Summertime tropospheric ozone assessment over the Mediterranean region using the thermal infrared IASI/MetOp sounder and the WRF-Chem model

S. Safieddine¹, A. Boynard¹, P.-F. Coheur², D. Hurtmans², G. Pfister³, B. Quennehen¹, J. L. Thomas¹, J.-C. Raut¹, K. S. Law¹, Z. Klimont⁴, J. Hadji-Lazaro¹, M. George¹ and C. Clerbaux¹,²

¹Sorbonne Universités, UPMC Univ. Paris 06; Université Versailles St-Quentin; CNRS/INSU, LATMOS-IPSL, Paris, France
²Spectroscopie de l'Atmosphère, Chimie Quantique et Photophysique, Université Libre de Bruxelles (U.L.B.), Brussels, Belgium
³Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA
⁴International Institute for Applied Systems Analysis, Laxenburg A-2361, Austria
Abstract

Over the Mediterranean region, elevated tropospheric ozone (O$_3$) values are recorded, especially in summer. We use the thermal Infrared Atmospheric Sounding Interferometer (IASI) and the Weather Research and Forecasting Model with Chemistry (WRF-Chem) to understand and interpret the factors and emission sources responsible for the high O$_3$ concentrations observed in the Mediterranean troposphere. Six years (2008-2013) of IASI data have been analyzed and show consistent maxima during summer, with an increase of up to 22% in the [0-8] km O$_3$ column in the eastern part of the basin compared to the middle of the basin. We focus on summer 2010 to investigate the processes that contribute to these summer maxima. Using two modeled O$_3$ tracers (inflow to the model domain and local anthropogenic emissions), we show that between the surface and 2 km, O$_3$ is mostly formed from anthropogenic emissions and above 4 km, is mostly transported from outside the domain or from stratospheric origins. Evidence of stratosphere to troposphere exchanges (STE) in the eastern part of the basin is shown, and corresponds with low water vapor mixing ratio and high potential vorticity.

1 Introduction

Tropospheric ozone (O$_3$) is a greenhouse gas, air pollutant, and a primary source of the hydroxyl radical OH, the most important oxidant in the atmosphere (Chameides and Walker, 1973; Crutzen, 1973). Previous observations and studies have shown that tropospheric O$_3$ over the Mediterranean exhibits a significant increase during summer time, especially in the east of the basin (Kouvarakis et al., 2000; Im et al., 2011; Gerasopoulos et al., 2005, 2006a; Richards et al., 2013; Zanis et al., 2014). Meteorological conditions such as frequent clear sky conditions (Fig. 1a) and high exposure to solar radiation (Fig. 1b) in summer enhance the formation of
photochemical $O_3$ due to the availability of its precursors. These precursors include carbon monoxide (CO), peroxy radicals generated by the photochemical oxidation of volatile organic compounds (VOCs) and nitrogen oxides ($NO_x = NO + NO_2$). Locally, the eastern part of the basin is surrounded with megacities such as Cairo, Istanbul, and Athens that are large sources of local anthropogenic emissions. The geographic location of the basin makes it a receptor for anthropogenic pollution from Europe both in the boundary layer (Fig. 1c) and the mid-troposphere (Fig. 1d). The threshold $O_3$ value for air quality standards for the European Union (of daily maximum of running 8-hour mean values of 60 ppbv) is exceeded on more than 25 days per year at a large number of stations across Europe, many of which are located to the south of Europe in the Mediterranean basin (EEA, 2012). The dynamical processes of the summer circulation over the Mediterranean were previously attributed to the Hadley cell considered as the driver of the major subtropical dry zones. Rodwell and Hoskins (1996) argued that during the June-August period, the zonal mean Hadley circulation has very little motion and cannot explain the dry season of North Africa and the Mediterranean. Rodwell and Hoskins (1996; 2001) suggested, through numerical simulations, that the Asian monsoon heating induces an equatorially trapped Rossby wave to its west that interacts with the mid-latitude westerlies, producing a region of adiabatic descent and triggering subsidence. Long term analysis of $dP/dt$ (units: Pa.s$^{-1}$, used to represent subsidence) shows indeed a positive enhancement over the Mediterranean region (Ziv et al., 2004) making the South Asian monsoon a fundamental driver of the summer circulation over the Eastern Mediterranean (Tyrlis et al., 2013). High $O_3$ values in the Mediterranean troposphere in the literature are attributed to different sources: Lelieveld et al. (2002) showed that in the upper troposphere, Asian pollution is transported from the east by the monsoon across the Mediterranean tropopause into the lower stratosphere. Liu et al., (2011) showed with long term model analysis that the dominant sources of $O_3$ in the Middle East
(including the Mediterranean) are the transport from Asia and local production. On the other hand, Gerasopoulos et al. (2005) have shown that the mechanism that controls surface O₃ seasonal variability in the eastern basin during summer is mainly the transport from Europe. Galani et al. (2003) detected with lidar measurements an increase of 10% of tropospheric O₃ between 4.5 and 6.5 km due to stratosphere to troposphere exchange events (STE). Zbinden et al. (2013) using aircraft data from MOZAIC (Measurements of OZone and water vapour by in-service Airbus airCraft programme) over 15 years (1994–2009), showed that the tropospheric O₃ columns in the east of the Mediterranean, reached a maximum reaching 43.2 DU during June-July. This recorded maximum exceeds the maximum recorded for Beijing for the same period, for example. Model calculation using WRF-Chem (Weather Research and Forecasting model coupled with Chemistry) and EMEP (European Monitoring and Evaluation Programme) MSC-W (Meteorological Synthesizing Centre-West) models of the Eastern Mediterranean during heat waves in 2007 showed that the daily maximum near surface O₃ is mostly sensitive to anthropogenic emissions of O₃ precursors (Hodnebrog et al., 2012). Im et al. (2011) found that the near surface ozone mixing ratios increases almost linearly with temperature by 1.0±0.1 ppb O₃ per Kelvin. STE processes can affect the tropospheric O₃ budget and impact air quality if transported to the boundary layer (Fiore et al., 2002). Stratospheric intrusions have been detected in the Mediterranean region, especially to the east side (Galani et al., 2003; Zanis et al., 2014), because it lies to the south of the North Hemisphere polar jet flowing over mid-latitudes (Stohl et al., 2000; Gerasopoulos et al., 2001). Understanding the factors that contribute to the O₃ maxima is important for developing control measures and prevents pollution build up. In this study we analyze O₃ and its sources at different altitudes in the Mediterranean troposphere. Section 2 introduces the model and observations data sets used in this study. In section 3, we analyze six years (2008-2013) of IASI tropospheric [0-8] km O₃ column seasonal variation above the whole
Mediterranean basin as well as at 15°E and 30°E, representative of what we henceforth refer as “middle of the basin” and “east of the basin” respectively. In section 4 we focus on summer 2010, as an example year, and validate the WRF-Chem model simulation with surface O₃ and IASI data, and then use the WRF-Chem model to assess the sources of O₃ in the troposphere. In section 5, we use IASI and WRF-Chem free tropospheric O₃ data to investigate potential stratosphere to troposphere exchange events. Discussion and conclusions are given in section 6.

