OZONE columns and profiles from ground based FTIR observations

(ESA-NIVR-KNMI project 2907 “OMI validation by ground based remote sensing: ozone columns and atmospheric profiles”, 2005-2008)

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Ground-based FTIR observations were performed within the framework of the ESA-NIVR-KNMI project 2907 entitled “OMI validation by ground based remote sensing: ozone columns and atmospheric profiles” for the purpose of OMI data validation. FTIR observations were carried out during the time frames August-October 2005, June-October 2006 and March-October 2007, mostly under cloud free and clear sky conditions and in some days from early morning to sunset covering the full range of solar zenith angles possible.

Ozone column and ozone profile data were obtained for the year 2005 using spectral modeling of the ozone spectral band profile near 9.6 microns with the MODTRAN3 band model based on the HITRAN-96 molecular absorption database. The total ozone column values retrieved from FTIR observations are biased low with respect to OMI-DOAS data by 8-10 DU on average, where they have a relatively small standard error of about 2%. FTIR observations for the year 2006 were simulated by MODTRAN4 modeling. For the retrieval of ozone column estimates and particularly ozone profiles from our FTIR observations, we used the following data sources to as input files to construct a priori information for the model: satellite Aqua-AIRS water vapor and temperature profiles; Aura-MLS stratospheric ozone profiles (version 1.5), TEMIS (KNMI) climatological ozone profiles and the simultaneously performed surface ozone measurements.

Ozone total columns obtained from our FTIR observations for year 2006 with MODTRAN4 modeling are matching rather well with OMITOMS and OMI-DOAS data where standard errors are 0.68 % and 1.11 %, respectively.

The observations performing during March 2007 - October 2007 were reduced according to the new approach to retrieve tropospheric ozone column and profiles. For final results we used new version AIRS (level 3,v005) T and H2O data. We have got the total ozone column values retrieved from FTIR observations 2007 which are biased low with respect to OMI-DOAS by –0.33 DU and to OMI-TOMS by –4.33 DU on average, where they have a relatively small standard error of about 1.4 %.

AURA-MLS data of version 2.2 which have become available in 2007 allow us to retrieve tropospheric ozone profiles. For some days Aura-TES tropospheric profiles were also available and were compared with our retrieved profiles for validation. A preliminary analysis of troposphere ozone variability was performed. Observation during the time frame March-October demonstrate daily photochemical variability of tropospheric ozone and reveal mixing processes during the night.

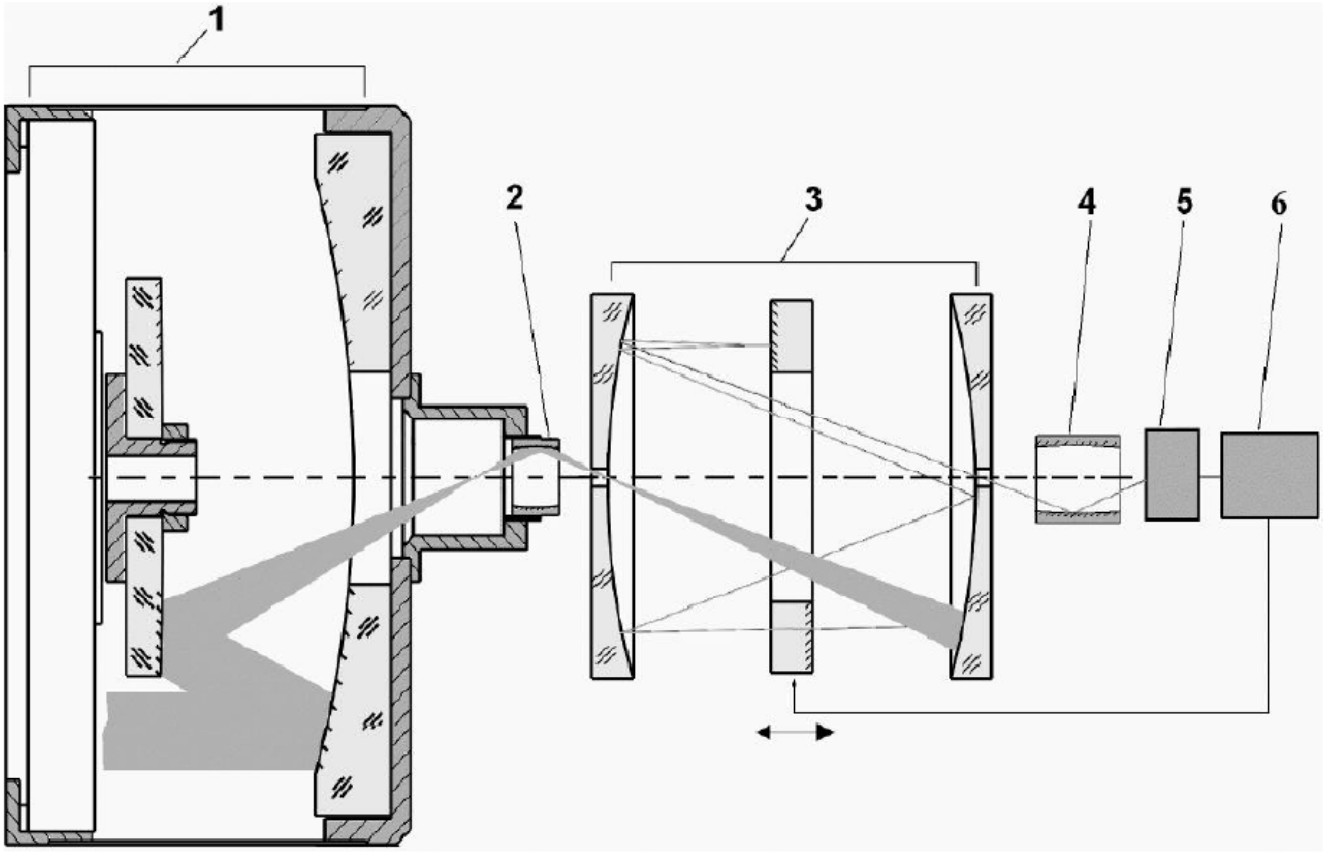

Figure 1. Structural and optical scheme of the FTIR spectrometer : 1 - fast lens; 2, 4 - ellipsoids for shift of image; 3 - interferometer ; 5 - detector; 6 - electronics block.

INTRODUCTION

It is common knowledge that the stratospheric ozone layer is very important for sustaining life on Earth - the ozone layer protects life on Earth from the harmful and damaging ultraviolet solar radiation. Ozone in the lower atmosphere, or troposphere, acts as a pollutant but is also an important greenhouse gas. Ozone is not emitted directly by any natural source. However, tropospheric ozone is formed under high ultraviolet radiation flux conditions from natural and anthropogenic emissions of nitrogen oxides (NOx) and volatile organic compounds (VOCs).

Satellite remote sensing is used to understand and quantify key processes in the global ozone budgets. Nowadays satellite observations are readily available for total ozone column and atmospheric ozone profiles. Nevertheless, ground based monitoring is important to validate and to complement space-based measurements and to clarify local/regional specific sources and sinks of this gas. Such ground based data can assist to derive the dynamical behavior of air pollution from space and ground-based observations and to check compliance to the pollutants transport models. They will also aid to the development of an environmental policy, in particular policies on greenhouse gases, on a local and regional scale.

OMI SATELLITE OBSERVATIONS

The Dutch-Finnish Ozone Monitoring Instrument (OMI) aboard the NASA Earth Observing System (EOS) Aura satellite is a compact nadir viewing, wide swath, ultraviolet-visible (270-500 nm) hyperspectral imaging spectrometer that provides daily global coverage with high spatial and spectral resolution. The Aura orbit is sun-synchronous at 705 km altitude with a 98 degrees inclination and ascending node equator-crossing time roughly at 13:45. OMI measures backscattered solar radiance in the dayside portion of each orbit and solar irradiance near the northern hemisphere terminator once per day. The OMI satellite data products are derived from the ratio of Earth radiance and solar irradiance.

The OMI TOMS and OMI DOAS total ozone column estimates are publicly available from the NASA DISC systems. The OMI-TOMS algorithm is based on the TOMS V8 algorithm that has been used to process data from a series of four TOMS instruments flown since November 1978. This lgorithm uses measurements at 4 discrete 1 nm wide wavelength bands centered at 313, 318, 331 and 360 nm. The OMI-DOAS algorithm [14] takes advantage of the hyper-spectral feature of OMI. It is based on the principle of Differential Optical Absorption Spectroscopy (DOAS) [9]. The lgorithm uses ~25 OMI measurements in the wavelength range 331.1 nm to 336.6 nm, as described in 14].

The key difference between the two algorithms is that the DOAS algorithm removes the effects of aerosols, clouds, volcanic sulfur dioxide, and surface effects by spectral fitting while the OMS algorithm applies an empirical correction to remove these effects. In addition, the TOMS algorithm uses a cloud height climatology that was derived using infrared satellite data, while the DOAS algorithm uses cloud information derived from OMI measurements in the 470 nm O2-O2 absorption band. The two algorithms also respond to instrumental errors very differently. Validation is key to quantify and understand these differences as a function of measurement geometry, season and geolocation.

