Comparison between Trace Gas Measurements Performed with the MAX- DOAS Technique During the FORMAT Campaign

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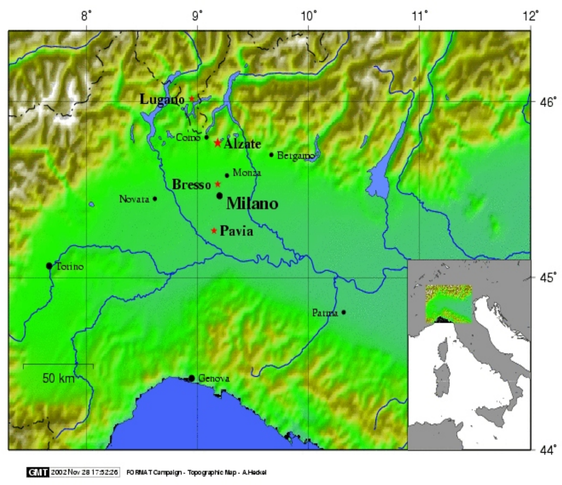
Introduction

In a period when populations in urban areas are expected to increase (more than 4% between 1995 and 2010), air pollution remains a significant issue in both health and environmental problems, leading to a higher incidence of diseases and damage on vegetation and materials.
Photochemical smog from incomplete combustion processes and burning of fossil fuel / biomass constitues one main source of air pollution in urban highly popullated regions.
Since reducing air pollution in urban areas constitues a major challenge in the next years, research programmes over the last decade strengthened the European research in atmospheric chemistry.
In order to improve the understanding on the impact of anthropogenic emissions, global measurements of key atmospheric constituents are required.
Measuring and modelling tools have undergone substantial improvements during the last decade, a large number of instruments and techniques being employed in carying out research studies.
DOAS (Differential Optical Absorption Spectroscopy) is an open path spectroscopic technique, useful for measuring trace gases of atmospheric interest with relatively large absorption cross-sections in the UV-visible wavelength range.
In contrast to satellite sensors, which may observe the free troposphere and the upper part of the boundary layer, ground based remote sensing instruments like MAX-DOAS observe the whole boundary layer where the highest mixing ratios are expected. In addition they are also sensitive to the free troposphere and stratosphere.
MAX-DOAS (multi-axis DOAS) provides off-axis measurements in addition to the zenith scattered light. Although a new method and yet to be proven for formaldechyde determinations, its estimated detection limit is about 1ppb for the troposphere.
A comparative overview on the analysis results of MAX-DOAS measurements taken at the same site by three different groups is presented. Though the same technique was used, differences existed regarding the data acquisition and analysis.

FORMAT project

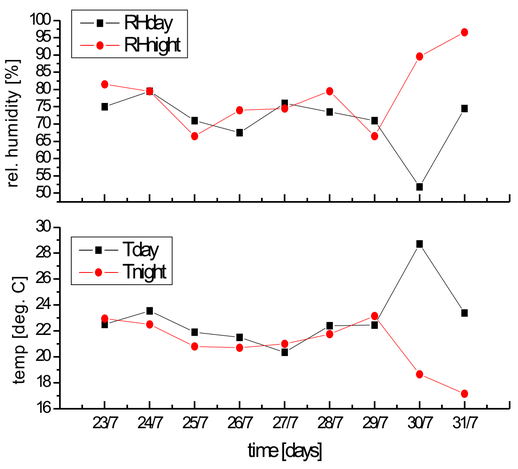
Formaldehyde is a good indicator of photochemical smog, so it is important to be able to measure it in an accurate way.
FORMAT (Formaldehyde as a tracer of photooxidation in the troposphere) is an atmospheric chemistry project whose single most important objective is to improve the measurement techniques that are used to measure this compound.
One major goal of the project is to obtain a better knowledge of the concentrations and distribution of formaldehyde in the troposphere over Europe and on a global scale (through analysis of satellite data), providing in this way better insight in the extent of fossil fuel and biomass burning.
This will improve the capability of atmospheric chemistry models to calculate formaldehyde and thereby predict smog episodes.
Po Valley (northern Italy) was chosen for running formaldehyde determinations, as a typical highly polluted and densly populated region.



