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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. Clerbaux^{1,2}

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 2361, Austria

Correspondence to: S. Safieddine (sarah.safieddine@latmos.ipsl.fr)

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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 results 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, while above 4 km it is mostly transported from outside the domain or from stratospheric origins. Evidence of stratosphere-to-troposphere exchange (STE) events in the eastern part of the basin is shown, and corresponds to a 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 summertime, 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 by 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 h 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 (unit: Pa s^{-1} , used to represent subsidence) indeed shows 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 O_3 seasonal variability in the eastern basin during summer is mainly the transport from Europe. Using lidar measurements, Galani et al. (2003) detected an increase of 10 % of tropospheric O_3 between 4.5 and 6.5 km due to stratosphere-to-troposphere exchange (STE) events. Zbinden et al. (2013), using aircraft data from the MOZAIC (Measurements of OZone and water vapour by in-service Airbus airCRAFT) program over 15 years (1994–2009), showed that the tropospheric O_3 columns in the east of the Mediterranean reached a maximum of 43.2 DU (Dobson units) 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 O_3 is mostly sensitive to anthropogenic emissions of O_3 precursors (Hodnebrog et al., 2012). Im et al. (2011) found that the near-surface ozone mixing ratios increase almost linearly with temperature by 1.0 ± 0.1 ppb O_3 per kelvin. STE processes can affect the tropospheric O_3 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 on the eastern side (Galani et al., 2003; Zanis et al., 2014), because it lies to the south of the Northern Hemisphere polar jet flowing over midlatitudes (Stohl et al., 2000;

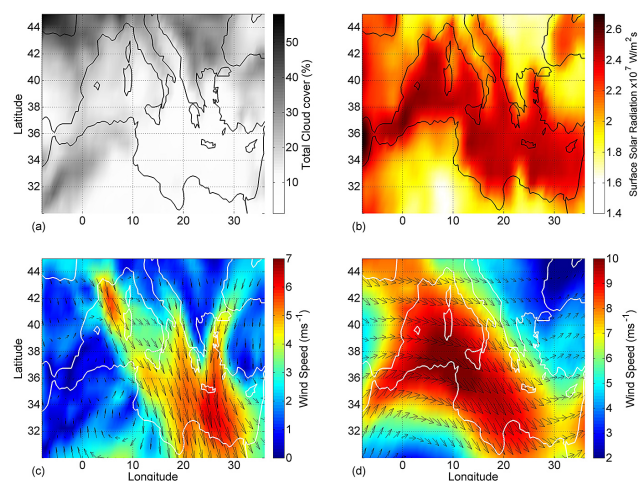


Figure 1. An example of the ECMWF (European Centre for Medium-Range Weather Forecasts) Reanalysis (ERA-Interim) for the period June–July–August (JJA) 2010 for (a) total cloud coverage, (b) 12:00 UTC solar radiation reaching the surface, (c) wind speed and direction averaged from the surface to 750 hPa, and (d) wind speed and direction averaged from 750 to 400 hPa.

Gerasopoulos et al., 2001). Understanding the factors that contribute to the O_3 maxima is important for developing control measures and preventing pollution buildup. In this study we analyze O_3 and its sources at different altitudes in the Mediterranean troposphere. Section 2 introduces the model and observations data sets used in this study. In Sect. 3, we analyze 6 years (2008–2013) of Infrared Atmospheric Sounding Interferometer (IASI) tropospheric [0–8] km O_3 column seasonal variation above the whole Mediterranean Basin as well as at 15 and 30° E, representative of what we henceforth refer to as “middle of the basin” and “east of the basin” respectively. In Sect. 4 we focus on summer 2010, as an example year, and validate the WRF-Chem model simulation with surface O_3 and IASI data, and then use the WRF-Chem model to assess the sources of O_3 in the troposphere. In Sect. 5, we use IASI and WRF-Chem free-tropospheric O_3 data to investigate potential STE events. Discussion and conclusions are given in Sect. 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 budget and spatiotemporal variability of O_3 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 $50 \text{ km} \times 50 \text{ km}$ and the vertical resolution is of 28 levels between the surface and 10 hPa. The

