

A. Ladstätter-Weißenmayer, J. Heland¹, R. Kormann², A. Richter, F. Wittrock,
H. Ziereis¹, and J. P. Burrows

Institute of Environmental Physics, University of Bremen, NW1,
Kufsteiner Straße, D-28359 Bremen, Germany

¹Institute of Atmospheric Physics, DLR, Oberpfaffenhofen, Germany

²Max-Planck-Institute for Chemistry, P.O. Box 3060, D-55020 Mainz

E-mail: lad@iup.physik.uni-bremen.de

Introduction

The aim of the international MINOS (Mediterranean Intensive Oxidant Study) is to quantify the main processes involved in the Mediterranean pollution build-up. Therefore the transport of polluted air masses e.g. from the European continent, the export of pollutants to other regions, and the chemical mechanisms that contribute to the built-up of oxidants have to be investigated.

During the MINOS campaign in August 2001 in-situ-measurements with the DLR research aircraft Falcon over the Mediterranean region up to altitudes of about 12 km were carried out to obtain the distributions and the profiles of different trace gases, such as nitrogen dioxide (NO₂) and formaldehyde (HCHO).

In this study the aircraft measurements and the satellite based GOME (Global Ozone Monitoring Experiment)-data were (a) compared in single GOME pixels to obtain a measure for the absolute uncertainties, and (b) used to observe the dynamic transport of polluted air masses in order to obtain information about their influence on chemistry and climate in the Mediterranean region.

GOME and Falcon Measurements

GOME was launched in April 1995 onboard ERS-2 into a near-sun-synchronous orbit at a mean altitude of 795 km to measure with a nadir-scanning double-monochromator the sunlight scattered from Earth's atmosphere and/or reflected by the surface in a wavelength region of 240 to 790 nm at a moderate spectral resolution of 0.17 to 0.33 nm. In addition solar irradiance is measured daily [Burrows et al. 1999].

In situ measurements of NO with a well characterized chemiluminescence detector (CLD) with a detection limit of 5% for NO [Ziereis et al., 1999] and the photolysis frequency of NO₂ (J_{NO2}), obtained from the sum of two filter radiometers (Meteo Consult GmbH) with 2 viewing geometry with a overall uncertainty of 17%, were performed with the DLR research aircraft Falcon. In addition airborne measurements like ozone measured with an UV-absorption- modified TE 49 instrument (Thermo Environmental) calibrated with a O₃ 41M ozone generator (ANSYCO) (detection limit 5%), meteorological parameters and HCHO measurements were carried out with an Aero Laser (AL4021) above the CML (similar measurement techniques are described in literature, elsewhere [Kelly et al. 1994, Macdonald et al. 1999])