Po Valley and the sites of the FORMAT 2002 campaign

Measurement Site Alzate

The first time interval (last 10 days of July) of the 2002 (summer) campaign was dedicated to an intercomparison period between the instruments, an action which took place in Alzate (45°46'N, 09°09'E, 384 m altitude).
Consecutively, two of the ground based DOAS instruments moved to Bresso (45°32'N, 09°12'E) and Pavia (45°18'N, 09°17'E), both locations in the Po Basin too (north and south of the city of Milan). There they were installed to operate for the next three weeks.
Light acquisition devices have been mounted on the top of a campaign conteiner, with viewing direction of the off axis measurements pointing to the west.



Weather in Alzate during the intercomparison

Experimental Setup

The instument of the Bremen univerisity:

Acton Research spectrograph ARC 500 (focal length 500 mm, 600 l/mm grating)

CCD Princeton Instruments (1100 x 330 Pixel)

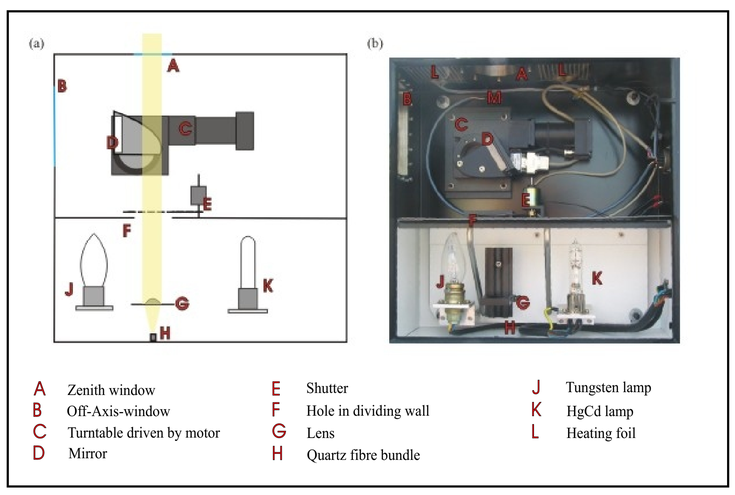
UV/vis wavelength region: 312 – 396 nm

Spectral resolution: ~0.5 nm

Targeted trace gases: O_3, No_2, O_4, BrO, HCHO.

Atmospheric observing mode: continuous alternating observations between zenith and horizon (4 off-axis viewing directions: 3°, 6°, 10° and 18°), by using a turning mirror moved by a computer controlled servomotor.

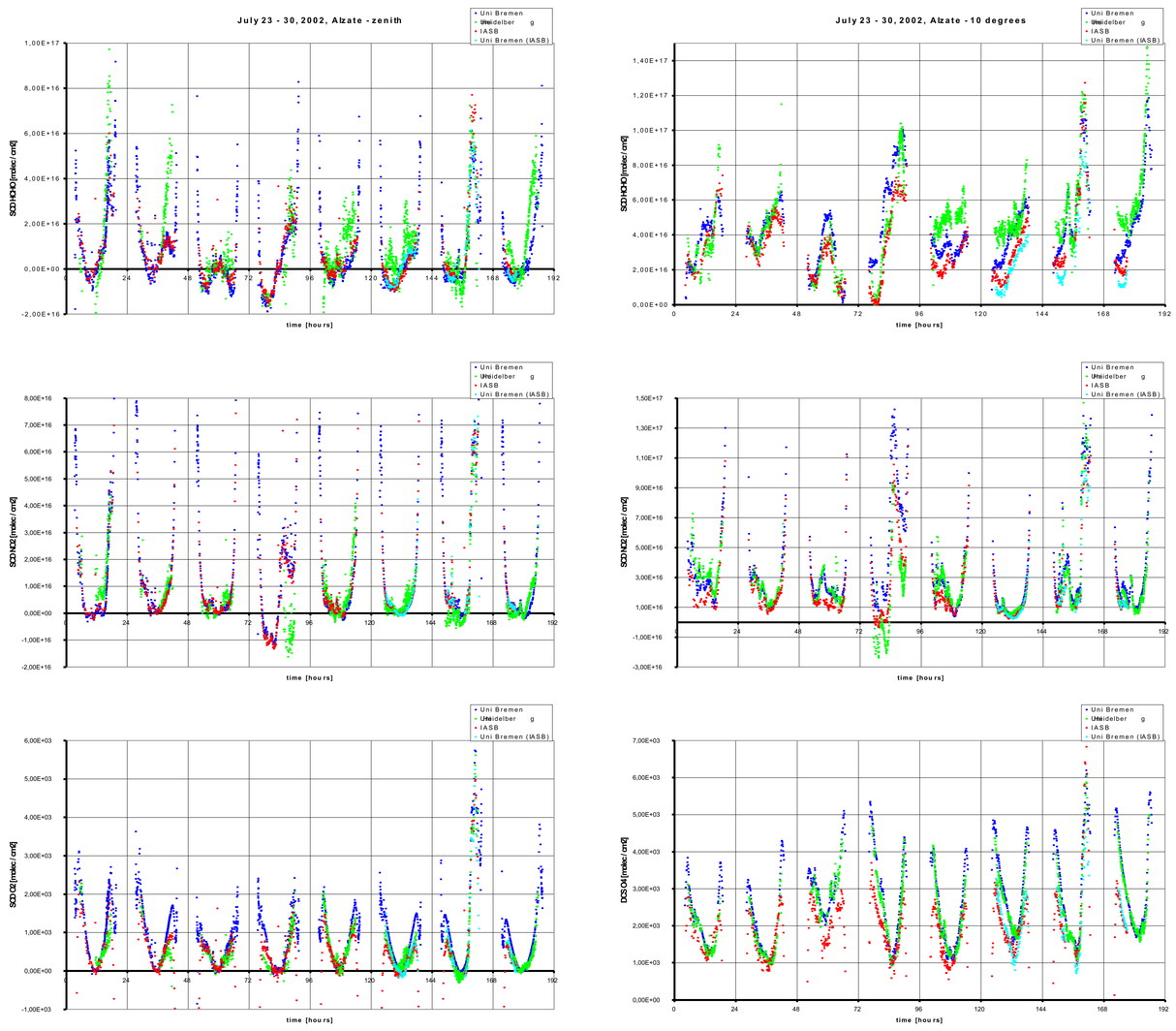
Daily calibration measurements were performed during nighttime.



