# FORMAT Campaign

Alzate (Po Basin, Northern Italy)

July – August, 2002

## first analysis results

2002, Dec. 4

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# Outline

- motivation for studying formaldehyde (HCHO)
- sources & chemistry of formaldehyde in the atmosphere
- scientific objectives of the project and aims of the campaigns
- campaign (summer – 2002)
- data analysis
- next campaign (2003?)

***FORMAT*** *= Formaldehyde as a tracer of (photo)oxidation in the troposphere*

# Motivation of project

HCHO – most abundant of the carbonyl compounds in the atmospere

HCHO - indicator of photochemical smog

HCHO, $O_3$, $NO_2$ and $SO_2$ dominate the tropospheric photochemistry

HCHO $\rightarrow$ influence on the oxidizing capacity of the atmosphere

HCHO – dangerous for health at concentrations above 0.1 ppm

# Atmospheric Formaldehyde Production (Sources)

*Background troposphere*: major product of the photooxidation of methane ($CH_4$ is the dominant precursor of HCHO)

*Close to the surface*:

- generated by the photooxidation of both methane & NMHC (biogenic & anthropogenic sources)
- byproduct of incomplete combustion processes (anthropogenic sources)
- naturally occuring: biogenic emissions (released in air by plants)
- generated by atmospheric chemical reactions of other pollutants

($HOCH_2CH_2O \rightarrow HCHO + CH_2OH$, $CH_2OH + O_2 \rightarrow HCHO + HO_2$)

# Atmospheric Formaldehyde Chemistry (Sinks)

**1.** Photolysis (in the near UV):

$HCHO + h\nu\ (\lambda < 360\ nm) \rightarrow H_2 + CO$ (ca. 55%)

$HCHO + h\nu\ (\lambda < 338\ nm) \rightarrow H + HCO$ (ca. 45%)

($\tau_{atm} \approx 3.8 \div 8.6$ h)

$H + O_2 + M \rightarrow HO_2 + M$

$HCO + O_2 \rightarrow HO_2 + CO,$ ($CO + OH \rightarrow H + CO_2$)

($\tau_{atm} \sim$ months)

**2.** $HCHO + OH \rightarrow H_2O + HCO$

($\tau_{trop} \approx 1.5$days)

**3.** $HCHO + HO_2 \leftrightarrow OOCH_2OH$

($\tau \approx 7$hrs at $[HO_2]=5\times10^{8}cm^{-3}$)

**4.** Hydrolysis: $HCHO\ (aq.) + H_2O \leftrightarrow H_2C(OH)_2$

## Scientific objectives of the project

- improvement of experimental techniques used as measurement methods for formaldehyde atmospheric determinations
- better knowledge about (regional- and global-scale) formaldehyde distribution and concentrations in the troposphere

## Goals of the campaign

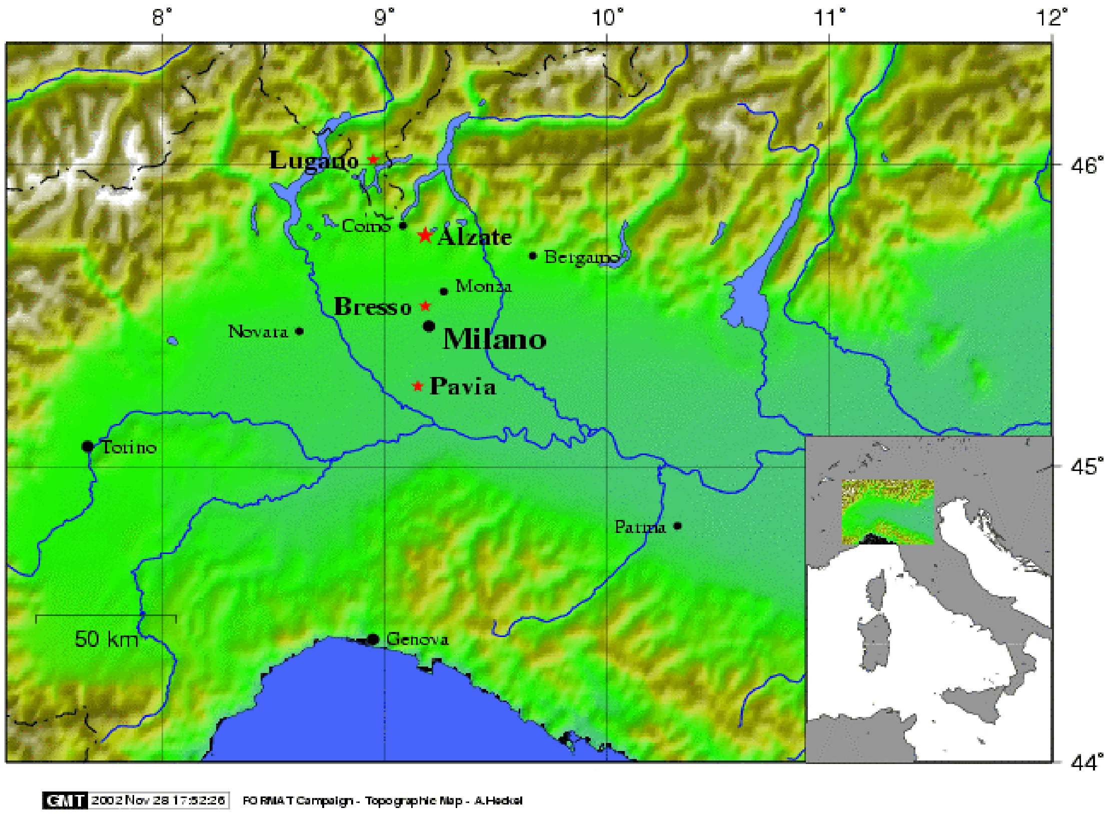
- validation of satellite data (GOME, SCHIAMACHY) regarding formaldehyde distributions in the area
- improvement of atmospheric chemistry models capabilities for calculating formaldehyde distributions and for using it as tracer of fossil fuel and biomass burning