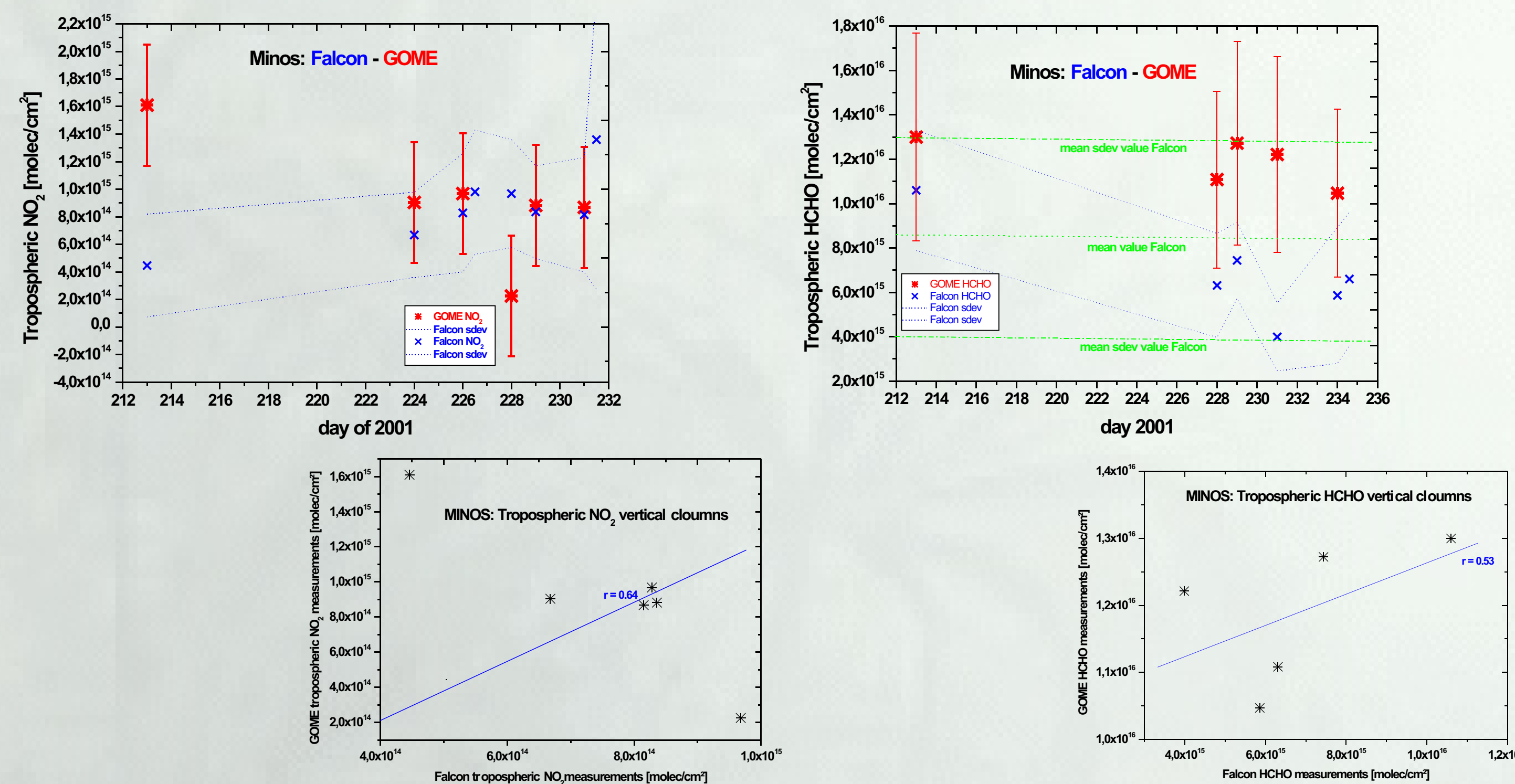


Figure 2 to 4: Comparison between the tropospheric amounts of NO₂ and HCHO for the GOME- and Falcon measurements during the MINOS campaign 2001 and the corresponding scatter-plots.

Analysis of Tropospheric NO₂ and HCHO

For the comparisons with airborne based Falcon measurements the data of GOME that means only cloud free pixels (less than 10% cloud cover, GOME pixels (4.5 s forward scan, 1.5 s back scan, the size of one GOME ground pixel is 40 x 320 km²) along the track of the Falcon (see fig. 1) were extracted and analysed to minimise the uncertainties for the direct comparisons of the tropospheric columns of NO₂ and HCHO.

GOME lv1-spectra were analysed by using the IUP Bremen Differential Optical Absorption (DOAS) algorithm, to derive first slant columns of the trace gases [Richter et al. 1998, 1999] and then to divide them by air mass factors (AMF) with the radiative transfer model GOMETRAN [Rozañov et al. 1997] to get vertical columns. Caused of the viewing mode of GOME the information based on the spectra is coming from the stratosphere and the troposphere therefore the Tropospheric Excess Method (TEM) is used for the retrieval of tropospheric NO₂. HCHO is mainly in the troposphere so the vertical columns of this trace gas can be determined directly.