2 Model and observational data

2.1 WRF-Chem model

In this study, we use the regional chemistry transport model WRF-Chem, Version 3.2 (Grell et al., 2005) to assess the O₃ budget and spatio-temporal variability of O₃ over the Mediterranean during summer 2010. The model domain shown in Fig. 2a is over Europe and the Mediterranean basin, the latter being the focus of this study (Fig. 2b). The horizontal resolution is of 50 km x 50 km and the vertical resolution is of 28 levels between the surface and 10 hPa. The meteorological initial and boundary conditions are based on the National Centers for Environmental Prediction (NCEP) Final (FNL) analyses with analysis nudging for wind, temperature, and humidity applied. Fields are provided every 6 hours with 1° horizontal resolution and 27 vertical levels from the surface up to 10 hPa. The chemical initial and boundary conditions, spatially and temporally varying (6 hours), are constrained by global chemical transport simulations from MOZART-4/GEOS-5 with 1.9° x 2.5° horizontal resolution (Emmons et al., 2010a). The WRF-Chem gas-phase chemical mechanism is that from Model for Ozone and Related Chemical Tracers, version 4 (MOZART-4) (Emmons et al., 2010a), which is coupled to the aerosol scheme Goddard Chemistry Aerosol Radiation and Transport (GOCART) model (Chin et al., 2002). The model also includes anthropogenic and fire emissions that are calculated off-line. The anthropogenic
emissions used within the WRF-Chem model were developed in the frame of the ECLIPSE European project using the Greenhouse gas and Air pollution Interactions and Synergies (GAINS) model. In addition to the ECLIPSE V4.0 anthropogenic emissions, ship emissions from the RCP 6.0 scenario (Fujino et al., 2006; Hijioka et al., 2008) were used. Biomass burning emissions are obtained from the Fire Inventory from NCAR (FINN V1) (Wiedinmyer et al., 2011). Biogenic emissions are calculated online from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006). The WRF-Chem simulation outputs are saved every 2 hours from 1 June 2010 until 31 August 2010.

