Variation of SCD with solar zenith angle (SZA) allows to determine the stratospheric VCD
- Sequential measurements at different elevation angle allow for the retrieval of the trace gas vertical distribution
- Measurements of an absorber with known vertical distribution (oxygen collision complex \(O_4\)) allow for the retrieval of aerosol extinction profiles
A typical MAX-DOAS Instrument
BrO DSCDs
OASIS Campaign, Barrow, AK, 2009

Clear sky
U-shaped profile → Stratospheric BrO
Low visibility
Separation of elevation angles → Tropospheric BrO

Elevation angle

01° 02° 05° 10° 20° 90°

-2 0 2 4 6 8 10 12 14 16

0 2 4 6


dSCD BrO
\(10^{14} \text{molec/cm}^2\)

dSCD O_4
\(10^{43} \text{molec}^2/\text{cm}^5\)
Monte-Carlo Modelling of Radiative Transfer

- **Aim:** to model the transport of radiation through the atmosphere as a function of:
  - Trace gas vertical profiles
  - Viewing geometry
  - Atmospheric state (T, p, humidity, aerosols, …)

- **Modelled quantities are:**
  - Radiances
  - (Box-) airmass factors
  - Derivatives of measured quantities with respect to atmospheric state parameters

Simulation of the radiative transfer through broken clouds

Backward modelling
Forward modelling

Random sampling of photon paths

Rayleigh
Cloud and aerosols
Absorption
Ground reflection

Deutschmann et al., JQSRT, 2013
Retrieval of Trace Gas and Aerosol Vertical Profiles

Spectra

DOAS Analysis

- Trace gas dSCDs
- Trace gas errors

Trace Gas Retrieval

- a priori trace gas profile
- a priori covariance

Aerosol Retrieval

- O$_4$ dSCDs
- O$_4$ errors
- Rel. Intensity
- Intensity errors

- Aerosol profile
- Aerosol opt. properties
- Retrieval covariance

Radiative Transfer Model
Example for Trace Gas and Aerosol Retrieval
CINDI Campaign, Cabauw/Netherlands, 2009

O₄ dSCDs

NO₂ dSCDs

Aerosol Profiles

NO₂ Profiles
Trace Gas and Aerosol Retrieval – Averaging Kernels
CINDI Campaign, Cabauw/Netherlands, 2009

02.07.2009, 12:00

Aerosol Averaging Kernel

NO$_2$ Averaging Kernel

Altitude [km]

$\Delta s = 1.9$

$\Delta s = 3.1$
Hohenpeißenberg, Germany
In collaboration with German Weather Service (DWD)
NO$_2$ Profiles, 8.7.2010

NO$_2$ Surface Mixing Ratio Comparison with in situ
Hohenpeißenberg, Germany

NO$_2$ Surface Mixing Ratio – Comparison with in situ measurements
Comparison of aerosol extinction profiles
CINDI Campaign, Cabauw, Netherlands,

July 3, 2009

July 4, 2009
MAX-DOAS Measurements of BrO and Aerosols in Barrow, Alaska during the OASIS field Campaign, February-April 2009

Udo Frieß and Holger Sihler

Frieß et al., The Vertical Distribution of BrO and Aerosols in the Arctic: Measurements by Active and Passive DOAS, JGR, 2011
200 km visibility
500 m visibility
100 m visibility
50 cm visibility
MAX-DOAS Measurements of BrO and Aerosols in Barrow, Alaska

Example for the Diurnal Variation of Aerosol Extinction

11:00 Extinction profiles - Barrow, Alaska 15:15

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MAX-DOAS Measurements of BrO and Aerosols in Barrow, Alaska

Comparison with Ceilometer

Ceilometer, vertical resolution degraded to MAX-DOAS

MAX-DOAS
MAX-DOAS Measurements of BrO and Aerosols in Barrow, Alaska

Comparison with Sun Photometer

- MAX-DOAS
- Sun photometer
- Sun photometer, quality filtered

Date 2009
MAX-DOAS Measurements of BrO and Aerosols in Barrow, Alaska
Direct measurement of the average trace gas concentration along the light path
Long-Path DOAS in Barrow
The Sending/Receiving Telescope
Long-Path DOAS in Barrow
Retro Reflector Setup

Long light path
Short light path
Comparison of BrO measured by LP-DOAS and CIMS (Chemical Ionisation Mass Spectrometry)

A comparison of Arctic BrO measurements by a chemical ionization mass spectrometer (CIMS) and a long path differential optical absorption spectrometer (LP-DOAS), submitted to J. Geophys. Res., 2010.
Tomographic LP-DOAS

- Numerous light paths with two LP-DOAS instruments using mirrors and retro-reflectors.
- The measured averaged concentrations along the light paths allow to reconstruct the concentration field using tomographic methods.