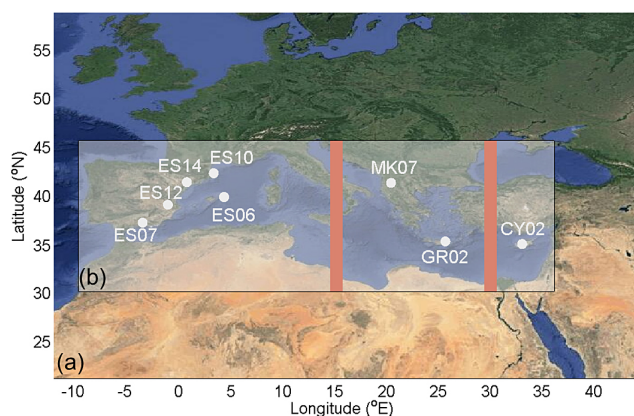


Figure 2. (a) The enlarged WRF-Chem model run domain. (b) IASI and WRF-Chem domain used in this study. White dots correspond to the location of the EMEP ground stations and the orange strips correspond to the longitudinal transects used in Figs. 5 and 10.

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 h 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 h), are constrained by global chemical transport simulations from MOZART-4/GEOS-5 with $1.9^\circ \times 2.5^\circ$ 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 offline. The anthropogenic emissions used within the WRF-Chem model were developed within the context 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 h from 1 June 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), as well as in other global and regional chemical transport models (Ma et al., 2002; Hess and Zbinden, 2013). Recently, this scheme was used for the

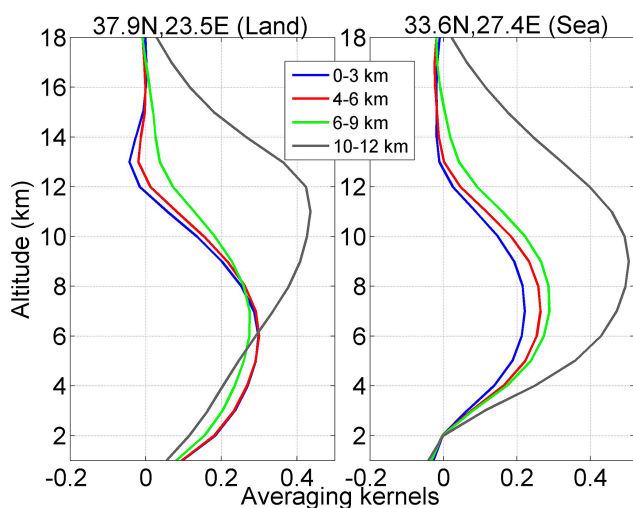
first time in the WRF-Chem model to quantify the contribution of transport on surface O_3 over California (Pfister et al., 2013). Here, we apply this scheme to keep track of the contribution of O_3 within the WRF-Chem domain. To determine O_3 sources, tagged NO_x is traced through the odd nitrogen species (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 and initial and boundary conditions. In the first one, the O_3 -ANTHRO tracer accounts for the anthropogenic regional tagged NO_x , while the second one, the O_3 -INFLOW tracer, accounts for tagged O_3 as well as all nitrogen species at the lateral boundaries of the regional model domain. The 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 the stratospheric O_3 is controlled by the lateral boundaries in this version of WRF-Chem, 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 the 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 $100\% - (O_3\text{-ANTHRO}\% + O_3\text{-INFLOW}\%)$. 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, a heat wave occurred in Russia that caused severe fires with high O_3 and O_3 precursor emissions that were probably transported to the Mediterranean region; this 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 with UV monitors. In this study, measurements at eight 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 eight stations used for validation are plotted in Fig. 2, and the corresponding details are listed in Table 1. Two more station data sets were available, GR01-Aliartos (38.37° N, 23.11° E) and IT01-Montelibretti (42.1° N, 12.63° E), for the same period. We disregarded the data from these stations because they show a 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.

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.