In this study, we use a tagging method for O_3 (Emmons et al., 2012), which has been applied in global models for diagnosing contributions for individual sources to O_3 (e.g. Lamarque et al., 2005; Pfister et al., 2006, 2008; Emmons et al., 2010b; Wespes et al., 2012), and in other global and regional chemical transport models (Ma et al., 2002; Hess and Zbinden, 2013). Recently, this scheme was used for the first time in the WRF-Chem model to quantify the contribution of transport on surface O_3 over California (Pfister et al., 2013). Here, we apply this scheme to keep track of the contribution of O_3 within the WRF-Chem domain. To determine O_3 sources, tagged NO_x is traced through the odd nitrogen species (e.g. PAN, HNO_3, organic nitrates) to account for NO_x recycling (Emmons et al., 2012). Two separate tracer runs were conducted with the same emissions, initial, and boundary conditions. In the first one, O_3-ANTHRO tracer accounts for the anthropogenic regional tagged NO_x, while the second one O_3-INFLOW tracer accounts for tagged O_3 as well as all nitrogen species at the lateral boundaries of the regional model domain. O_3-INFLOW tracer includes O_3 and O_3 precursors from all natural (including lightning and stratospheric O_3) and anthropogenic sources outside the regional modeling domain. Within the regional modeling domain, O_3-INFLOW undergoes transport and chemical processes, but is not produced from sources other than from reactions including the tagged species. Since in this version of WRF-Chem the
stratospheric O$_3$ is controlled by the lateral boundaries, O$_3$ from stratospheric intrusions within the regional domain would be labeled as O$_3$-INFLOW as well. More details about the tagging scheme are provided in Emmons et al. (2012). Two more tracers are available to complete the O$_3$ budget: O$_3$ from biogenic sources and O$_3$ from fires. Given that their contribution to the total budget in comparison with O$_3$-INFLOW and O$_3$-ANTHRO tracers is small (<10%), they are analyzed together in this study as “residuals” to the total budget and their contribution is defined as 100% - (O$_3$-ANTHRO% + O$_3$-INFLOW%). We focus our analysis on summer 2010, which corresponds to the year of the anthropogenic emission inventory used in the model. During July-August 2010, the Russian heat wave occurred that caused severe fires with high O$_3$ and O$_3$ precursors’ emissions that were probably transported to the Mediterranean region, and will be further investigated in this study.

2.2 EMEP data
The EMEP (European Monitoring and Evaluation Programme) O$_3$ hourly data (http://ebas.nilu.no/) are used to validate the WRF-Chem model at the surface. All ozone measurements within EMEP are done by UV monitors. In this study, measurements at 8 ground rural background sites during the summer of 2010 are used. Details on the EMEP observation system can be found in Hjellbrekke et al. (2012). The geographic locations of the 8 stations used for validation are plotted in Fig. 2 and the corresponding details are listed in Table 1. Two more station data were available, GR01-Aliartos (38.37°N, 23.11°E) and IT01-Montelibretti (42.1°N, 12.63°E). We disregarded the data from these stations because they show strong diurnal variation of 80-90 ppbv amplitude, and recurrent near zero O$_3$ concentrations throughout the period of the study, and were thus considered unreliable.

2.3 IASI satellite measurements
On board of the MetOp platforms, IASI was launched in October 2006 (IASI-1) and September 2012 (IASI-2). It has been sounding operationally the atmosphere since June 2007 (IASI-1) and January 2013 (IASI-2). IASI is a nadir looking Fourier transform spectrometer that probes the Earth’s atmosphere in the thermal infrared spectral range between 645 and 2760 cm\(^{-1}\), with a spectral resolution of 0.5 cm\(^{-1}\) (apodized) and 0.25 cm\(^{-1}\) spectral sampling. Global distributions of O\(_3\) vertical profiles are retrieved in near real time using a dedicated radiative transfer and retrieval software for the IASI O\(_3\) product, the Fast Optimal Retrievals on Layers for IASI (FORLI-O\(_3\)) (Hurtmans et al., 2012). The IASI FORLI-O\(_3\) observations are selected for scenes with cloud coverage below 13\%, and with RMS of the spectral fit residual lower than 3.5 \times 10^{-8} W/cm\(^2\).sr.cm\(^{-1}\). Details about the chemical components that can be measured by IASI can be found in Clerbaux et al. (2009), Coheur et al. (2009), Turquety et al. (2009), and Clarisse et al. (2011). IASI has the highest O\(_3\) sensitivity in the mid to upper troposphere (Safieddine et al., 2013). Figure 3 shows the partial column averaging kernel function for two specific observations above land and sea during June 2010. It can be seen that the sensitivity to the O\(_3\) profile is maximal around 4-10 km for both observations. IASI sensitivity near the surface is usually limited above the sea, as seen on the right panel of Fig. 3, and better over land as seen in the left panel, and with corresponding better thermal contrast (7.8\(^{\circ}\) above land, and 1.2\(^{\circ}\) above sea). In fact, IASI is able to detect several pollutants (e.g. carbon monoxide, ammonia, sulfur dioxide and ammonium sulfate aerosols), especially when large thermal contrast is combined with stable meteorological conditions leading to the accumulation of pollutants near the surface (Boynard et al., 2014).