GROUND BASED FTIR OBSERVATIONS

Ground based FTIR observations are performed with a Fourier Transform Infra-Red (FTIR) spectrometer, model ``Infralum FT 801", which was modernized for the task of monitoring the atmosphere by direct sun observations. The main advantage of this device is its small size and small sensitivity of the optical arrangement to vibrations. The working spectral range of the FTIR spectrometer is 2-12 microns (800-5000 cm-1) with the highest possible spectral resolution of about 1.0 cm-1.

Following the modernization in 2006 of our spectrometer and upadating the software for the initial treatment of the registered spectra, the system now allows us to average 2-99 individual spectra during the observation period. We averaged 4 single spectra as was recommended by the developers of the spectrometer device (Egevskaya et al.2001) to avoid a degradation of the averaged spectrum due to the recording of atmospheric instabilities at longer exposure times. Our averaged spectra have signal-to-noise ratios S/N of 150-200. We registered 3-4 averaged spectra during 2-3 minutes of recording time. Prior to further treatment of the observed spectra we checked the repeatability of these 3-4 spectra and choose the spectrum with the best signal-to-noise ratio S/N to be fitted with the model spectra

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MODTRAN SPECTRA MODELING AND ANALYSIS.

The column amounts of ozone (O3) molecules are recovered by using the radiation transfer codes MODTRAN3 and MODTRAN4, a moderate resolution model of transmission [1]. These codes are widely applied to the interpretation of ground based, airborne and spaceborne (satellite) observations of spectra of the Earth's atmosphere. The codes calculate atmospheric transmission and reflection of electromagnetic radiation with frequencies from 0 up to 50000 cm-1. The model uses a spherical source function for the light originating from the Sun and scattered from the Moon, and standard model atmospheres and user specified atmospheric profiles of gases, aerosols, clouds, fogs and even rain.

It uses a two-parameter (temperature and pressure) model of molecular absorption bands, which is calculated on the basis of a large array of previously accumulated data of spectral lines stored in the HITRAN database. MODTRAN uses absorption crosssection data for 12 light molecules (H2O, CO2, O3, CO, CH4, O2, NO, SO2, NO2, N2O, NH4 and HNO3), for heavy molecules - CFC (9 molecules) and for CLONO2, HNO4, CCl4 and N2O5. The calculations are carried out only in an local thermal equilibrium (LTE) approximation for the moderate spectral resolution (2 cm-1) which just corresponds to our observed Fourier spectra.

The Band Model parameters were re-calculated by us on the base of HITRAN-2004 according to the paper of (Shavrina et al. JGR, 2007).

For the new set of spectral data recorded during 2006, the model spectra were calculated with MODTRAN4 code (*Berk et al.* [1999]) and new Band Model input file which was prepared by us based on the HITRAN-2004 database of *Rothman et al.* [2005], the most recent and more complete version of molecular line database. The Band Model parameters, namely average absorption coefficient S/d and line density parameter $1/d$ were calculated as defined by *Bernstein et al.* [1996]:

$$S/d = \Sigma S_j/\Delta\omega;$$

$$1/d = (\Sigma S_j^{0.5})^2/\Sigma S_j/\Delta\omega$$

were S_j is the temperature-dependent line strength, $\Delta\omega$ is the width of the spectral interval ($\Delta\omega = 1cm^{-1}$ in this study), and the summation includes only lines within the interval.

The program MODTRAN works in four modes of radiative transfer: transmittance, thermal radiance, radiance with scattering of solar or lunar light and directly transmitted solar irradiance. We used the last mode to model solar spectrum and compare it with observed spectrum. High resolution solar irradiance data after Kurucz 1995 was used [10].

Measurements of surface ozone concentrations by the collocated ozonometer together with satellite remote sensing data from the Atmospheric Infrared Sounder Instrument (AIRS - http://disc.gsfc.nasa.gov/AIRS/) aboard the NASA EOS-Aqua platform and the Microwave Limb Sounder (MLS), http://avdc.gsfc.nasa.gov/Data/Aura/) aboard the NASA EOS-Aura platform were used for the construction of atmospheric ozone, temperature and water vapor input profiles for the MODTRAN4.3 code.

For the analysis of the 2006 FTIR observations we used MLS version 1.5 data, which then had a preliminary character. We modified the shape of the MLS stratospheric ozone profile to obtain a better fit to the MODTRAN4.3 model output and to our FTIR spectra of the ozone band around 9.6 microns.

5. Software developments

We developed in house a sophisticated procedure to analyze the observed ozone spectral band at 9.6 microns. To obtain the best fit to the observed spectral band profile we adhered to the following procedure:

a) We use the standard summer or averaged summer-winter MODTRAN model atmosphere as a reference model to compute a grid of Earth model atmospheres with different atmospheric columns and profiles of ozone. The construction of ozone input profiles, AIRS water vapor and CO_2 profiles are iterated in the case of a poor fit of model spectra to the observed spectrum (at the end of the process) by procedure in which these profiles are determined by two parameters: scaling (or fitting) factor and location (altitude) of the maximum of the molecular densities. Additionally for ozone we adopt two parameters determining the curvatures of upper and lower parts of the profile corresponding to upper and lower atmosphere layers near the ozone density maximum.

b) Using the MODTRAN4 code we compute a grid of the theoretical spectra associated with the grid of the model atmospheres.

c) To determine the best fit parameters we compare the observed and computed spectra with a two-step minimization procedure. Firstly, we determined the best fit to observed water vapor and CO_2 lines in the region $800 - 1240$ cm^{-1}, i.e., we exclude the ozone spectral band from the analysis. Secondly, we fit the observed spectrum with the grid of calculated ozone spectral band profiles using water vapor and CO_2 atmospheric profiles selected on the previous step. We choose the best fit in accordance with a minimal value of the sample variance.

Fortunately, in 2007 the all new and more precise version v2.2 of MLS data became available , that allows us to develop a new approach to the analysis: we now modified the input tropospheric ozone profile and we only scaled the stratospheric ozone profiles of Aura-MLS v2.2 data within 2-5 % (declared precision of these data) without any modification to its shape.

The tropospheric part of the input (a priori) ozone profile was constructed from surface ozone measurement and the TEMIS climatological (monthly averaged) ozone atmospheric profiles, which were downloaded from the TEMIS-KNMI website. In this way we tried to obtain the best possible fit of the model computed spectra to the FTIR observed spectral band on 9.6 microns. Aura-TES data available from the AVDC website were also used if they were available for observational days.

To modify the tropospheric ozone profiles we used a smooth function determined between the J1 and J2 points of altitude in the model atmosphere. For any J point of the model we then adopt:

$x=(J - J1) / (J\ 2 - J1)$, then

$P_J = P0_J * (1 + B * (\sin(x))^a)$,

determines the shape of the correction function, a and B determine the amplitude of changes of input tropospheric ozone profile, where B > -1 and a > 0.

Using the MODTRAN4 code we compute a grid of the theoretical spectra. To determine the best fit parameters, we compare the observed and computed spectra following a two-step optimization procedure: Firstly, we determined the best fit to observed water vapor lines in the spectral region 800 - 1240 cm-1, i.e., here we exclude the ozone band from the analysis. Secondly, we fit the observed spectrum around the 9.6 micron ozone band with the grid of calculated ozone bands including the previously determined best atmospheric water profile. Hence we determine tropospheric ozone profiles, total and tropospheric ozone column from the best fit of the modeled and observed ozone band spectra, where we included the unaltered Aura-MLS stratospheric profiles.