# FORMAT Campain (July – August 2002)

Alzate: $45^o46'$N, $09^o09'$E, 384m altitude

Bresso: $45^o32'$N, $09^o12'$E

Pavia: $45^o18'$N, $09^o17'$E



## Bremen Univ: MAX-DOAS (Alzate, July 20 – August 19) & AMAX-DOAS

Viewing directions: elevation angles: $3^o$, $6^o$, $10^o$, $18^o$ & $90^o$ (zenith)

azimuth: west (20.07. – 26.07. morning)

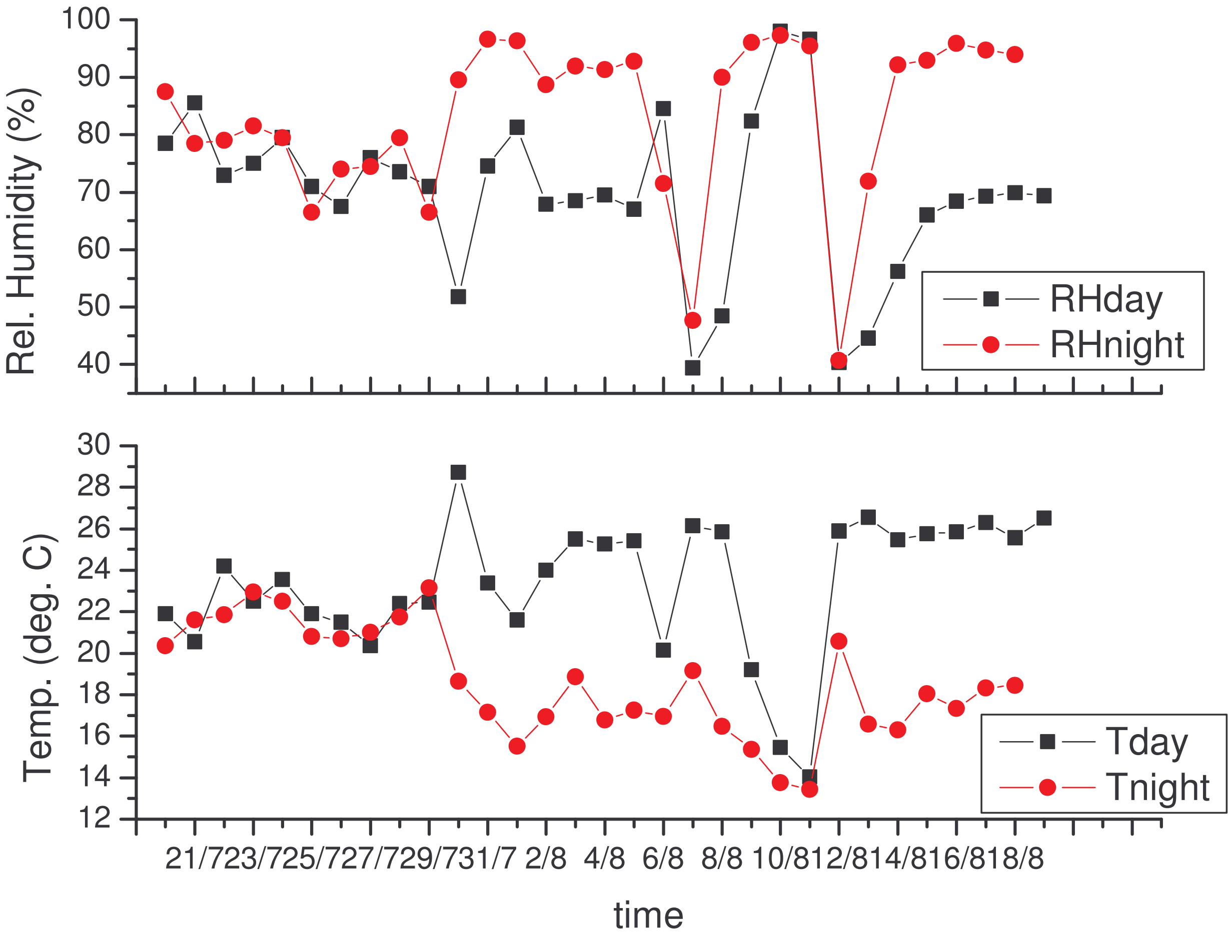
south (SSW: $35^o$ azimuth S) (26.07. morning – 19.08)