3 Tropospheric O\(_3\) seasonal variation as seen by IASI

To investigate the seasonal behavior of tropospheric O\(_3\) above the Mediterranean, we plot in Fig. 4 the [0-8] km partial tropospheric O\(_3\) column as seen by IASI, during 2008 to 2013. The data were averaged seasonally and daytime observations were used since the information content of
IASI-O$_3$ data is shown to be higher during the day (Clerbaux et al., 2009). We observe a similar tropospheric O$_3$ seasonal behavior each year. The weakest values are observed in winter (DJF) and autumn (SON), when solar activity is minimal. Increasing values in spring (MAM) are due to the increase of O$_3$ production from photochemistry, buildup of winter O$_3$ and its precursors, transport, and/or from O$_3$ of stratospheric origin integrating into the troposphere. The [0-8] km column reaches a maximum in summer (JJA) due to high photochemical O$_3$ production, horizontal transport into the region, or stratosphere to troposphere exchange, all of which will be investigated in detail in the following sections. Richards et al. (2013) detected a similar spatial distribution with the Global Ozone Monitoring Experiment-2 (GOME-2) during summers of 2007 and 2008, with values exceeding 32 DU at the east of the basin for the [0-6] km O$_3$ column.

To investigate further the higher values detected to the east of the basin, we analyze longitudinal transects of 1° width along 15°E (representing the middle of the basin) and 30°E (representing the east of the basin), and marked in orange in Fig. 2.

Figure 5 shows that during the period of 2008 to 2013, the summers in the east of the basin, notably at 30°E (plotted in red) are marked by elevated tropospheric [0-8] km O$_3$ values. The difference between the two O$_3$ columns at the 2 different longitudes was highest (4.7 DU-22 %) during June 2012. The highest recorded values were up to 30 Dobson units (DU) in July 2010 at 30°E. This period coincides with the 2010 Russian heat wave (Schubert et al., 2011) that caused severe fires with high O$_3$ precursors emissions (R’Honi et al., 2013). Further discussion is provided in section 4.2.
4 O₃ budget from the WRF-Chem model during summer 2010

From this section onwards, we focus our analysis on summer 2010, the year of the anthropogenic emission inventory used in the model. We evaluate the model then we discuss the O₃ budget at different altitude levels in the Mediterranean troposphere.

4.1 Model evaluation: comparison to EMEP and IASI

The model is evaluated by comparing O₃ concentrations with surface O₃ data from the EMEP stations (section 2.2), then free tropospheric O₃ data from IASI (section 2.3).

4.1.1 Comparison to EMEP surface monitoring stations

Linear spatial interpolation was applied to WRF-Chem data in order to correlate the model outputs and the EMEP data that were averaged every 2 hours to coincide with the model run output data. Figure 6 shows the individual time series of the data of the 8 stations used for the validation. Table 2 shows the individual O₃ correlation and bias between WRF-Chem and the EMEP for each of the stations used in this study during JJA 2010. The model simulates the surface O₃ with a correlation ranging from 0.41 (ES06) to 0.80 (ES12) and a mean value of 0.52. Figure 6 and Table 2 show that the model reproduces reasonably well the average amplitude of the daily cycle seen in the observation. For all stations except ES06 and ES10, the model underestimates the ground observation during the summer period with a mean normalized bias between -23.9% to -6.4%. The biases reported may be due to the resolution of the model resulting in a grid of around 50 km around the EMEP rural sites which may include other surface O₃ contributions. Other possible reasons include difficulties in simulating local flow patterns due to topography and land-sea circulation, as well as uncertainties in emissions and NOₓ concentrations (Pfister et al., 2013). Our results compare well with the study by Tuccella et al. (2012) that compared WRF-Chem to 75 EMEP stations over Europe during 2007, and found that hourly O₃ exhibit a correlation with observations ranging from 0.38 to 0.83. The largest discrepancy
observed, with modeled O\textsubscript{3} values larger than 80 ppbv, is for the station ES06-Mahon (39.87°N, 4.32°E), which might be due a particular uncertainty in the model emissions or dry deposition over this area.