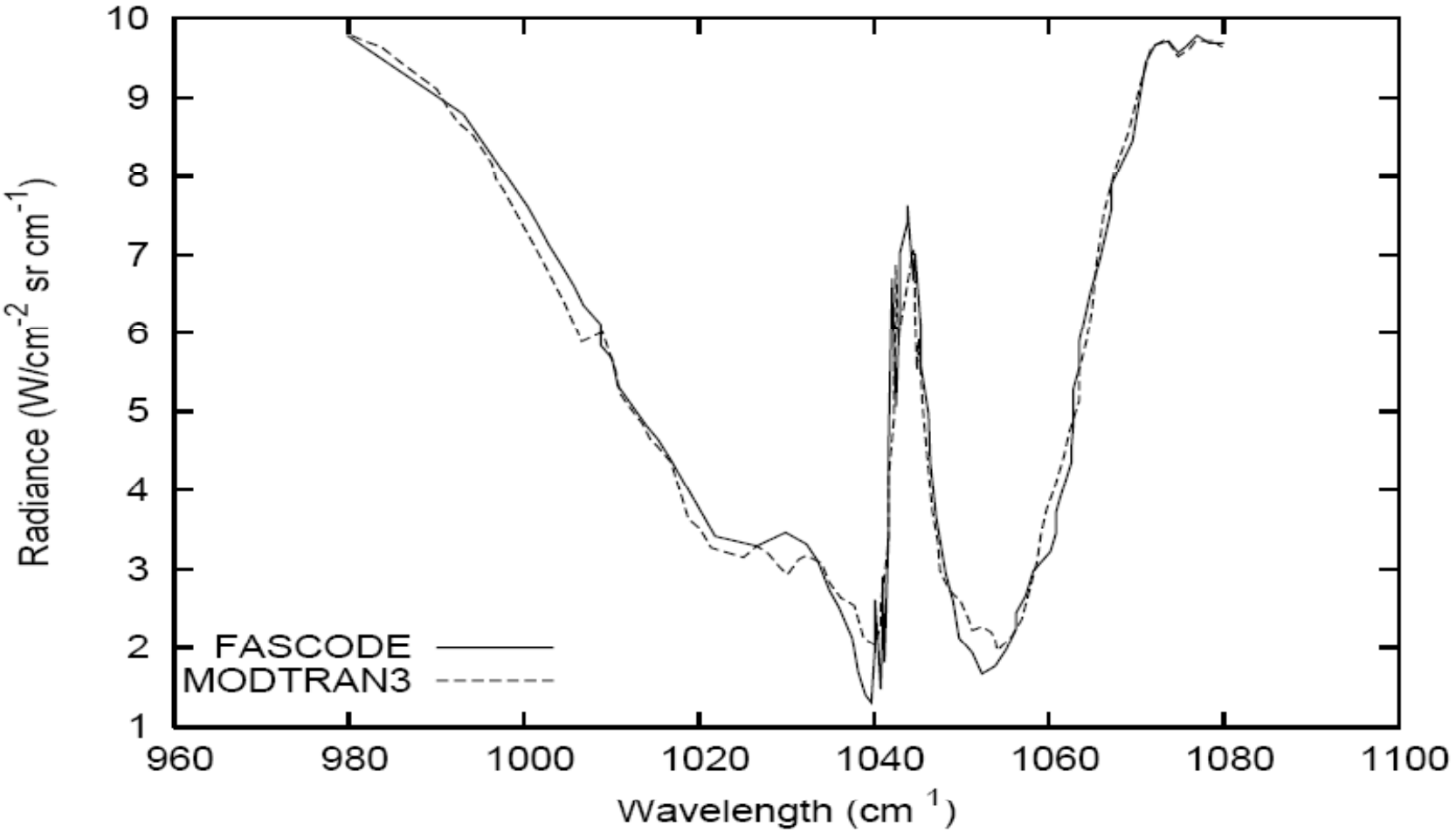


Figure 3. Comparison of MODTRAN (Band Model) and FASCODE (line-by-line) spectral radiance calculation for ozone 9.6 micron band (from *Bernstein et al.* [1996]). We estimate the value of the sample variance of these two spectra fit in the range of $981-1078$

In Fig. 3(b) we show the profiles of the ozone band at 9.6 micron calculated with MODTRAN3 and FASCODE (line-by-line modeling) from the paper of *Bernstein et al.* [1996] (The code FASCODE is not available for us, our own line-by-line code is now under development). We estimate the value of the sample variance S of these two spectra fit in the range of $981-1078\,\mathrm{cm}^{-1}$ as $S = \Sigma(F_{obs}-F_{comp})^2/N$ =6.9E−4, where F_{obs}, F_{comp} are the observed and computed residual intensities, N is the number of considered wavelengths. In the following we use this value of S as our coincidence criterion to choose the best fits of our model spectra to the observed ozone bands in the minimization procedure.

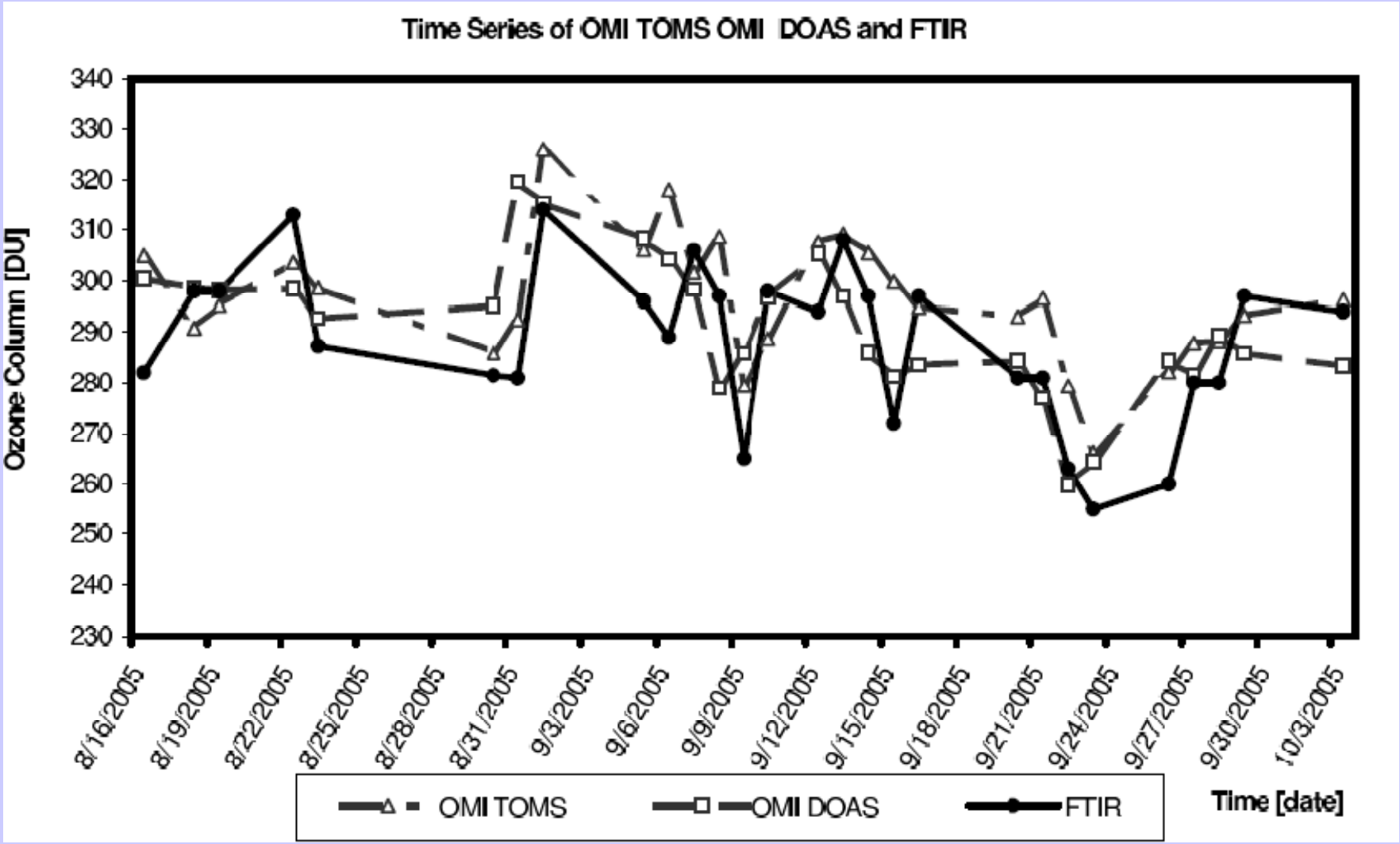


Figure 4a: Time series of OMI total ozone (OMI-TOMS and OMI-DOAS) and ground based FTIR total ozone data for 2005. Average difference of satellite minus ground based amounts to 8.45 DU and 3.19 DU for OMI-DOAS and OMI-TOMS respectively, with a 10.50 DU and 13.41 DU standard deviation (1.98 DU and 2.53 DU standard errors).