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

**Figure 3.** Random O₃ 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.

2.3 IASI satellite measurements

The MetOp satellites, launched in October 2006 and September 2012, each carry an IASI instrument, which have been operationally sounding the atmosphere since June 2007 (IASI-1) and January 2013 (IASI-2). The IASI instruments are nadir-looking Fourier transform spectrometers that probe 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 O₃ vertical profiles are retrieved in near-real time using a dedicated radiative transfer and retrieval software for the IASI O₃ product, the Fast Optimal Retrievals on Layers for IASI (FORLI-O₃) (Hurtmans et al., 2012). The IASI FORLI-O₃ observations are selected for scenes with cloud coverage below 13 % and with root mean square (rms) of the spectral fit residual lower than 3.5 × 10^{−8} W cm^{−2} sr cm^{−1}. Details about the chemical com-

ponents 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 O₃ 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 O₃ 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° above land, and 1.2° above sea). IASI is able to detect several pollutants (e.g., carbon monoxide, ammonia, sulfur dioxide, and ammonium sulfate aerosols), especially when a large thermal contrast is combined with stable meteorological conditions, leading to the accumulation of pollutants near the surface (Boynard et al., 2014).

3 Tropospheric O₃ seasonal variation as seen by IASI

To investigate the seasonal behavior of tropospheric O₃ above the Mediterranean, in Fig. 4 we plot the [0–8] km partial tropospheric O₃ column as seen by IASI during the period of 2008 to 2013. The data were averaged seasonally, and daytime observations were used since the information content of IASI O₃ data is shown to be higher during the day (Clerbaux et al., 2009). We observe a similar tropospheric O₃ 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 in O₃ production from photochemistry, buildup of winter O₃ and its precursors, transport, and/or from O₃ of stratospheric origin integrating into the troposphere. The [0–8] km column reaches a maximum in summer (JJA) due to high photochemical O₃ production, horizontal transport into the region, or STE, 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 the summers of 2007 and 2008, with values exceeding 32 DU at the east of the

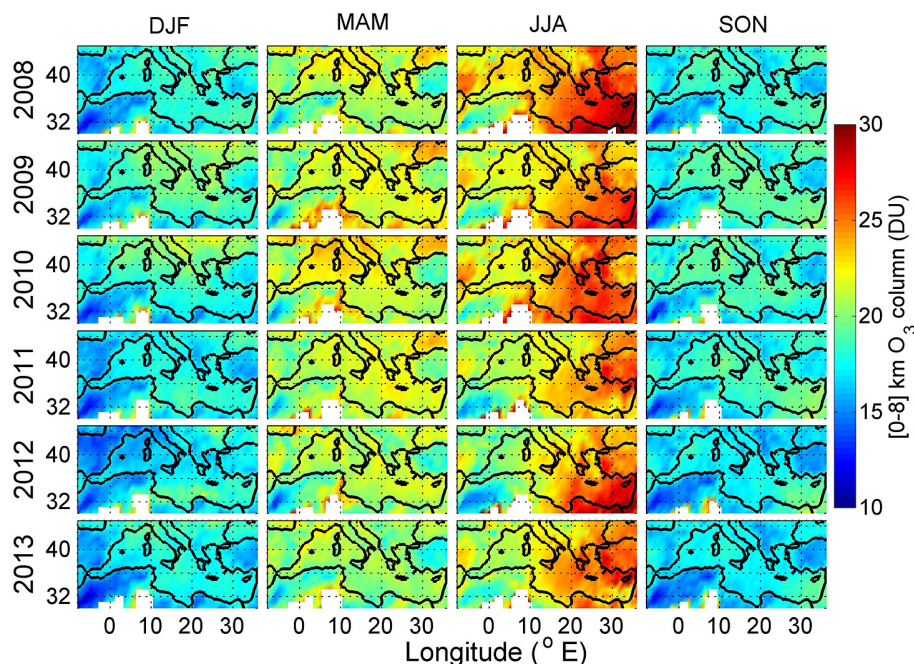


Figure 4. Six-year seasonal variation of [0–8] km integrated IASI O_3 column over the Mediterranean region for winter, spring, summer, and autumn. White pixels correspond to a filter applied to poor spectral fits because of emissivity issues in the FORLI radiative transfer above the Sahara.