## MAX-DOAS measurement parameters

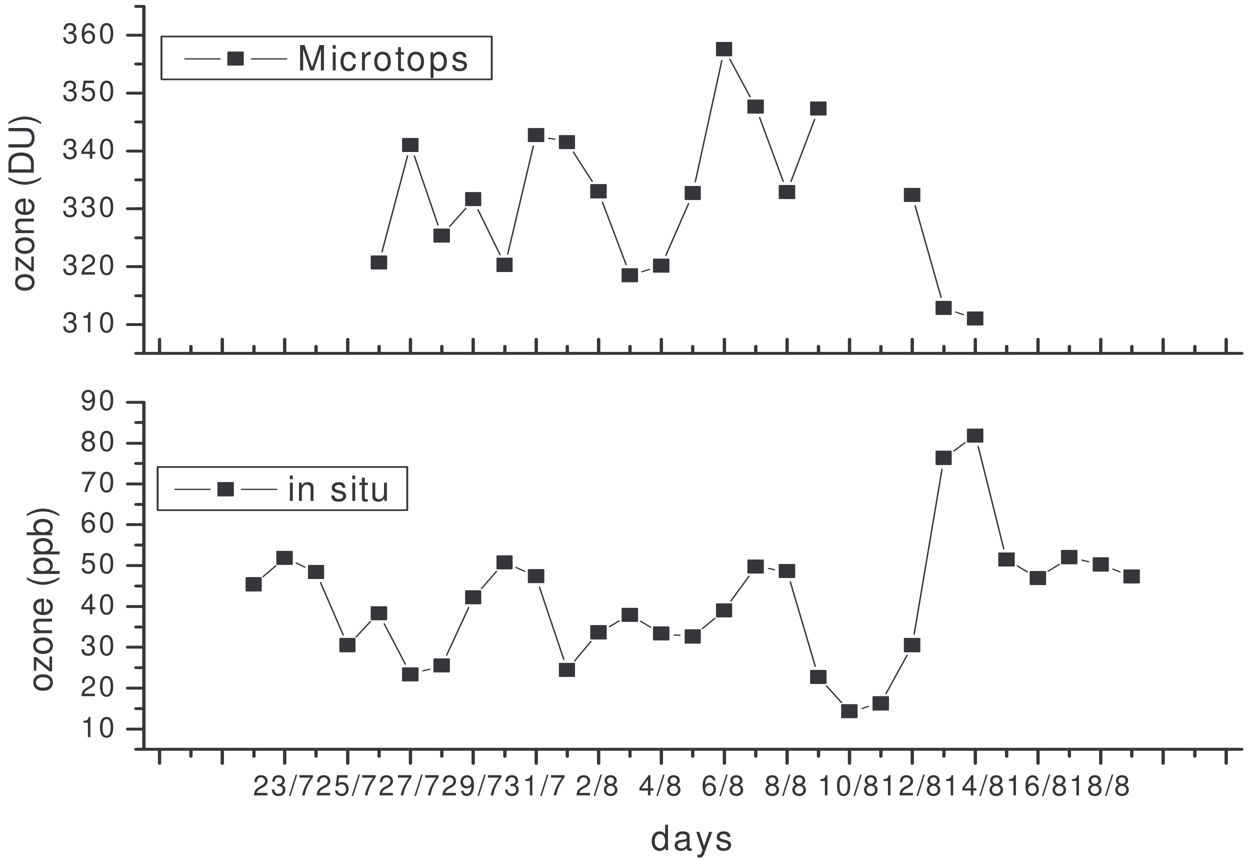
- wavelength interval: 311.5 – 396.5nm
- temporal resolution: min: 60 s, max: 550 s, typical: 300 s