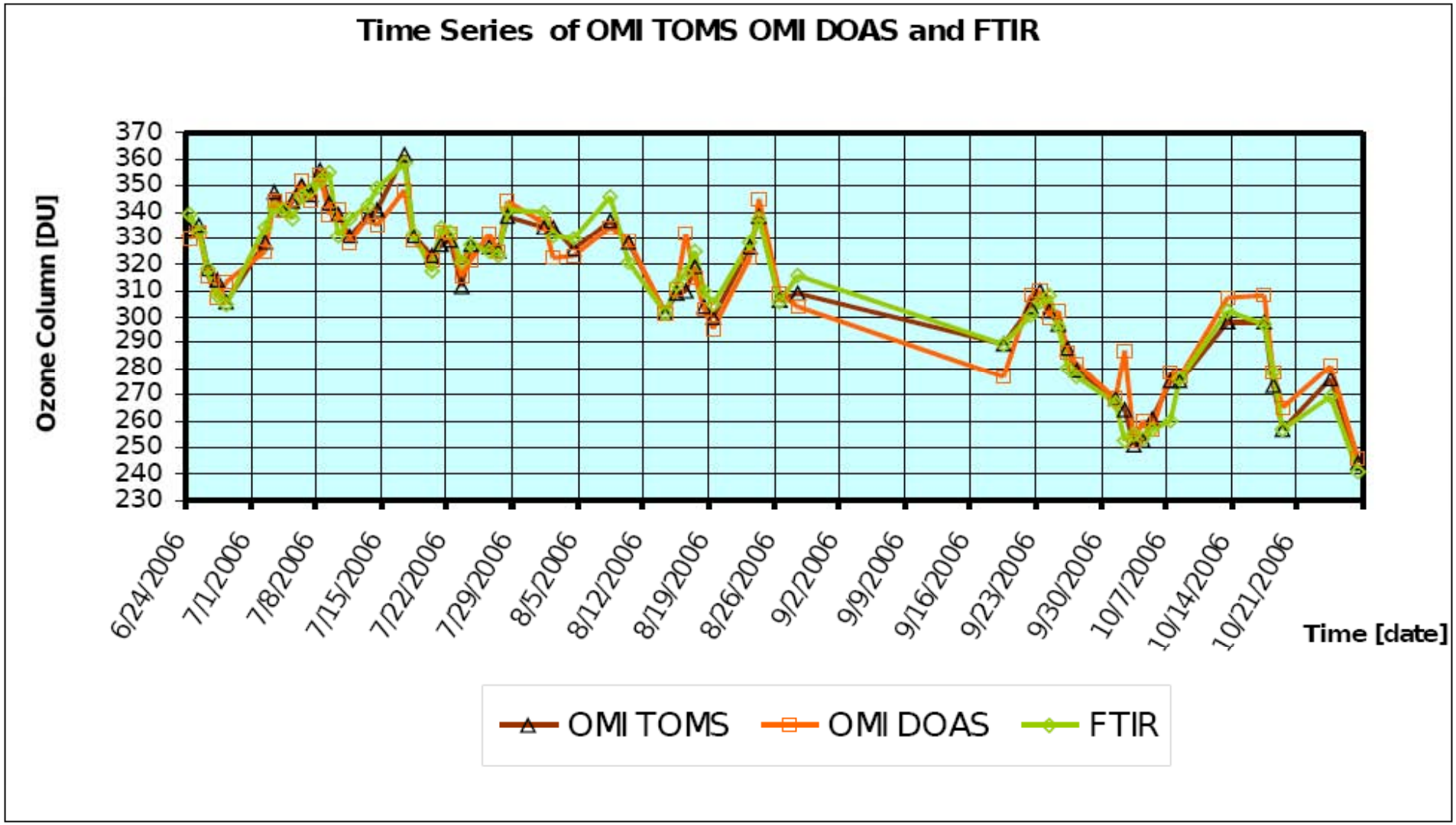


Figure 1: Time series of the OMI total ozone column and the ground based FTIR total ozone data of 2006 for the ground site of Kiev (MAO). Average difference of satellite minus ground based amounts to 0.37 DU and -0.25 DU for OMI-DOAS and OMI-TOMS respectively, with a 8.77 DU and 5.37 DU standard deviation (1.11 DU and 0.68 DU standard errors).

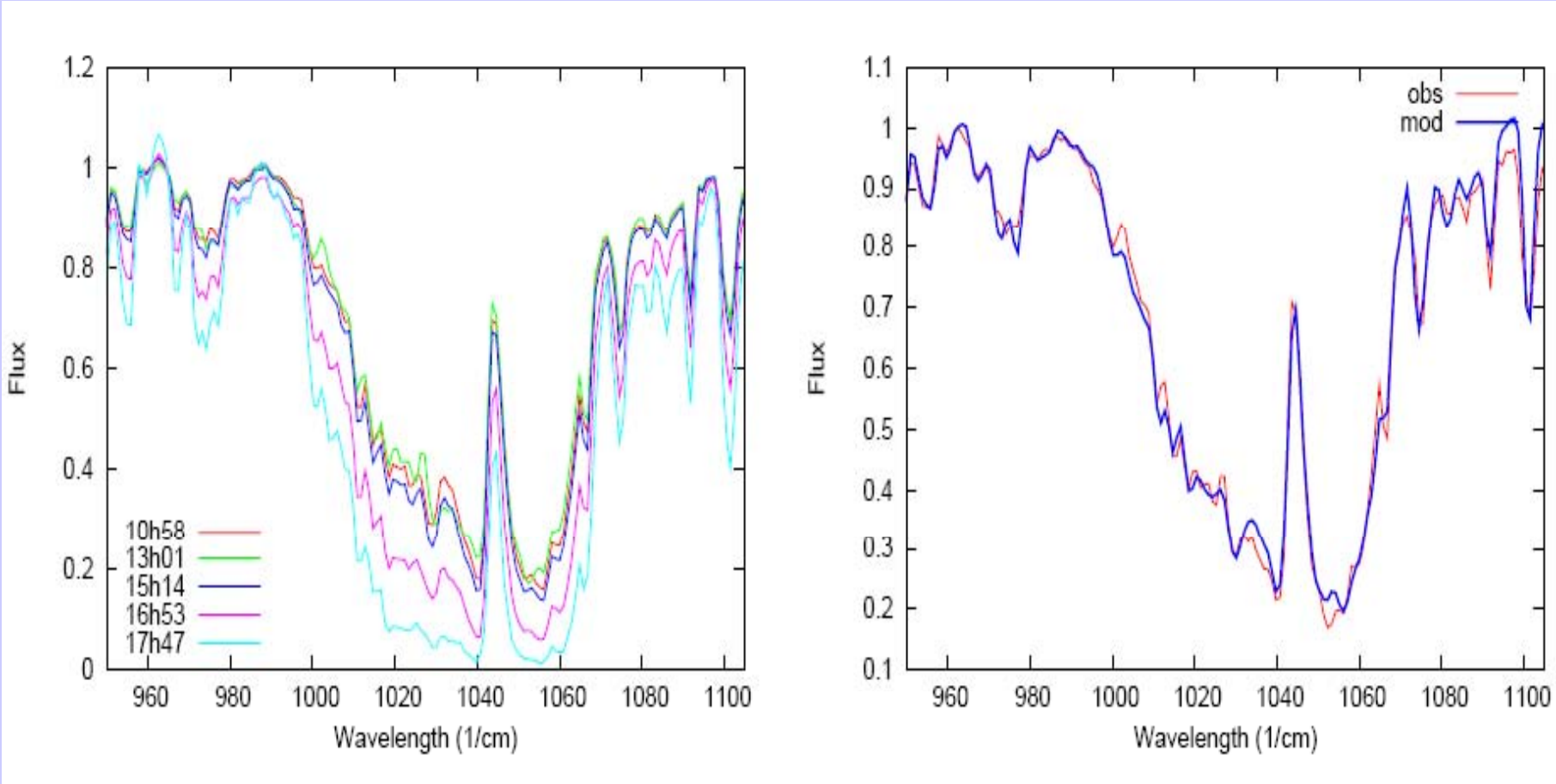
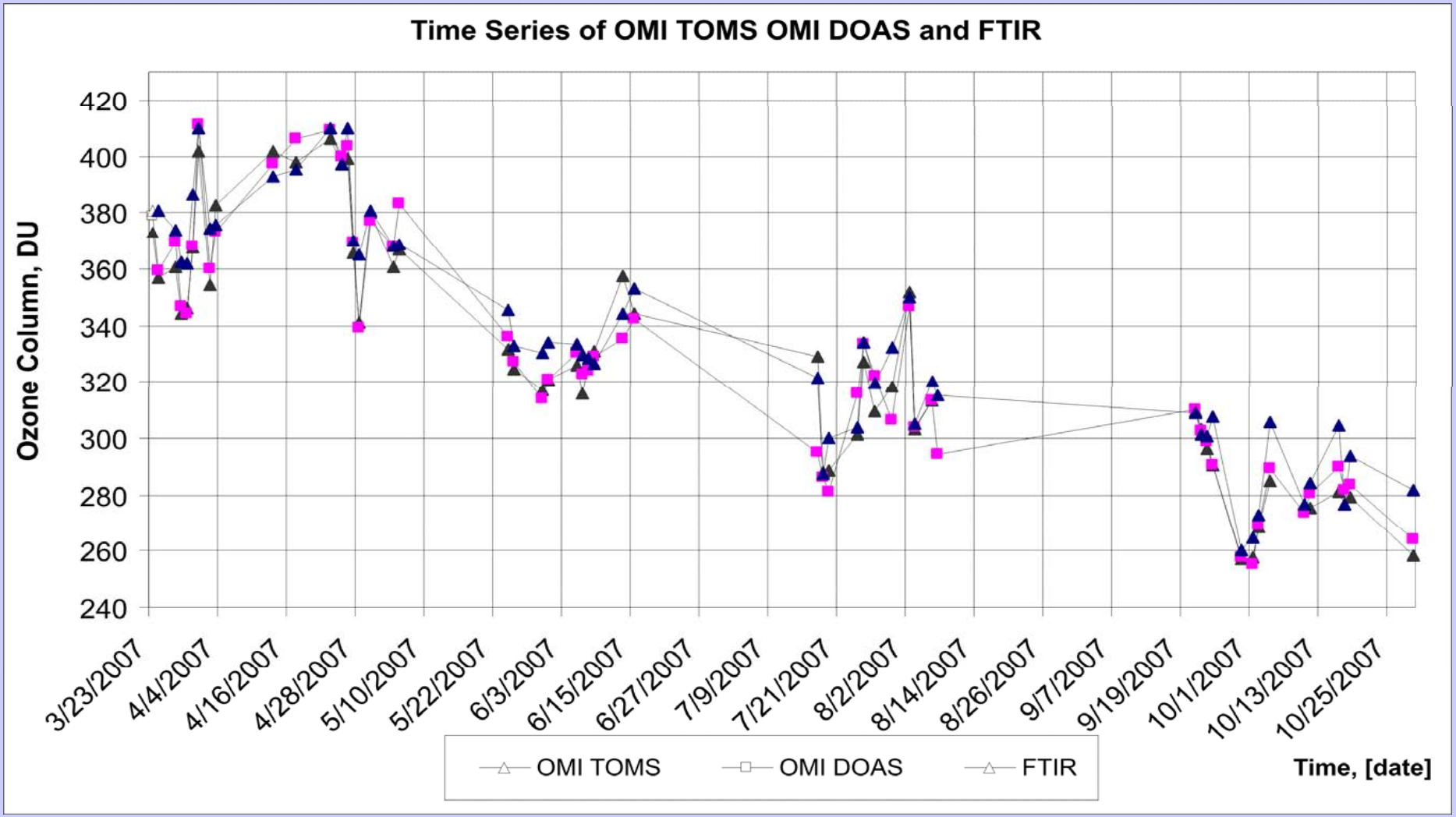


Figure 2: The observed FTIR spectra of the 9.6 micron ozone band for the 29th of September 2007 (29.09.07) (left) and the comparison of the observed FTIR spectra and modeled MODTRAN 4 spectra following the procedure for best fitting for the observation at 13h 01m local time on this day.