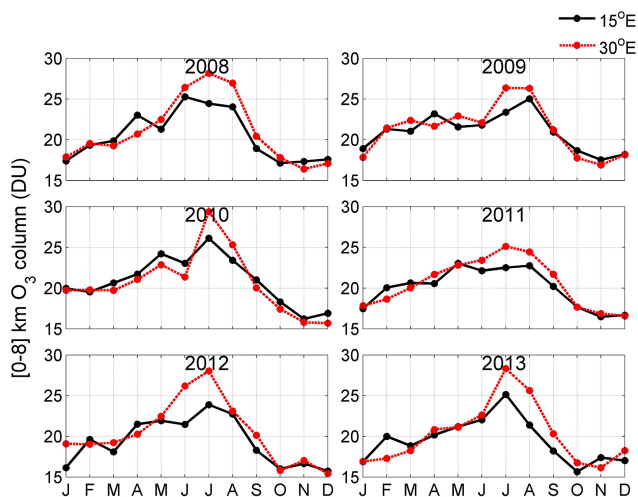


Figure 5. Six-year monthly variation of the integrated [0–8] km IASI O_3 column averaged over [30–45° N] at 15° E (in black) and 30° E (in red). Higher summer values are observed to the east of the basin at 30° E.

basin for the [0–6] km O_3 column. To further investigate 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), 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 DU in July 2010 at 30° E. This period coincides with the 2010 Russian heat wave (Schubert et al., 2011), which caused severe fires with high O_3 precursors emissions (R’Honi et al., 2013). Further discussion is provided in Sect. 4.2

4 O_3 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 O_3 budget at different altitude levels in the Mediterranean troposphere.

4.1 Model evaluation: comparison to EMEP and IASI

The model is evaluated by comparing O_3 concentrations with ground O_3 data from the EMEP stations (Sect. 2.2) and then free-tropospheric O_3 data from IASI (Sect. 2.3).

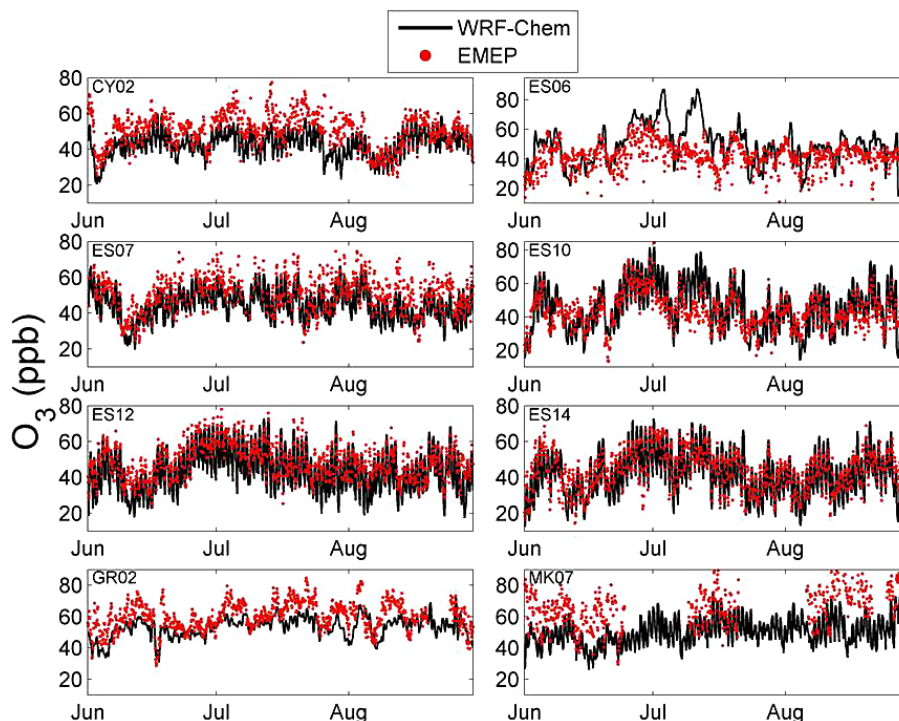


Figure 6. O₃ time series of EMEP and WRF-Chem data at the surface for the stations localized in Fig. 2 for the period JJA 2010.