4.1.2 Comparison to IASI observations

Averaged data for summer 2010 are used for the comparison of WRF-Chem and IASI O\textsubscript{3} [4-10] km free tropospheric column. The modeled profile is first linearly interpolated to the time and location of the retrieval. Then, the averaging kernels associated with each IASI measurement and its \textit{apriori} profile are applied to the interpolated modeled profile (of around 7 layers between 4 and 10 km). Figure 7 shows the spatial distribution of the [4-10] km integrated IASI and WRF-Chem model O\textsubscript{3} column along with the relative differences. We chose to analyze this part of the atmosphere in particular because IASI has a better sensitivity between 4 and 10 km over both land and water as shown in Fig. 3. The model reproduces well the spatial patterns seen by IASI during summer (JJA) 2010, with a correlation coefficient of about 0.93 and a summertime mean bias of 6.1 DU (25%) (not shown). The model underestimation of the [4-10] km O\textsubscript{3} column might due to the difficulties in resolving the high O\textsubscript{3} concentrations observed in transported plumes over large distances (Pfister et al., 2013). On the other hand, the high discrepancies seen over northern Africa, might be due to IASI poor spectral fits above surfaces with sharp emissivity variations particularly above the desert (Hurtmans et al., 2012), leading to a possible overestimation of the real profile. We analyzed the IASI total retrieval error for the [4–10] km partial column and we found that it is on average around 7% in the model domain, and between 7 and 12% where the discrepancies between the model and IASI are the highest.

4.2 Origins of boundary layer O\textsubscript{3} over the Mediterranean
Modeled O₃ concentrations are illustrated in Fig. 8 (a-c) at the surface, 1 and 2 km during JJA 2010. At the surface, modeled O₃ exhibits the highest values downwind the European continent. At 1 and 2 km the whole eastern part of the basin is characterized by high O₃ mixing ratios. In order to investigate possible sources of high O₃, we run the model with 2 different tracers of pollution: O₃-ANTHRO and O₃-INFLOW as described in section 2.1. O₃-ANTHRO (Fig. 8 d-f) assesses the possible anthropogenic contribution of O₃ at different altitudes, while O₃-INFLOW (Fig. 8 g-i), provides an estimate of transport of O₃ including the stratosphere. The residual plots plotted in panels (j-l) show the completion of the O₃ budget, and represent the O₃ contribution from fires and biogenic sources. These plots show that the residual contribution is between 0 and 10% inferring that the O₃-ANTHRO and O₃-INFLOW combined are responsible of 90 to 100% of the total O₃ budget over the model domain, at the different altitudes of Fig. 8 and 9. The surface shows a high contribution for the anthropogenic emission tracer (O₃-ANTHRO > 85%), with almost zero contribution of the inflow tracer. This shows the importance of local emissions to the O₃ surface concentration. At 1 km, the highest contribution is also for the anthropogenic tracer (up to 75-80%), whereas the result is mixed at 2 km between the 2 tracers (around 50-60% for O₃-ANTHRO and 40-50% for O₃-INFLOW), suggesting that up to 50% of the O₃ available at 2 km is being transported. The rest of the O₃ plotted in the residual plots (panels j-l) and decreasing with altitude is suggested to be from fire sources, as the extended domain (Fig 2a) used in the study includes parts of the region hit by the Russian fires of summer 2010.

4.3 Origins of free tropospheric O₃ over the Mediterranean

O₃ concentrations at 4, 6 and 8 km in Fig. 9 (a-c) show that the eastern part of the basin is subject to much higher O₃ values, reaching up to 100 ppbv between 6 and 8 km (see further discussion in section 5). The anthropogenic contribution decreases with altitude, whereas the O₃ inflow
contribution increases. The northeastern corner of the modeled domain in panels (d-f) show anthropogenic contribution between 20 and 40%. This might be due to important vertical transport and mixing in the free troposphere. These values can be correlated with the O₃ residuals plotted in panels (j-l). These panels show an O₃ signature in the north eastern corner of the domain. This signature is probably related to the emitted O₃ precursors from fires sources in the model domain (Fig. 2) and lifted to the upper troposphere due to convective movements during the Russian fires of summer 2010. We can also suppose that certain anthropogenic O₃ precursors, like NOₓ, near the fire sources were also transported with the same convective movements to the same part of the domain and contributed eventually to the production of anthropogenic O₃ in that region. Panels (g-i) show that 70 to 100% of the available O₃ between 4 and 8 km does not come from local sources. The high values are likely due to long-range transport of pollution from outside the study region or transport of air masses from the stratosphere that we will discuss in the following section. The low values recorded in the residual plots in panels (j-l) show that the O₃ budget in the free troposphere over this region is controlled almost exclusively by local anthropogenic sources and transport.