The total ozone column values retrieved from FTIR observations 2007 are biased low with respect to OMI-DOAS by –0.33 DU and to OMI-TOMS by –4.33 DU on average, where they have a relatively small standard error of about 1.4 %.

Date	Time H, min	ZSA, grad	TOC, DU	OMI-TOMS, DU	OMI-DOAS, DU	Tr.OC, DU our , TES	Surface O3, ppb	Htrop, km
28.03 2007	8 54 10 47 13 12 14 46 16 51 17 51 18 21	70.434 58.459 47.469 52.131 67.169 76.192 80.375	364.24 363.57 361.39 363.94 363.54 359.91 366.27	344.2 353.2	356.0 363.2	47.15 36.06 44.13 46.72 46.33 43.54 44.93	27.3 40.2 48.8 65.9 64.0 56.5 57.3	12.0
23.04 2007	9 22 11 15 14 35 15 40	57.622 43.200 42.879 50.375	411.01 410.30 410.27 409.54	412.0” 414.7	414.5 417.6	48.06 47.34 47.30 46.57	18.7 32.8 44.1 46.5	12.5
9.06.07	6 39 8 44 11 56 16 08 17 53	75.28 55.66 29.93 45.92 62.42	348.37 341.53 346.05 352.76 349.56	347.6	349.6	38.40 31.70 35.47 36.38 39.56	20 22 42.8 51 57	12.0
14.06. 2007	6 52 7 05 9 05 12 06 17 45	73.20 71.21 52.25 28.96 60.75	355.54 351.04 352.81 348.72 357.36	347.6	349.6	42.9 44.75 39.81 42.86 44.76	14 13 15 46 50	12.0

References: “ 22.04.07 OMI total column value = 448 DU;

18.07. 2007	13 35 14 52 16 10 17 20 18 15 19 27	29.93 36.16 46.62 58.23 66.19 77.39	287.12 294.07 290.91 294.39 292.85 296.60	291.5	289.6	44.32 51.27 49.37 51.60 50.09 53.80 53.55*	72 85 95 67 58 46	12.6
29.09. 2007	10 35 13 01 15 14 16 37 17 47	57.722 52.756 61.211 71.676 82.059	269.21 260.34 260.38 261.44 266.62	261.2 260.2	263.9 260.9	29.96 32.64 32.31 33.73 38.92	13.0 29.0 39.0 40.0 35.0	13.0
1.10.07	8 08 9 49 13 22 16 21 17 41	79.704 65.672 53.971 70.201 81.844	271.75 261.95 264.68 271.41 277.23	261.7	264.9	30.31 28.09 30.69 37.42 43.24	8.0 18.0 40.0 45.0 39.0	12.5
2.10.07	8 31 9 43 12 58 15 20	76.545 66.709 53.897 63.019	279.16 276.51 271.42 274.80	270.9	269.1	40.43 37.78 34.93 36.08 39.19*	8.0 12.0 43.0 47.0	12.5

References: * TESL3 tropospheric ozone column;

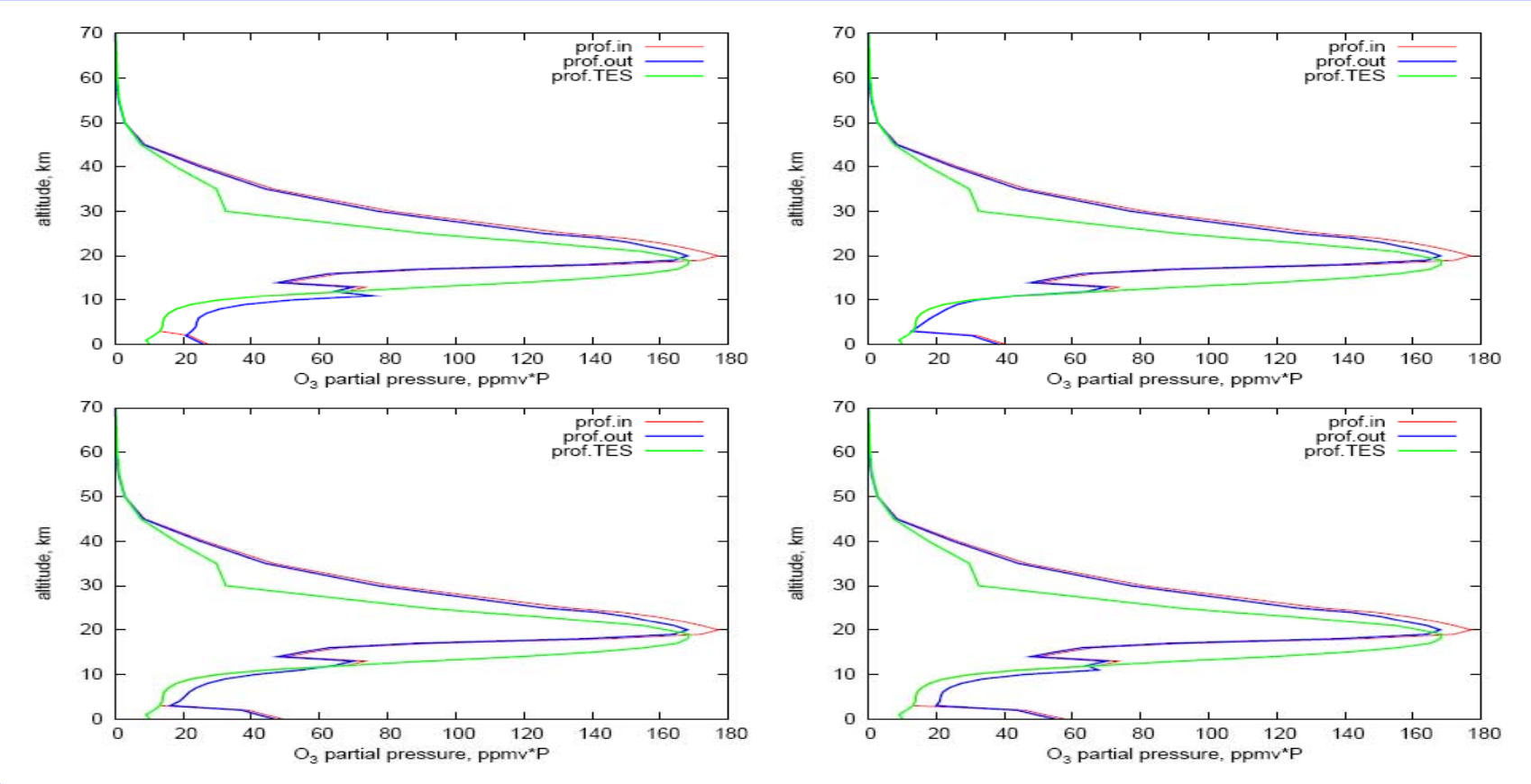


Figure 3: The retrieved ozone atmospheric profiles for the 28th of March 2007 , 8h54m and 10h47m (upper figures) local time, and 13h12m and 18h21m (lower figures) local time. From these figures one observes the low ozone concentrations in the boundary layer for the morning observation at 8h54m LT. Here most probably ozone titration by NO as emitted from cars during the morning traffic is taking place. From the 10h47m LT observation we see the abatement of tropospheric ozone, most clearly over the vertical range 2-11km. The enhancements of ozone due to the photochemical processes in the atmosphere are seen in the lower two figures. Our simultaneously performed surface ozone measurements reflect this dynamics also with the supportive values 27.3 ppb, 40.2 ppb, 48.8 ppb, and 57.3 ppb recorded for exactly these moments in time. For the comparison, we also show the Aura-TES ozone vertical profile for the 28th of March 2007, which can be considered as the valid satellite profile in the troposphere only.