How to fit a long light path into a compact setup

Design of Active DOAS Instrument

Fibre Bundle

Main Mirror

Atmosphere

Light Path

Retro Reflector Array

CE-DOAS Principle

$I_{in}$

HR - Mirrors $R > 99.9\%$

$d \approx 0.5...2m \rightarrow$ Optical Path Length $0.5km...10km$

$I_{zero \ reflection}$

$+I_{two \ reflection}$

$+I_{four \ reflection}$

$+\ldots=I$
The NO$_2$ CE-DOAS Instrument

Cavity:
- $R \approx 99.975$ (@445nm)
- Opt. Path Length $L_0 \approx 1.8$km

- Weight $\sim 5$kg
- Blue Led (Peak at 445nm)
- Fit Range 436nm - 453nm

- Det. Limit 1ppb @ 2s
  <0.5ppb @ 10s
The NO$_2$ CE-DOAS Instrument
CE-DOAS Theory

• Optical density is calculated relative to intensity transmitted by a "zero air" filled resonator.

\[
\ln \left( \frac{I(\lambda)}{I_0(\lambda)} \right) = D_{CE}(\lambda) = L_{eff}(\lambda) \left( \sum_i \bar{c}_i \sigma_i(\lambda) + \epsilon_b(\lambda) \right)
\]

• Difference to LP-DOAS:
  • Wavelength dependent path length
  • Path length must be calibrated:
    -> Purge cavity with gases of known extinction

We use an alternating purge with Helium and zero air
CE-DOAS Theory

- Length of optical light path depends on extinction in the resonator. **Strong absorber** \(\rightarrow\) shorter light path.

\[ L_{eff}(\lambda) = L_0(\lambda) \cdot \frac{D_{CE}(\lambda)}{\exp(D_{CE}(\lambda)) + 1} \]

with \( \ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = D_{CE}(\lambda) \)

[Platt et. al. 2009]

- Path length correction depends on **absolute** optical density.
- Direct correction with meas. \(D_{CE}\) possible but requires:
  - light source with very stable intensity
  - very stable optomech. setup
  \(\rightarrow\) Difficult to achieve.
  \(\rightarrow\) Temp. stab. of LED required

\[ L_0 = 1.8 \text{ km} \]
Mobile Meas. in Hong Kong Dec. 13-20, 2010

Central area of Hong Kong

LP-DOAS Light Path
Open Path CE-DOAS Measurements of IO in Antarctica

- Open path CE-DOAS
- Spectral region: 425-455 nm
- Mirror distance: ~1.9 m
- Light source: blue LED
- Spectrometer: Avantes AvaSpec-ULS2048
- Ring-down system with PMT tube
- Light path ~6 km
- Detection limit for IO ~0.5 ppt
- Power consumption: ~30 W
- Dimensions: 220 x 30 x 40 cm³, ~ 30 kg
- Temperature range: -45°C to +30°C
Summary

• Atmospheric remote sensing allows for the contact-free detection of atmospheric constituents (trace gases, aerosols, clouds...)

• DOAS is a versatile measurement technique:
  – Simultaneous measurement of numerous atmospheric trace gases
  – Very sensitive (< 1 ppt for some species)
  – Inherently self-calibrating
  – Can be operated from various platforms (ground, air-borne, balloon-borne, satellite borne)

• MAX-DOAS:
  – Allows for the determination of stratospheric and tropospheric trace gases and aerosols
  – Simple and robust instrumentation suitable for field experiments and long-term measurements

• LP-DOAS:
  – Very accurate measurement of the mean concentrations of trace gases along a light path of several km

• CE-DOAS:
  – Compact setup with high sensitivity due to light paths of several km on a desktop