**Intercomparison period**: July 20 – August 3

# Weather conditions



# Ozone measurements



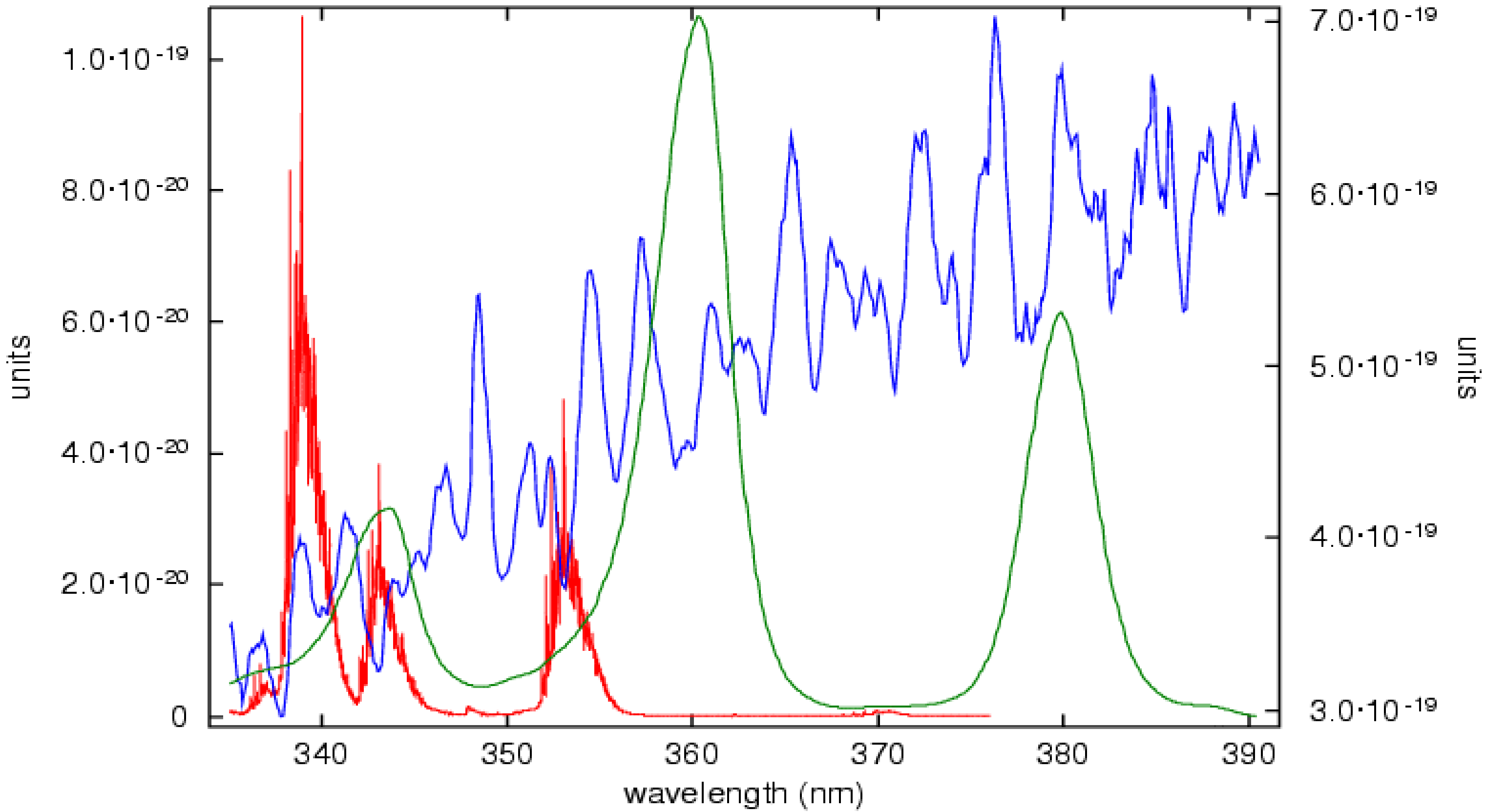

Microtops measurements $\rightarrow$ depending on clouds

*in situ* determinations – every 10 min.

## Data analysis

- wavelength fit range: HCHO 335.0 – 357.0nm

$O_4$ & $NO_2$ 355.0 – 390.5nm



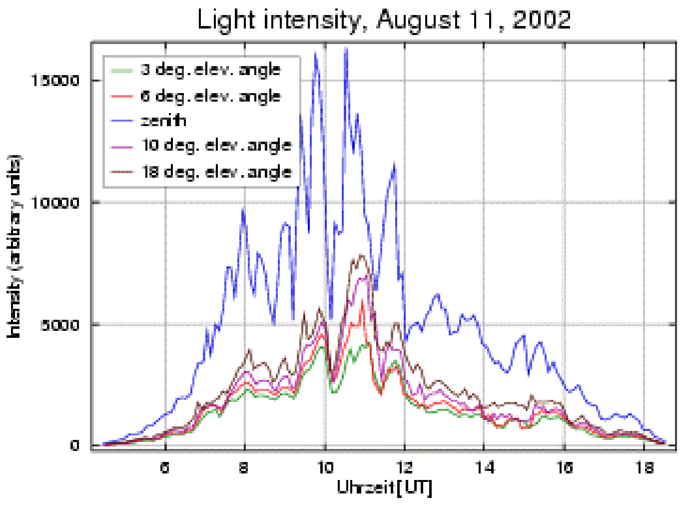

Analyzed trace gases absorbtion spectrum in the fitting intervals

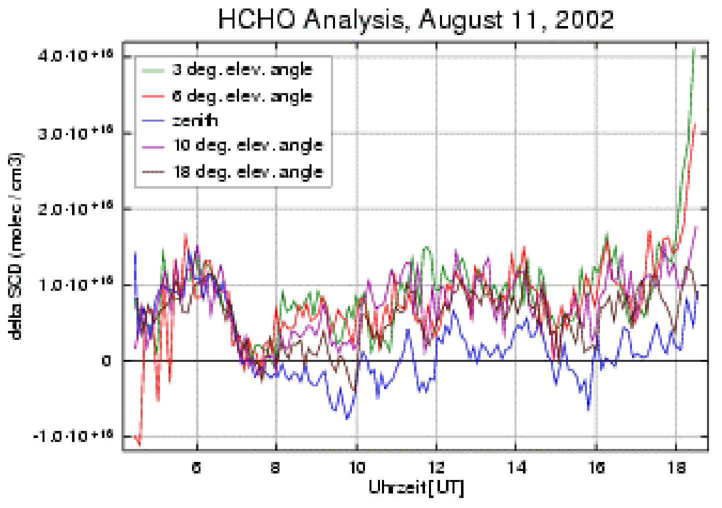
# Reference Spectra for HCHO analysis

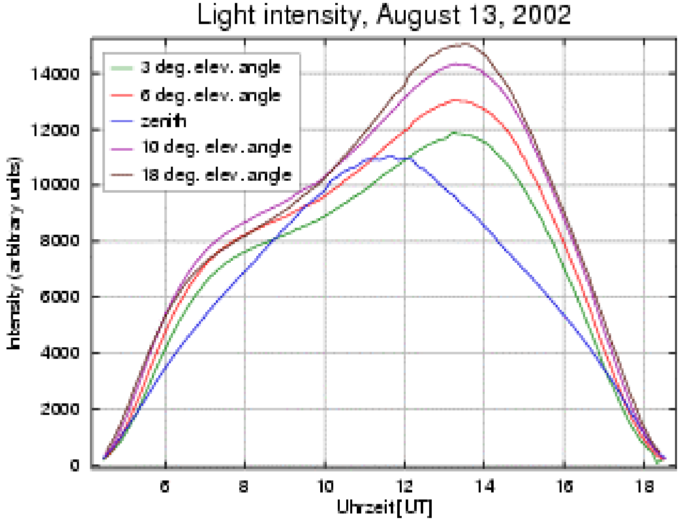
| Molecule | Temperature [K] | Reference |
|---|---|---|
| HCHO | 293 | Meller and Moortgaat |
| NO2 | 220 | Van Daele et al. (1997) |
| O3 | 241 | GOME |
| O3 | 221 | GOME |
| 04 | 296 | Greenblatt et al. (1996), corrected |
| BrO | 228 | Wahner (1990) |
| Ring | - | Vountas (1997) |