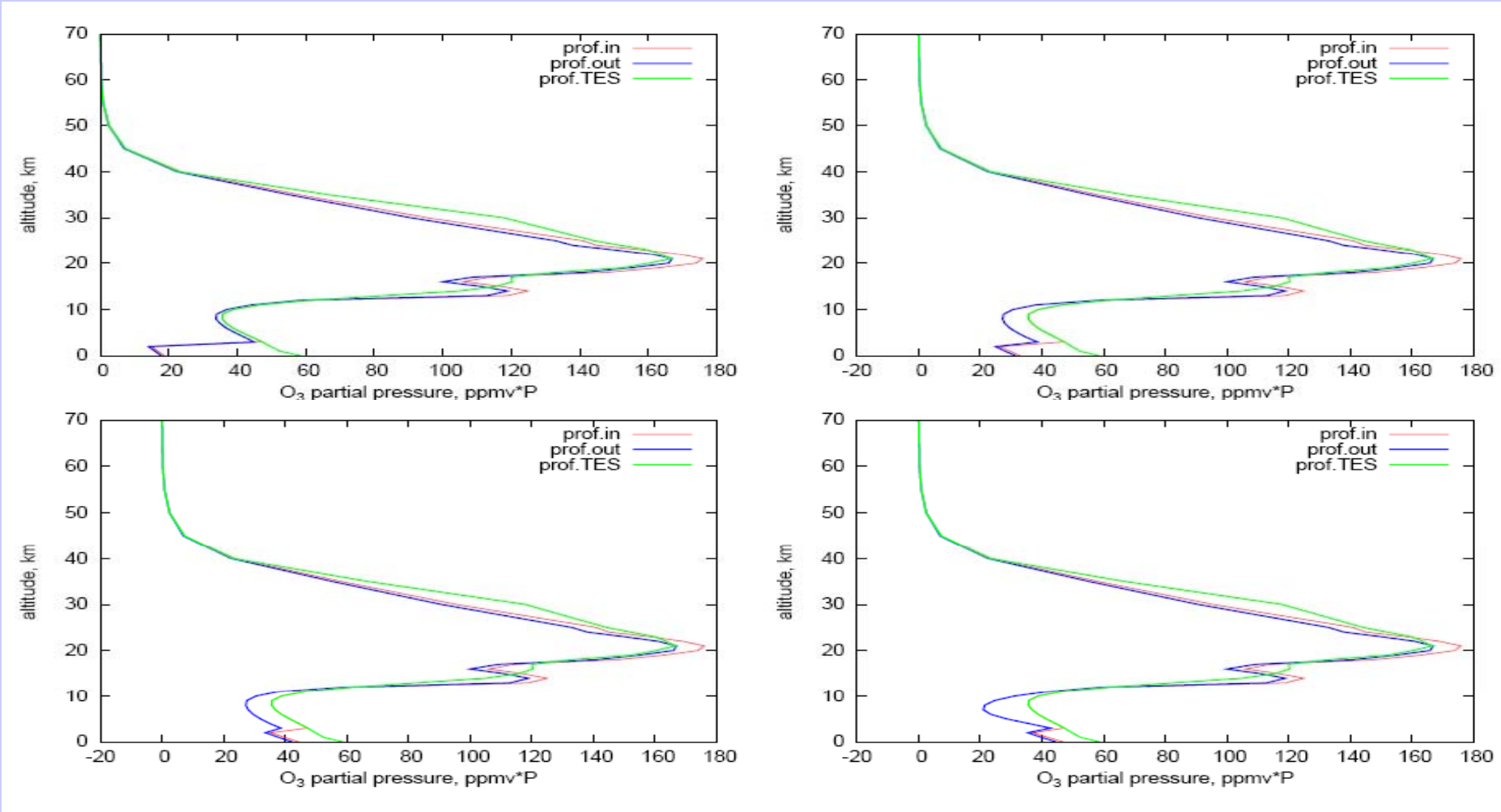


Figure 3: The retrieved ozone atmospheric profiles for the 23rd of April 2007, 09h22m and 11h15m (upper figures) local time, and 14h35m and 15h40m (lower figures) local time. On this day the values of both total ozone columns (411.0 DU by FTIR) and tropospheric ozone columns are very high. Possibly we are here observing a stratospheric intrusion event as the highest OMI value of total ozone column in 2007 was 448 DU for the 22nd of April 2007.

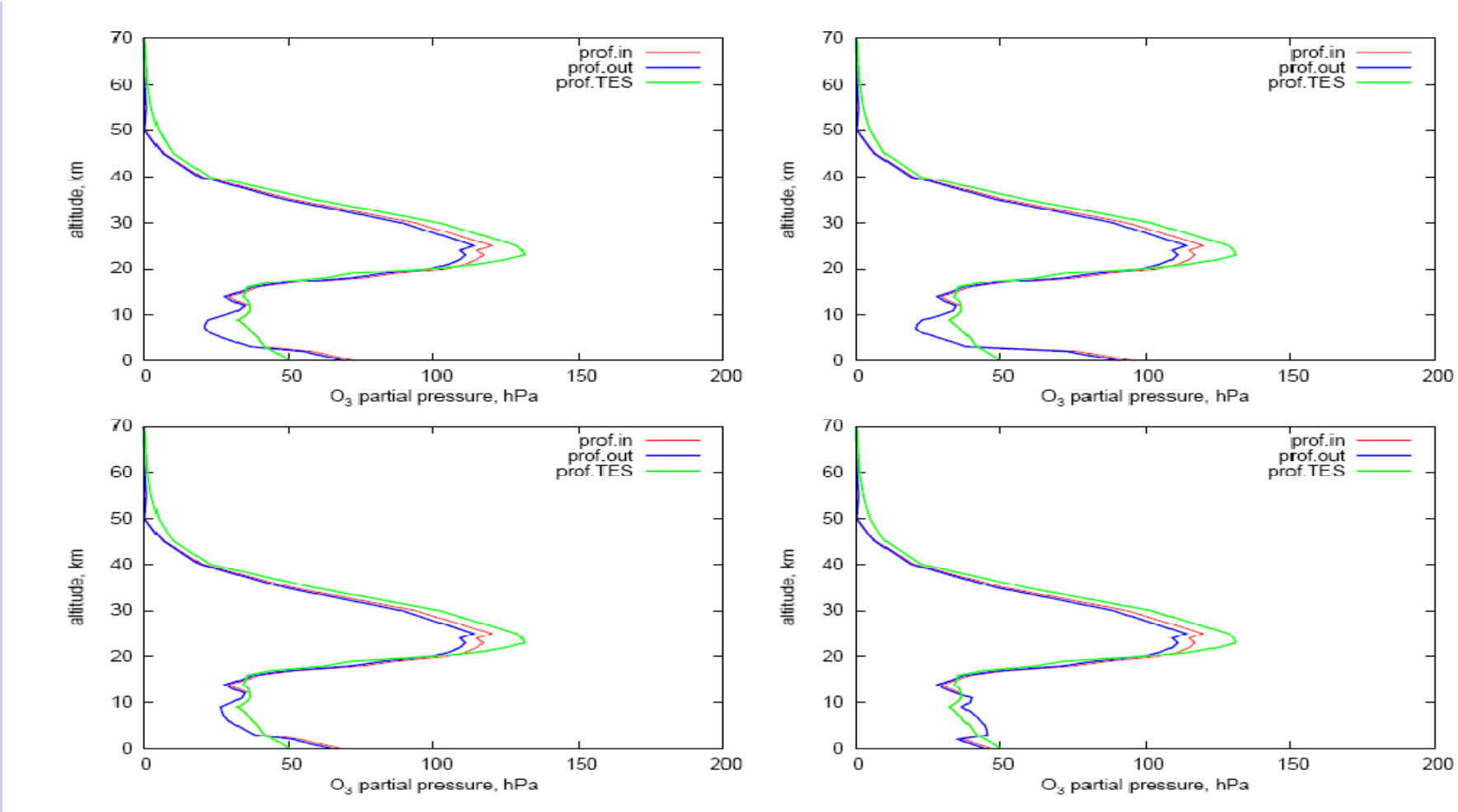


Figure 4: The retrieved ozone atmospheric profiles for the 18th of July 2007, 13h35m and 16h10m (upper figures) local time, and 17h20m and 19h27m (lower figures) local time. The very high tropospheric ozone columns and surface ozone concentrations (see Table2 for the exact numbers) and their daily dynamics are characteristic for episodes of strongly enhanced surface and tropospheric ozone due to tropospheric photochemistry. Please note that on this day the total ozone column is rather low (291.5 DU)