Setup of the Bremen telescope

The instrument operated by the Heidelberg university was similar in termes of detection device, with differences regarding the geometry of the light acquisition module: 2 telescopes (windows) directed into the zenith and 3 telescopes for each of the two off-axis viewing directions (3° and 10°). Typically once a day (some time interval between 8 - 15) all telescopes were pointed toward zenith for calibration purposes.
The instrument of the Brussels institute (IASB) only observed zenith and one off-axis direction (10°) in a sequential mode.

Comparison of Results



Ground based measurements were taken simultaneously by several groups employing zenith and off-axis viewing geometries within the MAX-DOAS technique.
The tropospheric trace gases of interest (HCHO, NO_2 and O_4) were investigated in the near-UV spectral region by recording diurnal spectra and retrieving their trends during day-time.
A comparison between the results of the analysis is presented, in terms of time series for these compounds, observed at 90 degrees (zenith) and 10 degrees elevation angles above horizon.

- Uni Bremen, Uni Heidelberg, respectively IASB notations denote results achieved by every team for own data set and with own retrieval algorithms.
  Slant columns for analysed absorbers show larger values for smaller elevations, since tropospheric concentrations are higher for these gases than stratospheric concentrations. This demonstrates the capability of MAX-DOAS technique to derive also vertical profile information.
  Diurnal trends show excellent agreement for some of the days, as well as poor agreement for other days.
- Uni Bremen (IASB) notation denotes retrieval performed by the Bremen team on data acquired with the instrument of the Brussels group.
  In this case, differences in the values with respect to the IASB results must have been caused by the algorithms only.

In the DOAS method, a multicomponent spectrum has to be deconvoluted, so the results may depend on the deconvolution process, especially when mixing ratios close to the detection limits have to be estimated.

The results prove that significant levels of HCHO and the other compounds were present during the campaign despite reduced emissions (holiday time) and unusual weather conditions (showers prevented the accumulation of high atmospheric concentrations).
After the intercomparison period, values from different sites around Milan indicate the presence of these gases in the whole area, providing a picture of the horizontal and temporal distribution.

Conclusions

An intercomparison study has been performed on data acquired during the last 10 days of July, when all three MAX-DOAS instruments involved in the 2002 FORMAT campaign made measurements at the same site.
This study suggests the importance in obtaining a better understanding of the differences between the various devices using the DOAS ground-based measurement technique and the data analysis tools in order to reduce the disagreements that occur in reporting results.

Selected References

Acknowledgements

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See also: www.doas-bremen.de