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 h to coincide with the model run output data. Figure 6 shows the individual time series of the data of the eight 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 reasonably well reproduces 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 relative error between -23.9 and -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 that 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 NO_x concentrations (Pfister et al., 2013). Our results compare well with the study by Tuccella et al. (2012), which compared WRF-Chem to 75 EMEP stations over Europe during 2007 and found that hourly O₃ exhibits a correlation with observations ranging from 0.38 to 0.83. The largest discrepancy observed, with modeled O₃ values larger than

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

Station name	Corr. coeff. with WRF-Chem	Bias (ppbv)	MRE (%)
CY02	0.63	7.78	−14.2
ES06	0.41	+7.26	+20.9
ES07	0.77	−7.24	−13.4
ES10	0.72	+1.43	+3.6
ES12	0.80	−5.96	−12.7
ES14	0.78	−2.99	−6.4
GR02	0.62	−7.38	−11.3
MK07	0.57	−16.65	−23.9

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 O₃ [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 a priori profile are applied to the interpolated modeled profile (of around seven layers between 4 and 10 km). Figure 7 shows

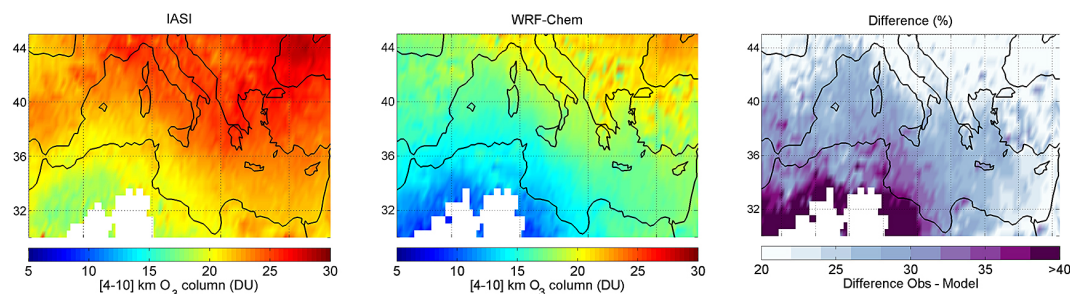


Figure 7. Average [4–10] km O_3 column for JJA 2010 from IASI and WRF-Chem and their relative difference (%). White pixels correspond to a filter applied to poor spectral fits above the Sahara.