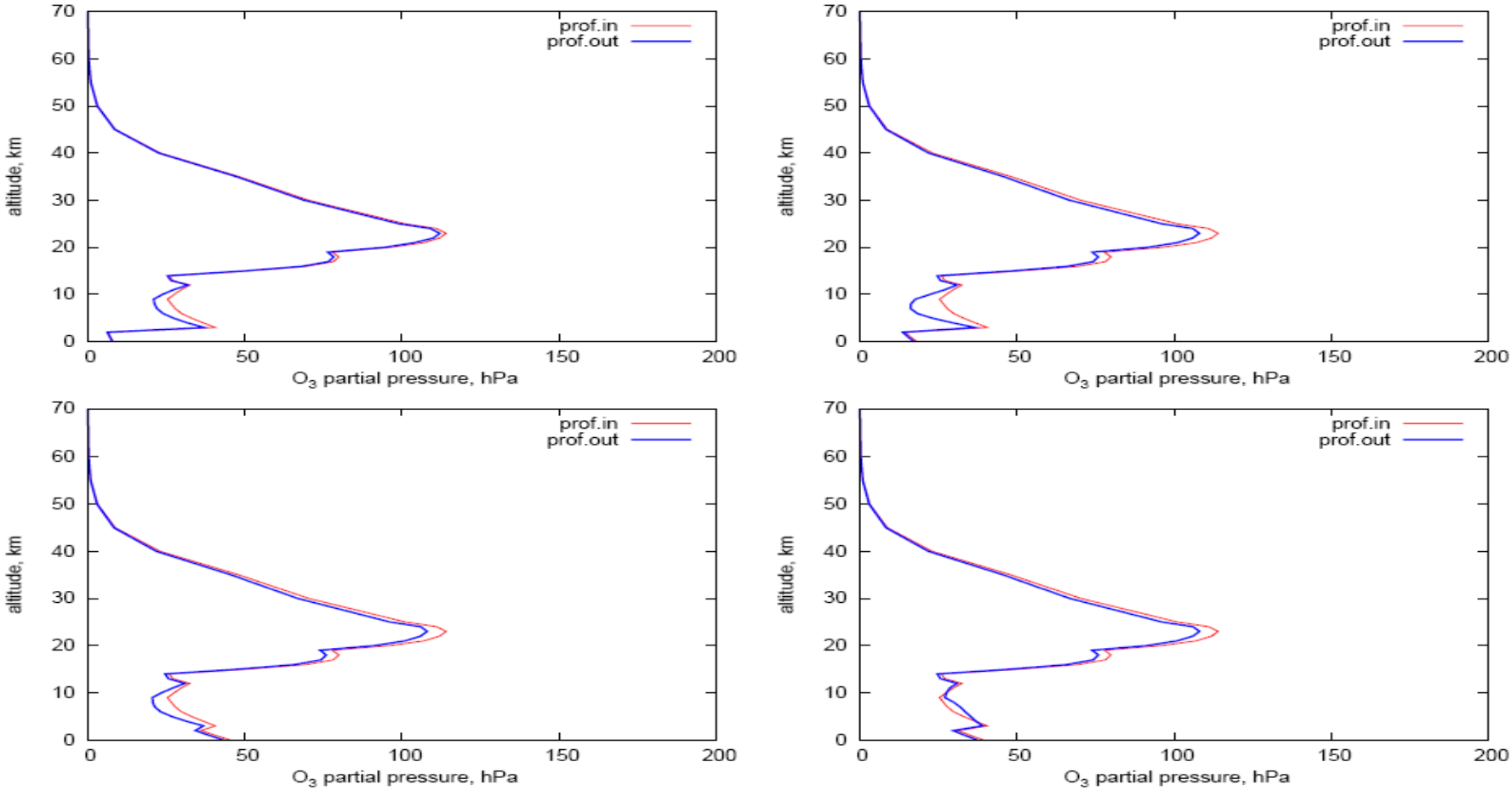


Figure 6: The retrieved atmospheric ozone profiles for the 1st of October 2007, 08h08m and 9h49m (upper figures) local time and 16h21m and 17h41m (lower figures) local time. Please note that on this day the FTIR total ozone column is rather low, only 262 DU. Nevertheless, we can see the daily dynamics of tropospheric ozone: in the morning ozone titration by NO and rather high ozone concentrations later in the afternoon due to photochemistry.. Unfortunately, for this day Aura-TES data are absent and hence the tropospheric part of the input ozone profile for the MODTRAN modeling process was constructed on the basis of the TEMIS monthly averaged data.

CONCLUSION

We have obtained a long track record of ground based FTIR total ozone column observations over the years 2005- 2007. Our estimates of the total ozone columns agree well with OMI satellite remote sensing data. Differences are in the percentile range. We note some significant differences under insufficiently clear sky conditions, which are indicative of the influence of clouds on FTIR observations.

AURA-MLS data of version 2.2 become available in 2007. We have got the total ozone column values retrieved from FTIR observations 2007 which are biased low with respect to OMI-DOAS by –0.33 DU and to OMI-TOMS by –4.33 DU on average (as mean value and –0.05 and –2.98 respectively as median one), where they have a relatively small standard error of about 1.4 %.

AURA-MLS data of version 2.2 allow us to retrieve tropospheric ozone profiles. For some days AURA-TES tropospheric profiles were also available and were compared with our retrieved profiles for validation. A preliminary analysis of troposphere ozone variability was performed. Observations during March-October demonstrate daily photochemical variability of tropospheric ozone and reveal mixing processes during the night.

The work presented here is the first step towards ozone profile retrievals on a regular basis. For this we need to further develop our retrieval procedures and we need to perform testing of our model calculations through line-by-line radiation transfer model calculations alike FASCODE. Since we do not have this code available we need to develop such coding in the near future ourselves. The procedure of quantitative comparison of our retrieved profile and other available data must be developed.

Line by line approach

*No additional suggestions for opacity computations;

*Direct computations of every line core and wings;

*Voigt function is adopted for the line profile;

*We compute blending lines using the detailed abundances information + isotopes!

*Spectra are smoothed AFTER the radiative transfer solution.

- **ACKNOWLEDGEMENTS**

- The authors are grateful to the AVDC, AURA-MLS and AIRS website administrations for providing the necessary satellite remote sensing data. The work of the authors from MAO NASU was partly supported by the grant of STCU (2005-2007) and by Space Agency of Ukraine (2007).

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(http://hirlam.knmi.nl/omi/research/validation/ao/documents.html)
13. OMI AO Progress Report no 3,
(http://hirlam.knmi.nl/omi/research/validation/ao/documents.html)
14. OMI AO Progress Report no 4,
(http://hirlam.knmi.nl/omi/research/validation/ao/documents.html)

An investigation of ozone and planetary boundary layer dynamics over the complex topography of Grenoble combining measurements and modeling

O. Couach et al., 2003 (Atmos.Chem.Phys. 3, 549-562)

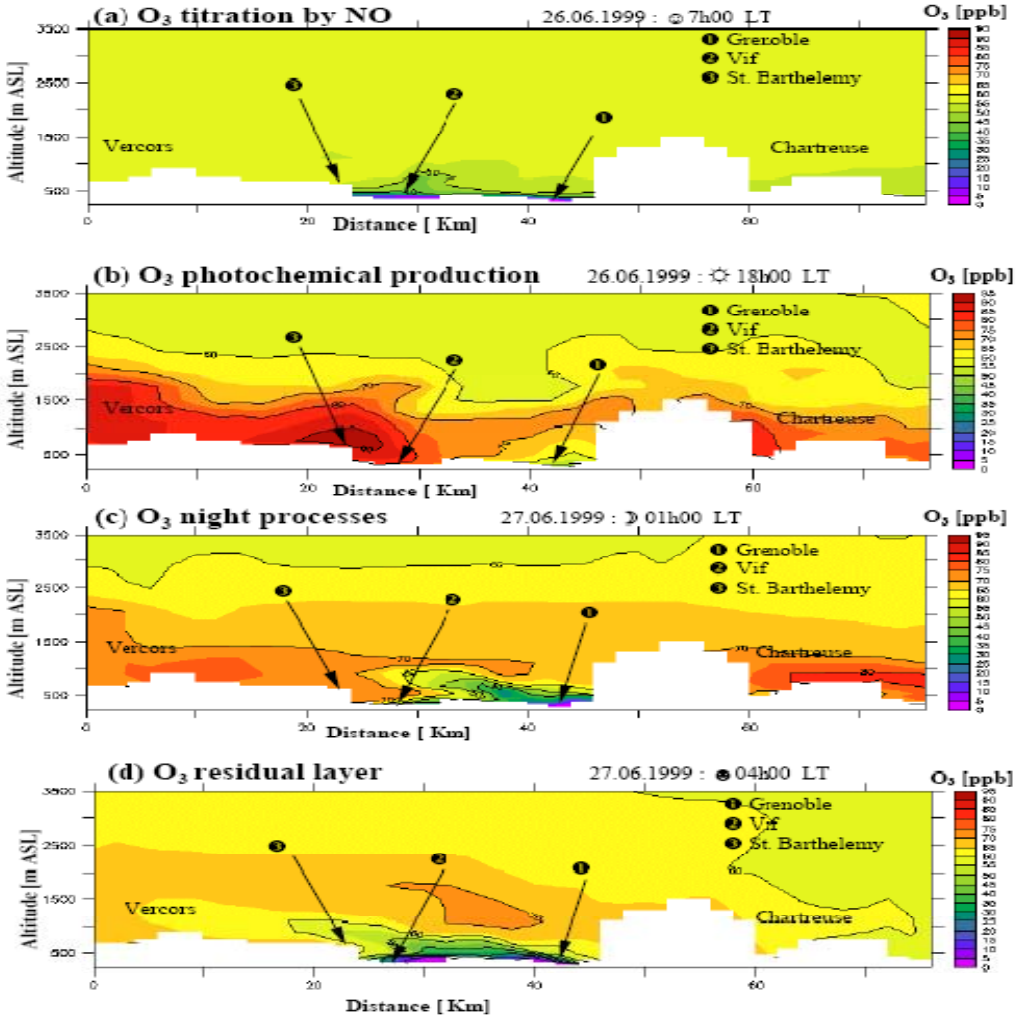

Fig. 10. Simulated ozone dynamics in a south to north (Vif – Grenoble) 50 km transect from the ground to 3500 m ASL on the vertical dimension. The ozone NO titration in the morning **(a)**, the ozone photochemical production **(b)**, the night ozone processes **(c)** and the ozone residual layer formation **(d)** are represented here.