For getting the tropospheric NO₂ based on Falcon measurements the NO₂ photolysis frequency J(NO₂), the measured O₃ and NO were implemented in the photostationary steady state equation [e.g. Atkinson, 2000] where the temperature-dependent rate constant was calculated from the data given in Sander et al. [2000]. The analysis of the HCHO data is based of profiles from a height of 600 m up to 13 km averaged in 2 km altitude bins. The standard deviations are between 0.5 ppb at the lowest and 0.2 ppb at the highest level. Taking into account the ozone cross sensitivity the detection limit is calculated from the RMS (1 sigma) of the zero

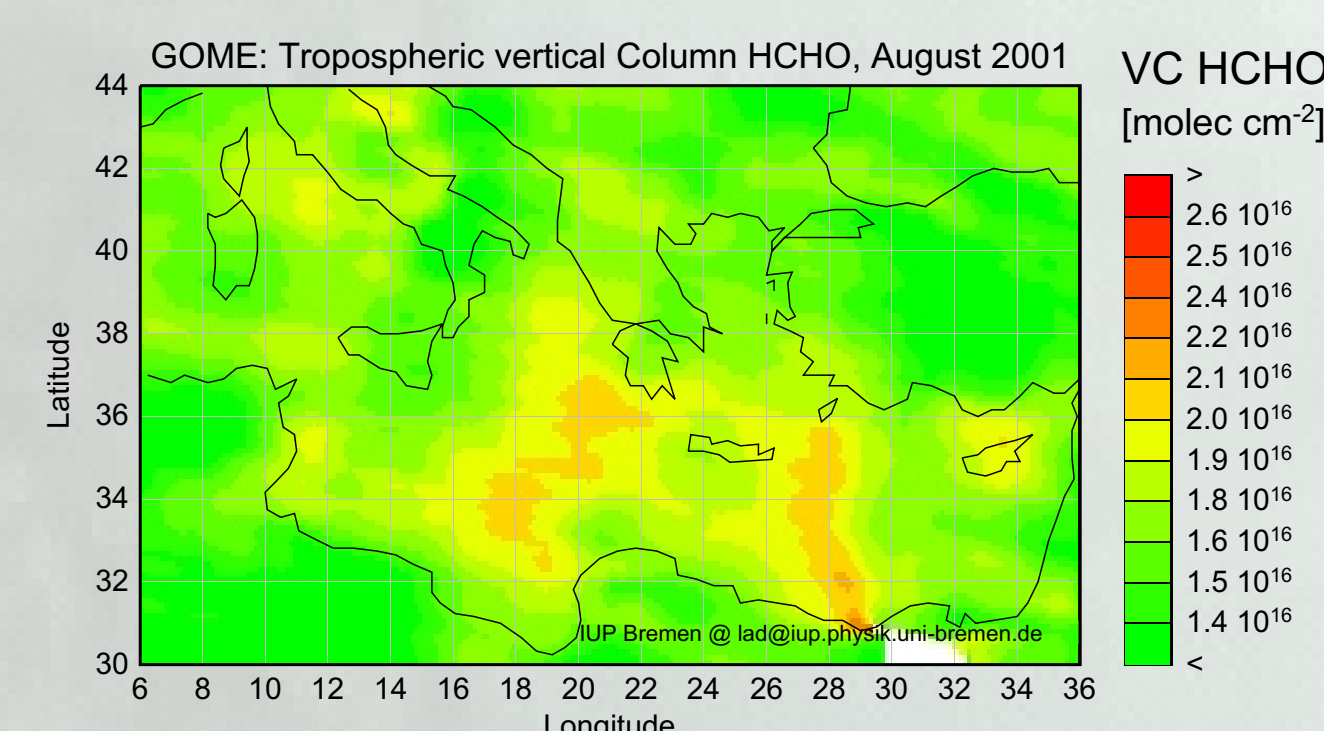


Figure 5: Tropospheric amounts of HCHO for the Mediterranean region during the time period of August 2001.