5 WRF-Chem and IASI detection of stratosphere-troposphere exchange events

Figures 4, 5 and Fig. 9 (a-c) showed that the eastern part of the Mediterranean basin in summer is subject to high O₃ mixing ratios at 4, 6 and 8 km. In order to further investigate the sources and processes responsible for these enhancements, modeled and observed IASI O₃ vertical profiles in the troposphere were examined, during summer 2010, to try to detect possible stratosphere to troposphere exchange (STE) events.

Figure 10 shows the tropospheric O₃ vertical distributions along 15°E (mid-Mediterranean) and 30°E (eastern Mediterranean) for IASI (panels a and b) and WRF-Chem, smoothed with the IASI
averaging kernels (panels c and d) for JJA 2010. Between 4 and 8 km, panels (b) and (d) show higher values of O\textsubscript{3} in the eastern part of the basin (30°E) with concentrations ranging between 50 and 100 ppbv for IASI and 40 to 100 ppbv for WRF-Chem (WRF-Chem underestimates IASI as shown in Fig. 7).

Since stratospheric intrusions within the regional domain are included in the O\textsubscript{3-INFLOW} tracer, it is useful to use other stratospheric tracers to distinguish the transport from the stratosphere. The potential vorticity (PV) and the water vapor mixing ratio (Q\textsubscript{vap}) measurements can be used as markers of transport from the upper troposphere-lower stratosphere (UTLS) to the troposphere: elevated O\textsubscript{3} and PV, and low Q\textsubscript{vap} values, would indicate that high free troposphere values are due to downward transport from the UTLS (Holton et al., 1995). Here, we study PV and Q\textsubscript{vap} at 4, 6, and 8 and 10 km calculated from the WRF-Chem model run parameters. Figure 11 shows that starting 4 km, higher PV and lower Q\textsubscript{vap} values start to develop to the east of the basin. At 8 and 10 km, the highest PV values (1.5 to 2 pvu) (potential vorticity unit, 1pvu =10\textsuperscript{-6} m\textsuperscript{2} K kg\textsuperscript{-1} s\textsuperscript{-1}), and the lowest Q\textsubscript{vap} values (0.0-0.10 g.kg\textsuperscript{-1}) are recorded to the east of the basin, in comparison with low PV values in the mid and to the west of the basin (0.5-1), with high Q\textsubscript{vap} values (0.1-0.15). The high PV/low Q\textsubscript{vap} values to the east are in accordance with Fig. 9 and 10, strongly suggesting that this part of the basin is subject to transport from the UTLS into the free troposphere. In fact, at 30°E and around 37°N-39°N (panels b and d of Fig. 10) both IASI and the model suggest a stratospheric intrusion. It corresponds to PV values between 1.4 and 2 pvu at 8 km and Q\textsubscript{vap} values around 0.05 g.kg\textsuperscript{-1}. In a recent study, Zanis et al. (2014) using 12 year climatology (1998-2009) of the ERA-interim reanalysis, also detected frequent events of STE with PV ranging between 0.4 and 1.4 pvu and specific humidity values between 0.01 and 2 g.kg\textsuperscript{-1} between 700 and 250 hPa during July and August to the east of the basin, in accordance with our results for summer 2010 at 4, 6 and 8 km.
6 Discussion and conclusions