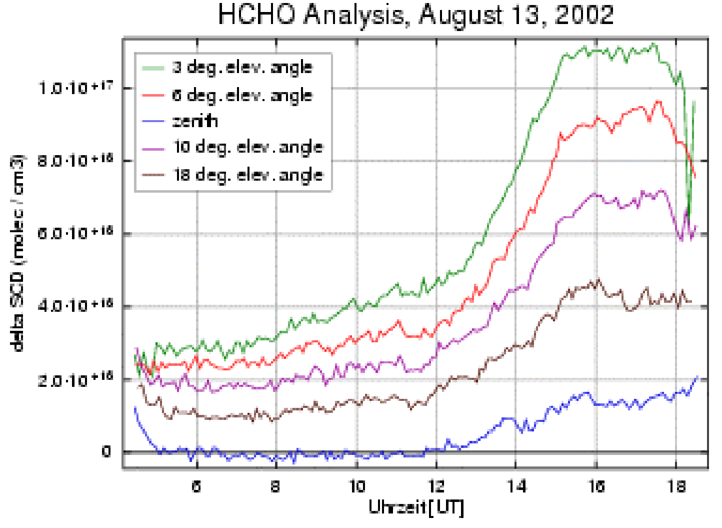
Polynomial: degree 5 (6 coefficients)