Results and Conclusion

During the MINOS campaign GOME data were compared in view to tropospheric NO₂ and HCHO. These case studies showed a good agreement (with the exception in the heights of the tropopause) between both measuring systems. Considering the standard deviation of tropospheric columns of NO₂ and HCHO all GOME data are in the range of the airborne measurements. (regarding in addition the scatter-plots for both trace gases). The globally tropospheric e.g. HCHO amounts of GOME reflect the polluted situation over the Mediterranean region; values of ~1.9 ppb in maximum were reached in summer 2001 during the MINOS campaign. Comparing these results with back trajectories information about the sources e.g. biomass burning can be obtained.

References

- Atkinson, R., Atmospheric chemistry of VOCs and NO_x, Atmos. Environ., 34, 2063-2101, 2000.
- J.P. Burrows, M. Weber, M. Buchwitz, V. Rozanov, A. Ladstätter-Weißenmayer, A. Richter, R. DeBeek, R. Hoogen, K. Bramstedt, K.-E. Eichmann, M. Eisinger, and D. Perner: The Global Ozone Monitoring Experiment (GOME): Mission Concept and First Scientific Results, J. Atmos. Sci., 56, 151-175, 1999
- Kelly, T.J. and C.R. Fortune, Continuous monitoring of gaseous formaldehyde using an improved fluorescence approach. International Journal of Environmental Analytical Chemistry, 1994. 54: p. 249-263.
- Macdonald, A.M., H.A. Wiebe, S.M. Li, H. Dryfhout-Clark, K. Asalian, G. Lu, D. Wang, C.L. Schiller, G.W. Harris, A.L. Sumner, and P.B. Shepson, Results of a formaldehyde intercomparison study in Ontario, 1999, Atmospheric Environment Service, Ontario, Canada.
- Richter, A., and F. Wittrock, and J. P. Burrows, GOME observations of tropospheric BrO, in European Symposium on Atmospheric Measurements from Space, ESA WPP-161, vol. 1, pp.407-413, 1999
- Rozañov, D., D. Diebel, R. J. Spurr, and J. P. burrows, GOMETRAN: A radiative transfer model for the satellite project GOME the plane parallel version, J. Geophys. Res., 102, 16683, 1997
- S. P. Sander, R. R. Friedl, W. B. DeMore, D. M. Golden, C. E. Kolb, M. J. Kurylo, R. F. Hampson, R. E. Huie, M. J. Molina, G. K. Moortgat, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Supplement to Evaluation 12: Update of Key Reactions", JPL Publication 00-3, NASA Panel for Data Evaluation, Evaluation Number 13, March 8, 2000, Jet Propulsion Laboratory, Pasadena, California, 2000
- Ziereis, H. H. Schlager, P. Schulte, I. Köhler, R. Marquardt, and C. Feigl, In situ measurements of the NO_x distribution and variability over the eastern North Atlantic, J. Geophys. Res., 104, 16021-16032, 1999.