MODTRAN4

The models calculate atmospheric transmittance, atmospheric background radiance, single-scattered solar and lunar radiance, direct solar and lunar irradiance and multiple-scattered solar and thermal radiance. The spectral resolution of LOWTRAN 7 is 20 cm^{-1} FWHM (Full Width at Half-Maximum) in averaged steps of 5 cm^{-1} in the spectral range of 0 to 50,000 cm^{-1} or 0.2 μm to infinity. The MODTRAN resolution is 2 cm^{-1} FWHM in averaged steps of 1 cm^{-1}. A single parameter band model (Pressure) is used for molecular line absorption in LOWTRAN 7, while MODTRAN utilizes (Pressure, Temperature and a line width). The effects of molecular continuum-type absorption; molecular scattering, aerosol and hydrometeor absorption and scattering are all included. Representative atmospheric aerosol, cloud and rain models are provided within the code with options to replace them with user-modeled or measured values. Spherical refraction and earth curvature (ray bending) are considered in the calculation of the atmospheric slant path and attenuation amounts along the path.

New atmospheric constituent profiles[10] containing separate molecular profiles (0 to 120 km) for thirteen (13) minor and trace gases are provided for use with both models. Six reference atmospheres, each defined by temperature, pressure, density and mixing ratios for H_2O, O_3, CH_4, CO and N_2O, all as a function of altitude (selected from the U.S. Standard Supplements, 1966[11] and the U.S. Standard Atmosphere 1976[12]) allow a wide range of climatological choices.

For LOWTRAN 7, Pierluissi and Maragoudakis[13] have developed separate band models and band model parameters for the absorbing molecules: H_2O, O_3, N_2O, CH_4, CO, O_2, CO_2, NO, NO_2, NH_3 and SO_2 (see section 4.1). Analytic transmittance functions (double-exponential) replace numerical tables stored in previous LOWTRAN models. These band model parameters were developed with and based on degraded line-by-line spectra[14] and validated against laboratory measurements. Modifications to the water vapor continuum absorption at 1 and 10 μm are included in both models. These corrections were based on a series of laboratory and field measurements[15,16,17,18].

For MODTRAN 2, Anderson et al[19] have developed band model parameters from the HITRAN 1992[20] database with pressure and temperature dependence and a defined line width (see section 3). Besides its more recent and accurate derivation, the MODTRAN model also contains geometrical corrections to some long-standing problems with short and long horizontal-like paths[21], errors currently existing in the older versions of LOWTRAN and FASCODE.

Many new features were introduced between MODTRAN 2 (1992) (Acharya *et al.*, 1993) and MODTRAN3.5 (1996). These include:

- A second multiple scattering option based on the multiple stream discrete ordinate DISORT algorithm (Stamnes *et al.*, 1988);
- A new CO_2 mixing ratio input option for scaling the profile;
- "Heavy" molecule (e.g., CFCs) cross-section spectra and profiles;
- A set of surface reflectivity (albedo) options;
- Upgrades to the cloud and rain models;
- New solar TOA (top of the atmosphere) irradiance databases;
- Wavelength / frequency inputs in cm^{-1}, μm and nm;

MODTRAN3.7

MODTRAN3.7 includes a number of upgrades to the aerosol models. The built-in aerosol models are no longer confined to fixed regions, but can be independently moved to any region and can be stretched, compressed, overlapped and scaled. The user-supplied spectral parameter input schemes for aerosols have also been improved.

In addition, extensive modifications now allow MODTRAN to incorporate NOVAM, the Navy Oceanic Vertical Aerosol Model (Gathman and Davidson, 1993). Here, NOVAM is used as a stand-alone code, which is first executed to produce an output file consisting of spectral- and altitude-dependent aerosol extinction, absorption, and asymmetry parameters.

MODTRAN4 adds the following features:

- Two Correlated-*k* (CK) options: the standard option which uses 17 *k* values (absorption coefficients) per spectral bin and a slower, 33 *k* value option primarily for upper-altitude (>40 km) cooling rate and weighting function calculations;

- An option to include azimuth dependencies in the calculation of DISORT solar scattering contributions ;

- Upgraded ground surface modeling including parameterized forms for spectral BRDFs (Bidirectional Reflectance Distribution Functions) and an option to define a ground image pixel (H2) different from its surrounding surface.

- A high-speed option, most appropriate in short-wave and UV spectral regions, that uses 15 cm-1 band model parameters);

- Scaling options for water vapor and ozone column amounts;

- Improved, higher spectral resolution, cloud parameter database (not aerosols); and

- More accurate Rayleigh scattering and indices of refraction.

1.2 Radiation Transport Upgrades

In addition to adding the above features, many improvements have been made to MODTRAN's radiation transport algorithms. These include:

- Using the new HITRAN96 database (Rothman *et al.*, 1992; Rothman *et al.*, 1998) to generate the band model parameters;
- Reformulating the absorption coefficient and line spacing band model parameters, and the temperature dependence of the Lorentz half-widths (Bernstein *et al.*, 1995) (MODTRAN3.5);
- Lowering the minimum of the band model parameter temperature grid to 180 K for linear interpolation modeling of the Antarctic tropopause (MODTRAN3.5);
- Improving the band model line tail treatment by more carefully accounting for the line center locations (MODTRAN3.5) and increasing the line tail calculation resolution to 0.25 cm-1 (MODTRAN3.7);
- Applying the "linear-in-tau" method to thermal radiance multiple scattering terms (MODTRAN3.5).

Model	Model Atmosphere	WSS and WHH Default Wind Speed (m/s)
0	User-defined (Horizontal Path)	6.9
1	Tropical	4.1
2	Mid-latitude summer	4.1
3	Mid-latitude winter	10.29
4	Sub-arctic summer	6.69
5	Sub-arctic winter	12.35
6	U.S. Standard	7.2
7	User-define	6.9

Species
pressure
temperature
water vapor (H_2O)
carbon dioxide (CO_2)
ozone (O_3)
nitrous oxide (N_2O)
carbon monoxide (CO)
methane (CH_4)
oxygen (O_2)
nitric oxide (NO)
sulfur dioxide (SO_2)
nitrogen dioxide(NO_2)
ammonia (NH_3)
nitric acid (HNO_3)

Table 9. Various Names for the Heavy Molecular Gases, (WMOLX(J), J = 1, 13).

1	$CC1_3F$	F11	CFC-11
2	CCl_2F_2	F12	CFC-12
3	$CClF_3$	F14	CFC-13
4	CF_4	F14	CFC-14
5	$CHClF_2$	F22	CFC-22
6	$C_2Cl_3F_3$	F113	CFC-113
7	$C_2Cl_2F_4$	F114	CFC-114
8	C_2ClF_5	F115	CFC-115
9	$ClONO_2$		
10	HNO_4		
11	$CHCl_2F$		
12	CCl_4		
13	N_2O_5		

Evaluation of tropospheric and stratospheric ozone trends over Western Europe from ground-based FTIR network observations (C. Vigouroux et al. 2008, Atmos.Chem.Phys. Discuss., 8, 5007–5060, 2008)

Within the European project UFTIR (Time series of Upper Free Troposphere observations from an European ground-based FTIR network), six ground-based stations in Western Europe, from 79 N to 28 N, all equipped with Fourier Transform infrared (FTIR) instruments and part of the Network for the Detection of 5 Atmospheric Composition Change (NDACC), have joined their efforts to evaluate the trend of several direct and indirect greenhouse gases over the period 1995–2004. The retrievals of CO, CH4, C2H6, N2O, CHClF2, and O3 have been optimized. Using the optimal estimation method, some vertical information can be obtained in addition to total column amounts. The observed total column ozone trends are in agreement with previous studies:

1) no total column ozone trend is seen at the lowest latitude station Izan˜a (28 N);

2) slightly positive total column trends are seen at the two mid-latitude stations Zugspitze and Jungfraujoch (47 N), only one of them being significant;

3) the highest latitude stations Harestua (60 N), Kiruna (68 N) and Ny-A˚ lesund (79 N) show significant positive total column trends. Following the vertical information contained in the ozone FTIR retrievals, we provide partial columns trends for the layers: ground-10 km, 10–18 km, 18–27 km, and 27–42 km, which helps to distinguish the contributions from dynamical and chemical changes on the total column ozone trends. We obtain no statistically significant trends in the ground–10 km layer for five out of the six ground-based stations. We find significant positive trends for the lowermost stratosphere at the two mid-latitude stations, and at Ny-A˚ lesund. We find smaller, but significant trends for the 18–27 km layer at Kiruna, Harestua, Jungfraujoch, and Iza ˜na. The results for the upper layer are quite contrasted: we find significant positive trends at Kiruna, Harestua, and Jungfraujoch, and significant negative trends at Zugspitze and Iza˜na.