# Comparing between luminosity conditions

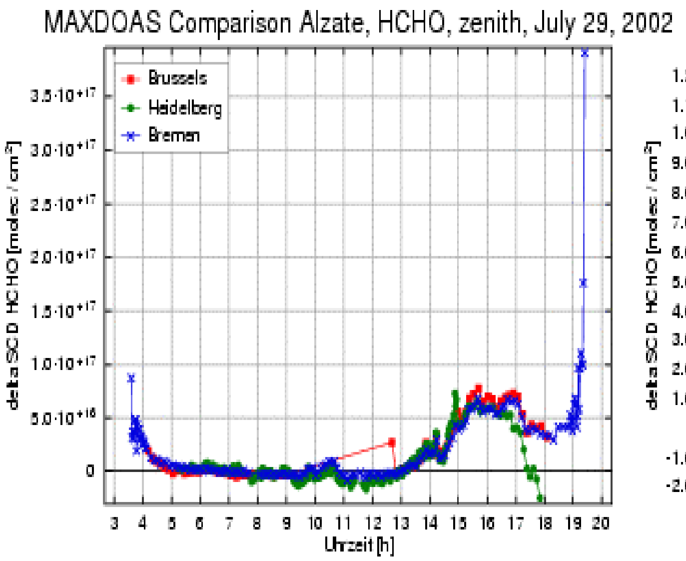


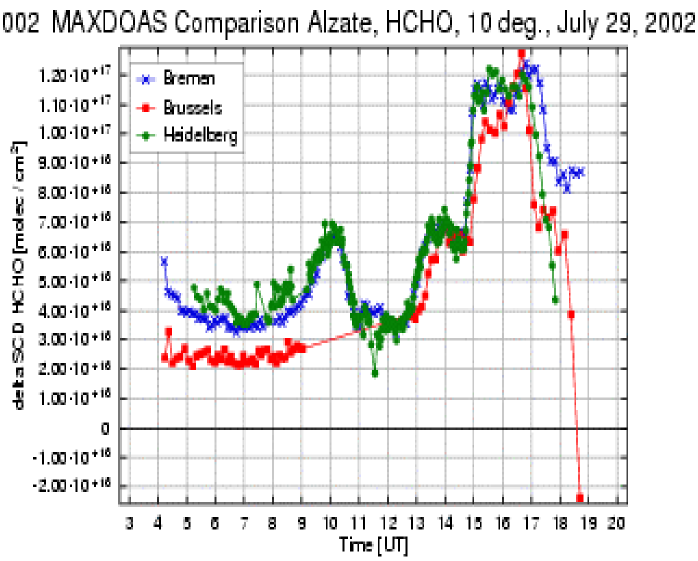



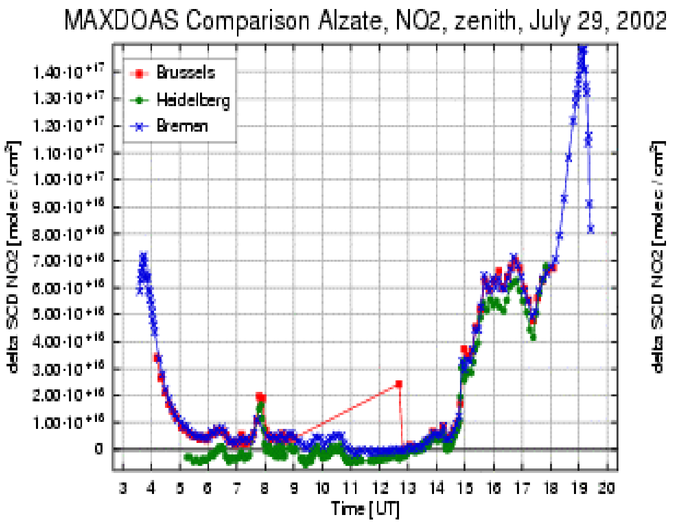



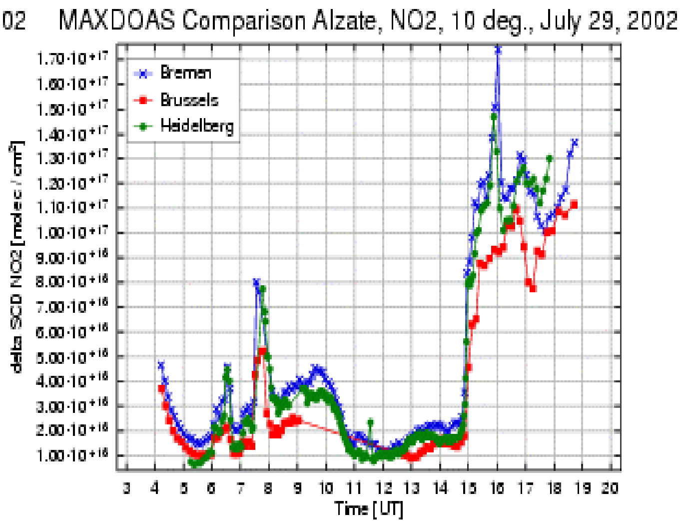



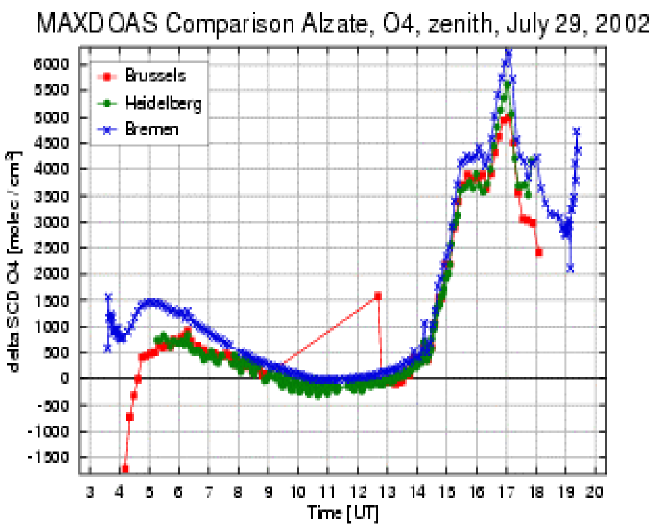
# Intercomparison period (July 22 – August 3)