Acknowledgements

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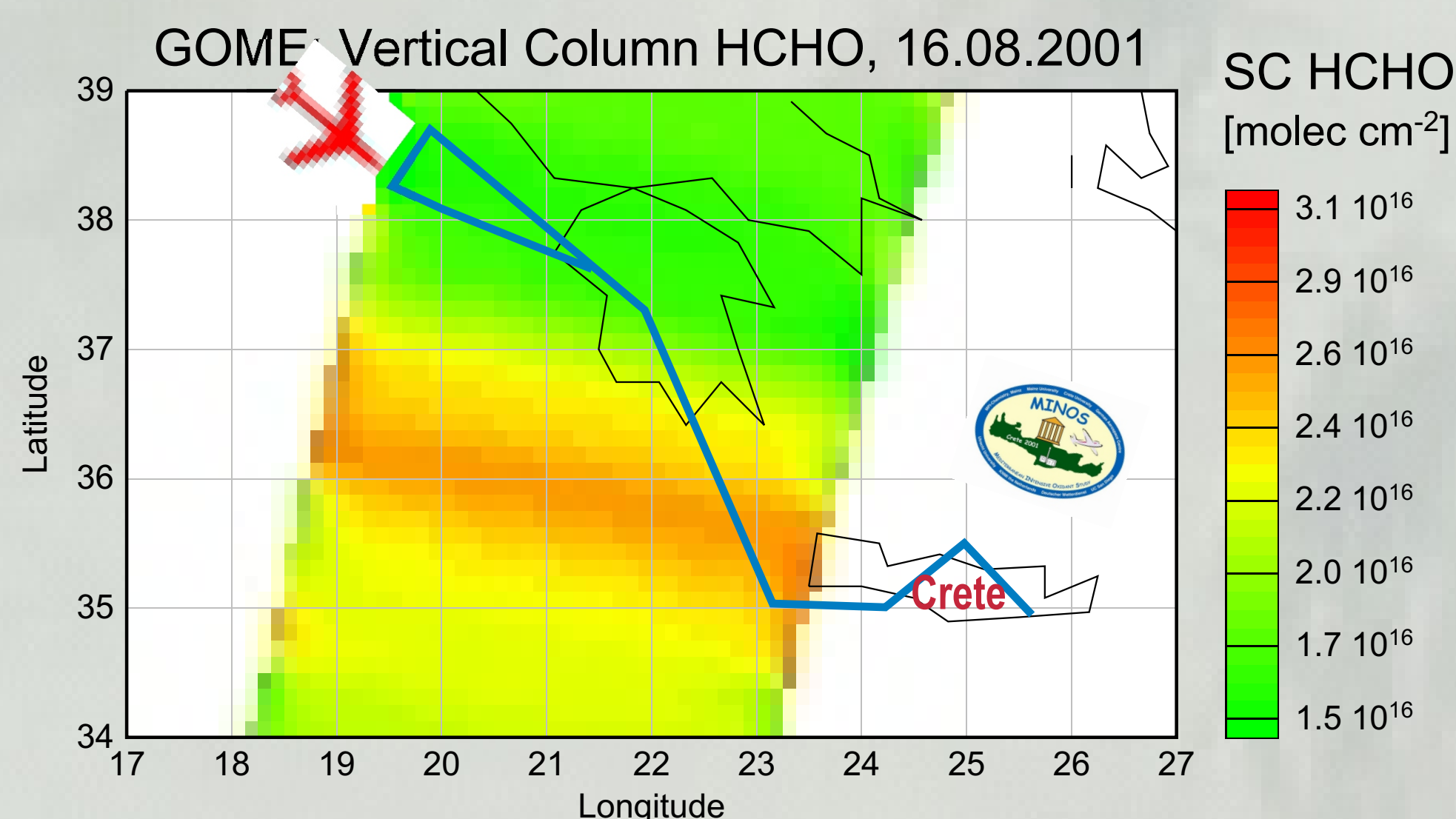


Figure 1: Extracted GOME pixels (e.g. Vertical columns of HCHO) along the Falcon track (marked in blue) on the 16th of August 2001 during the MINOS campaign

The results of GOME and of airborne based measurements were compared for NO₂ and HCHO. For the trace gas NO₂ only flights on six days whereas for HCHO only data of 5 days (because for this trace gas only the center pixels were used for the comparison) in August 2001 could be compared caused by the overflights of GOME (see fig.2 and 3). The GOME-data that means only pixels under cloud free conditions (less than 10%) were analysed to obtain the tropospheric columns for the trace gas NO₂ and HCHO during the MINOS campaign in July and August 2001.

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The comparison for the tropospheric columns of NO₂ and HCHO shows a good agreement for both measuring systems considering the standard deviation. For the trace gas NO₂ the measured GOME data are in this cases a factor of 1.4 higher than the Falcon results taking into account each common data point (coloured in blue) whereas a factor of 1.9 can be observed for the same comparison for HCHO. This factor of 1.9 can be scaled down to 1.4 regarding the mean value of all flight data for HCHO (coloured in green). Looking at the monthly mean value for August 2001 detected with GOME (see fig. 6) a maximum value of 2.4*10¹⁶ can be observed over the Mediterranean region. That means concerning that most of the HCHO molecules are in a atmospheric layer from 0-5 km a mixing ratio of ~ 1.9 ppb was detected.

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