Six years of tropospheric O$_3$ observations provided by the IASI mission above the Mediterranean are shown. Tropospheric [0-8] km O$_3$ columns show a consistent seasonal behavior over the period 2008-2013 with pronounced maxima in summer with higher values to the east of the basin. A complementary study by Doche et al. (2014) using IASI data at 3 km height, also showed 6 years recurrent O$_3$ summer maxima in July to the east of the basin. Since IASI has a lower sensitivity in the lower troposphere and above the sea, anthropogenic emission contribution to the boundary layer O$_3$ is not well captured by the instrument. However, IASI is able to detect in the free to upper troposphere, where its sensitivity is the highest, high tropospheric O$_3$ values to the east of the basin during the 6 years. Focusing on summer 2010, we use IASI and the regional chemical transport model WRF-Chem to interpret these maxima. A tagging scheme is used to keep track of O$_3$ from anthropogenic sources in the domain (O$_3$-ANTHRO) and O$_3$ from inflow at the domain boundaries and stratosphere (O$_3$-INFLOW). Our results show that transport plays an essential role in the O$_3$ budget over the Mediterranean troposphere and that summer O$_3$ maxima over the region are recorded especially in the eastern part of the basin. Even though high local anthropogenic emissions are responsible to 60-100% of O$_3$ in the boundary layer (surface-2 km), as demonstrated by the anthropogenic O$_3$ tracer of the WRF-Chem model, above 2 km, O$_3$ is mainly transported. Kalabokas et al. (2007, 2013) showed that the highest ozone concentrations in the low troposphere are associated with large-scale subsidence of ozone-rich air masses from the upper troposphere. However, Zanis et al., (2013) using model simulations reported, that at the low troposphere, long distance transport and local photochemical processes dominate. In the free troposphere, WRF-Chem shows that vertical and lateral transport of O$_3$ take place represented by the O$_3$-INFLOW tracer which is responsible for 70-100% of O$_3$ at 4, 6 and 8 km. In the Eastern
Mediterranean, Roelofs et al. (2003) showed important contributions to elevated O$_3$ in the middle troposphere by transport from the stratosphere. More recently, Hess and Zbinden (2013) showed that stratospheric inter-annual O$_3$ variability drives significantly the O$_3$ variability in the middle troposphere, between 30° and 90°N but not the overall trend which is largely affected by transport processes. The increase in O$_3$ seen by the model and the IASI instrument in the eastern part of the Mediterranean basin suggests that stratosphere to troposphere exchange (STE) events contribute to elevated ozone in the upper free troposphere. This is further shown in the WRF-Chem simulations that predict elevated potential vorticity (PV) and water vapor mixing ratio ($Q_{\text{vap}}$) over the same region. This result is in agreement with many previous studies e.g. Butkovic et al. (1990); Varotsos and Cracknell (1993); Kalabokas and Bartzis (1998); Kalabokas et al. (2000, 2007); Kouvarakis et al.(2000); Lelieveld et al.(2002); Sprenger and Wernli (2003); Papayannis et al. (2005); Gerasopoulos et al. (2006b); Akritidis et al. (2010); Zanis et al. (2013); Doche et al. (2014) that have shown the occurrence of STE events in the eastern Mediterranean region in summer. Since O$_3$ maxima have the potential to strongly impact regional air quality and climate (e.g. Hauglustaine and Brasseur, 2001), the present study further demonstrate the importance of quantifying and analyzing O$_3$ and its sources at different altitudes in the atmosphere. Quantifying long term trends and a distinction between the different sources is crucial. This should be possible with observations and model runs over longer time scales with additional tracers to identify all O$_3$ sources.

Acknowledgments. IASI is a joint mission of EUMETSAT and the Centre National d’Etudes Spatiales (CNES, France). The IASI L1 data are distributed in near real time by EUMETSAT through the EumetCast system distribution. The authors acknowledge the French Ether atmospheric database (www.pole-ether.fr) for providing the IASI L1C data and L2 temperature
data. This work was undertaken under the auspices of the O3M- SAF project of the EUMETSAT
and supported by the European Space Agency (ozone CCI project). The French scientists are
grateful to CNES and Centre National de la Recherche Scientifique (CNRS) for financial support.
The research in Belgium is funded by the Belgian State Federal Office for Scientific, Technical
and Cultural Affairs and the European Space Agency (ESA Prodex arrangement). P.F. Coheur is
Senior Research Associate with F.R.S-FNRS. Support is also acknowledged from the EU FP7
ECLIPSE (Evaluating the Climate and Air Quality Impacts of Short-Lived Pollutants) project
(no. 282688).

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Table 1: List of geographic location of the EMEP O₃ monitoring ground stations used in this study, with the corresponding altitude above mean sea level.

<table>
<thead>
<tr>
<th>Code</th>
<th>Station name</th>
<th>Latitude (°)</th>
<th>Longitude (°)</th>
<th>Altitude (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY02</td>
<td>Ayia Marina</td>
<td>35.04</td>
<td>33.06</td>
<td>532</td>
</tr>
<tr>
<td>ES06</td>
<td>Mahón</td>
<td>39.87</td>
<td>4.32</td>
<td>78</td>
</tr>
<tr>
<td>ES07</td>
<td>Víznar</td>
<td>37.30</td>
<td>-3.53</td>
<td>1265</td>
</tr>
<tr>
<td>ES10</td>
<td>Cabo de Creus</td>
<td>42.32</td>
<td>3.32</td>
<td>23</td>
</tr>
<tr>
<td>ES12</td>
<td>Zarra</td>
<td>39.08</td>
<td>-1.10</td>
<td>885</td>
</tr>
<tr>
<td>ES14</td>
<td>Els Torms</td>
<td>41.39</td>
<td>0.73</td>
<td>470</td>
</tr>
<tr>
<td>GR02</td>
<td>Finokalia</td>
<td>35.31</td>
<td>25.66</td>
<td>250</td>
</tr>
<tr>
<td>MK07</td>
<td>Lazaropole</td>
<td>41.32</td>
<td>20.42</td>
<td>1332</td>
</tr>
</tbody>
</table>

Table 2. Pearson correlation coefficient, bias and the corresponding mean normalized bias (MNB) of each EMEP and WRF-Chem ground station data localized in Fig. 2, for the period JJA 2010.