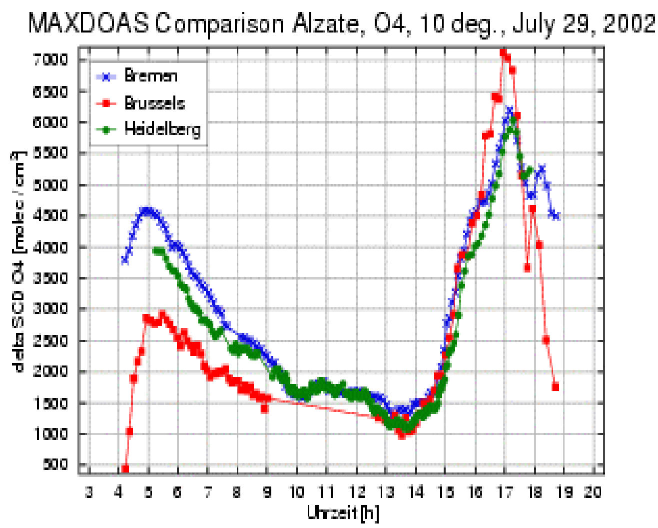


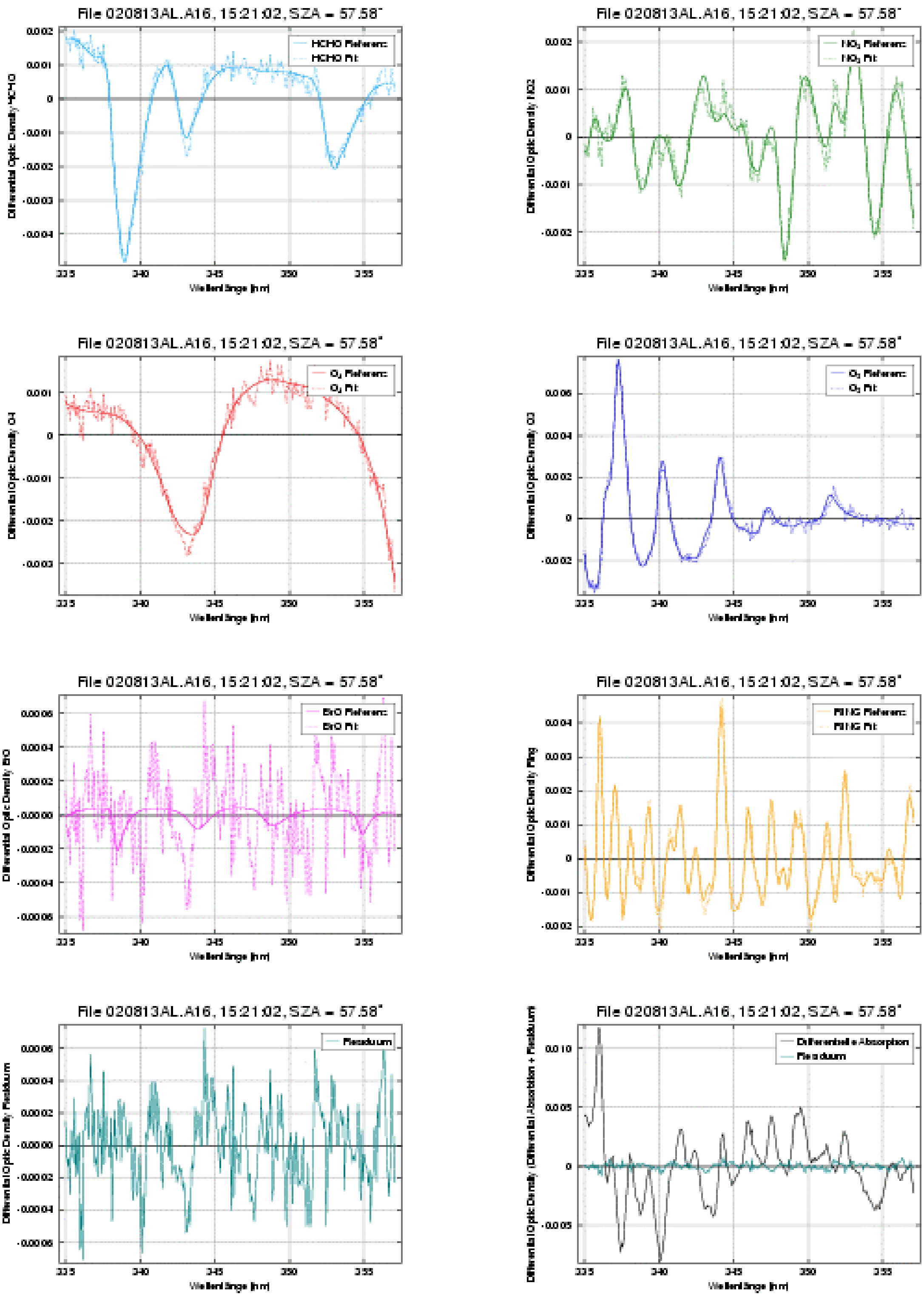



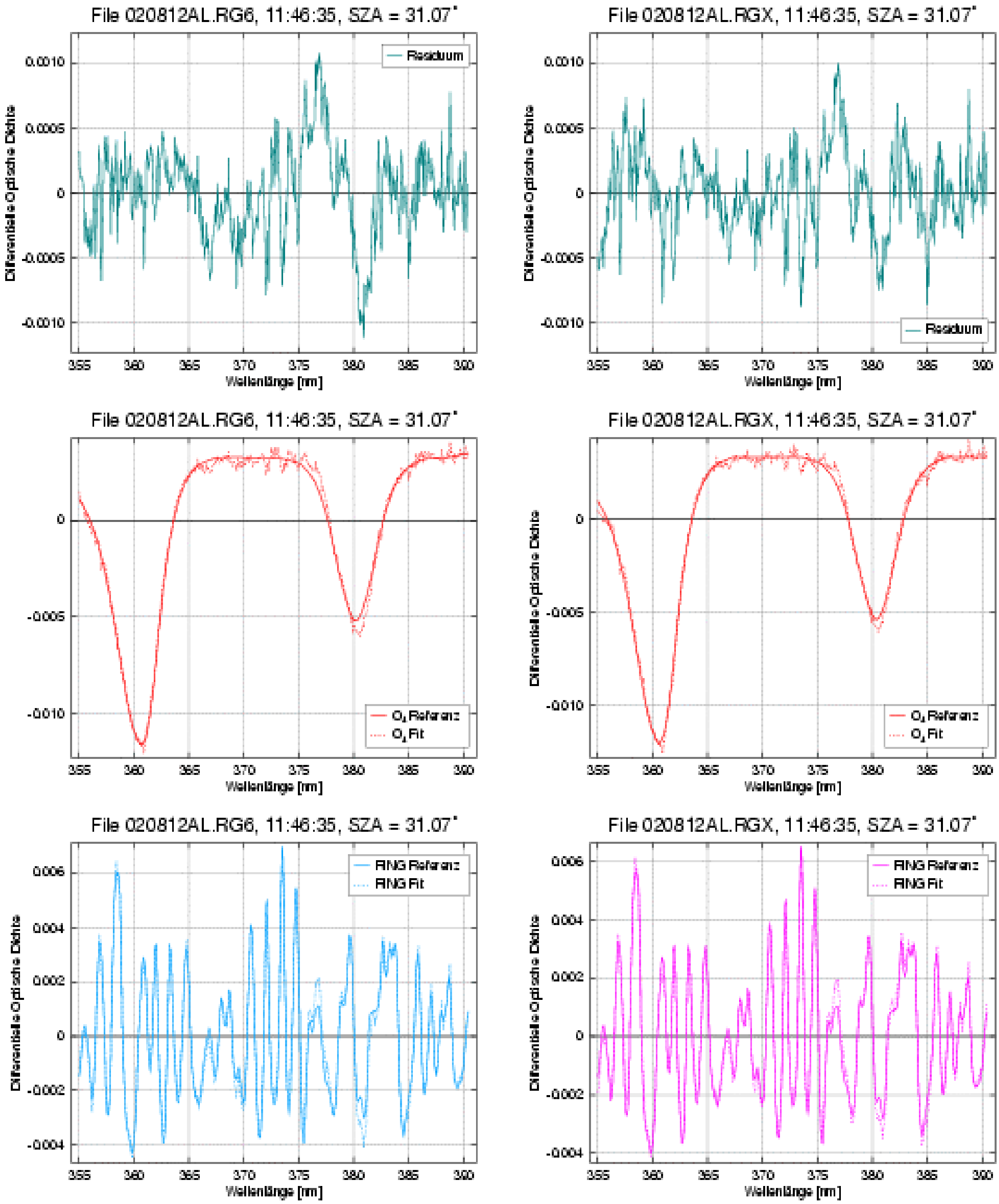



# Typical DOAS analysis for HCHO evaluation

# ($3^o$ elevation, 13.08.2002, 15:21 UT)

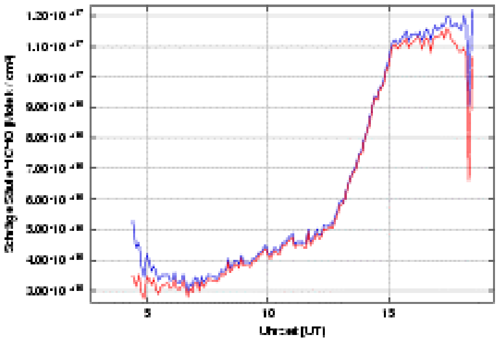


# Improving $O_4$ evaluation

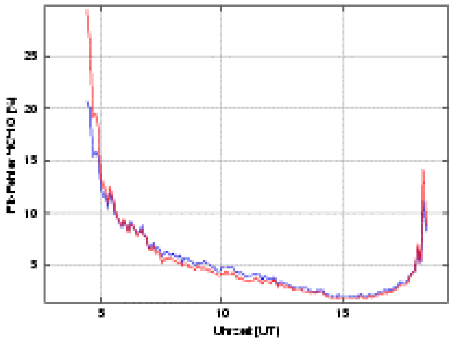


# Influence of improved Ring upon HCHO evaluation

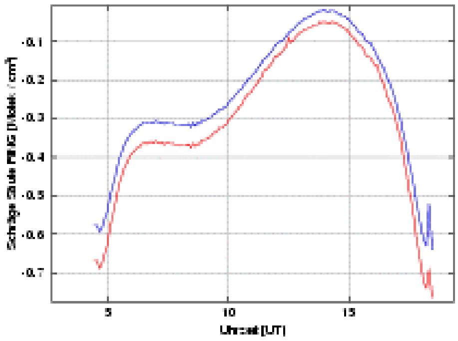
Schräge Säule HCHO , 13.08.02



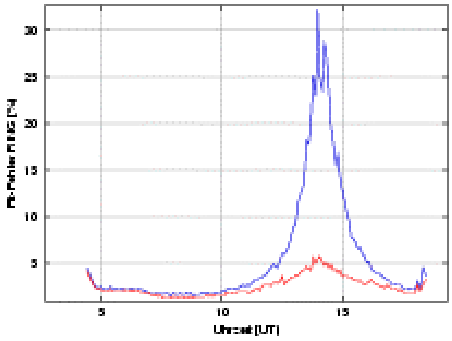
Fit-Fehler HCHO , 13.08.02



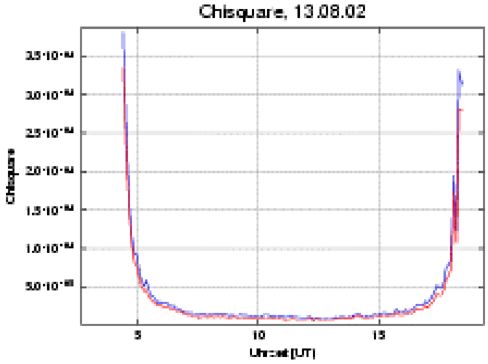
Schräge Säule RING , 13.08.02



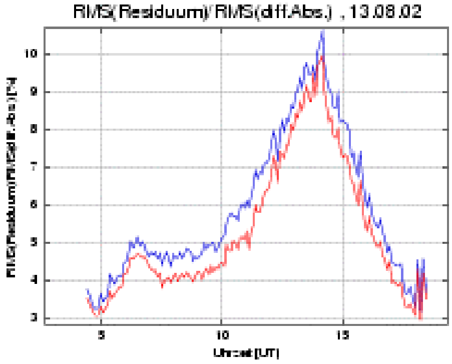
Fit-Fehler RING , 13.08.02



Chisquare, 13.08.02



RMS(Residuum)/RMS(diff.Abs.) , 13.08.02



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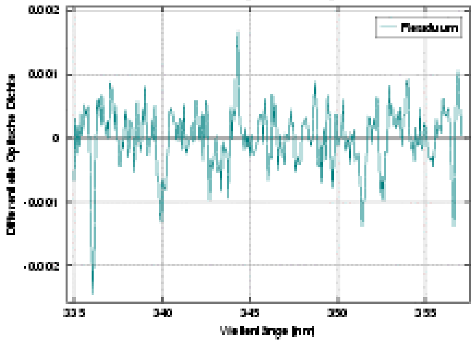

File 020813AL.RF1, 05:24:02, SZA = 80.24°