<table>
<thead>
<tr>
<th>Station name</th>
<th>Corr. Coef. With WRF-Chem</th>
<th>Bias (ppbv)</th>
<th>MNB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY02</td>
<td>0.63</td>
<td>-7.78 (-14.2%)</td>
<td></td>
</tr>
<tr>
<td>ES06</td>
<td>0.41</td>
<td>+7.26 (+20.9%)</td>
<td></td>
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<tr>
<td>ES07</td>
<td>0.77</td>
<td>-7.24 (-13.4%)</td>
<td></td>
</tr>
<tr>
<td>ES10</td>
<td>0.72</td>
<td>+1.43 (+3.6%)</td>
<td></td>
</tr>
<tr>
<td>ES12</td>
<td>0.80</td>
<td>-5.96 (-12.7%)</td>
<td></td>
</tr>
<tr>
<td>ES14</td>
<td>0.78</td>
<td>-2.99 (-6.4%)</td>
<td></td>
</tr>
<tr>
<td>GR02</td>
<td>0.62</td>
<td>-7.38 (-11.3%)</td>
<td></td>
</tr>
<tr>
<td>MK07</td>
<td>0.57</td>
<td>-16.65 (-23.9%)</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. An example of the ECMWF (European Centre for Medium-Range Weather Forecasts) Reanalysis (ERA-Interim) for the period June-July-August (JJA) 2010 for: (a) total cloud coverage, (b) 12:00 UTC solar radiation reaching the surface and (c) wind speed and direction averaged from the surface to 750 hPa and (d) wind speed and direction averaged from 750 to 400 hPa.
**Fig. 2.** (a) The enlarged WRF-Chem model run domain. (b) IASI and WRF-Chem domain used in this study. White dots correspond to the location of the EMEP ground stations and the orange strips correspond to the longitudinal transects used in Figures 5 and 10.

**Fig. 3.** Random $O_3$ averaging kernels over the Mediterranean: the functions are for the [surface-3], [4-6], [6-9], and [10-12] km partial columns characterizing a retrieval for an observation chosen randomly above land (Greece, left panel) and above the sea (right panel) during June 2010.
Fig. 4. Six years seasonal variation of [0-8] km integrated IASI O₃ column over the Mediterranean region for winter, spring, summer and autumn. White pixels correspond to a filter applied on poor spectral fits, because of emissivity issues in the FORLI radiative transfer above the Sahara desert.
Fig. 5. Six years monthly variation of the integrated [0-8] km IASI O$_3$ column averaged over [30°N-45°N] at 15°E (in black) and 30°E (in red). Higher summer values are observed to the east of the basin at 30°E.
**Fig. 6.** O$_3$ time series of EMEP and WRF-Chem data at the surface for the stations localized in Fig. 2, for the period JJA 2010.

**Fig. 7.** Average [4-10] km O$_3$ column for JJA 2010 from IASI and WRF-Chem and their relative difference (%). White pixels correspond to a filter applied to poor spectral fits above the Sahara desert.
Fig. 8. WRF-Chem spatial distributions of (a-c) O$_3$ mixing ratios (ppbv), (d-f) O$_3$ anthropogenic tracer relative contributions (%), (g-i) O$_3$ inflow tracer relative contribution, and (j-l) the residual (100%-(O$_3$-ANTHRO%+O$_3$-INFLOW%)) averaged over the period JJA 2010 at the surface, 1 km and 2 km. Note that the colorbar for the residual plots is different.
Fig. 9. Same as Fig. 8 but for 4, 6 and 8 km.
Fig.10. Mean latitude-altitude cross sections of IASI-O$_3$ (a-b) and modeled-O$_3$ (c-d) averaged over JJA 2010 at 15°E (left) and 30°E (right). Black line corresponds to the dynamical tropopause height.
Fig. 11. WRF-Chem (a) potential vorticity (PV) at 4, 6, 8 and 10 km over the Mediterranean region for JJA 2010 and (b) water vapor mixing ratio ($Q_{vap}$) for the same vertical levels and time period.