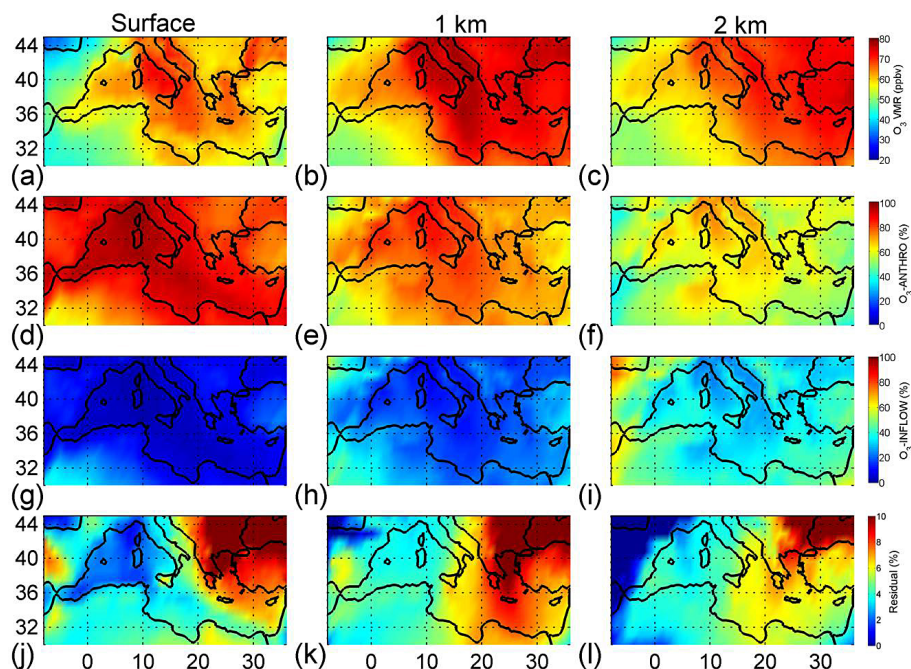


Figure 8. WRF-Chem spatial distributions of (a–c) O_3 mixing ratios (ppbv), (d–f) O_3 anthropogenic tracer relative contributions (%), (g–i) O_3 inflow tracer relative contribution, and (j–l) the residual ($100\% - (O_3\text{-ANTHRO } \% + O_3\text{-INFLOW } \%)$) averaged over the period JJA 2010 at the surface and 1 and 2 km. Note that the color bar for the residual plots is different.

the spatial distribution of the [4–10] km integrated IASI and WRF-Chem model O_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 the spatial patterns seen by IASI during summer (JJA) 2010 well, 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_3 column might be due to the difficulties in resolving the high O_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 poor spectral fits from IASI 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 (not shown here) and 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_3 over the Mediterranean

Modeled O_3 concentrations are illustrated in Fig. 8a–c at the surface and 1 and 2 km during JJA 2010. At the surface, modeled O_3 exhibits the highest values downwind from the European continent. At 1 and 2 km the whole eastern part of the basin is characterized by high O_3 mixing ratios. In

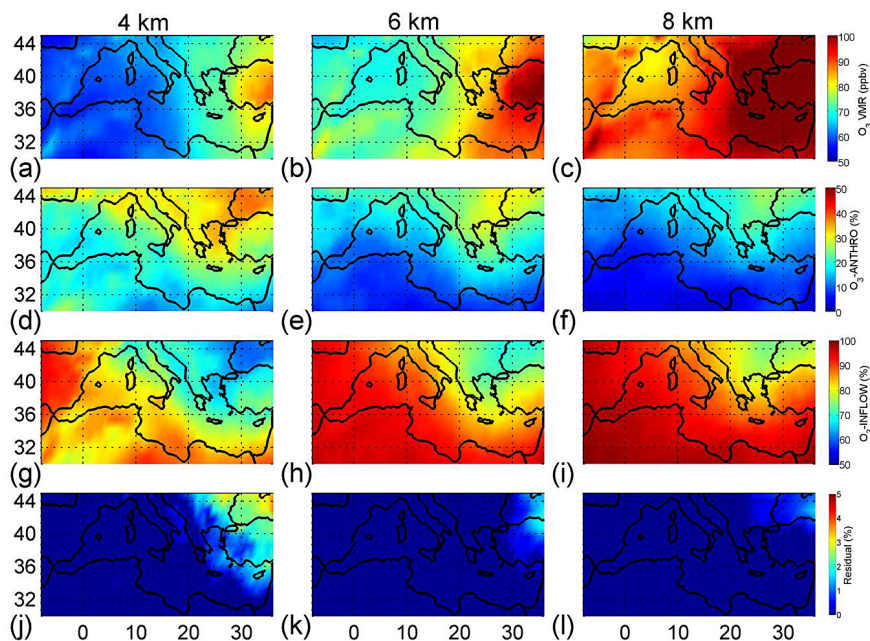


Figure 9. Same as Fig. 8 but for 4, 6, and 8 km.

order to investigate possible sources of high O_3 , we run the model with two different tracers of pollution, O_3 -ANTHRO and O_3 -INFLOW, as described in Sect. 2.1. O_3 -ANTHRO (Fig. 8d–f) assesses the possible anthropogenic contribution of O_3 at different altitudes, while O_3 -INFLOW (Fig. 8g–i) provides an estimate of transport of O_3 , including the stratosphere. The residual plots plotted in panels j–l show the completion of the O_3 budget, and represent the O_3 contribution from fires and biogenic sources. These plots show that the residual contribution is between 0 and 10 %, inferring that O_3 -ANTHRO and O_3 -INFLOW combined are responsible for 90 to 100 % of the total O_3 budget over the model domain at the different altitudes of Fig. 8. The surface shows a high contribution from the anthropogenic emission tracer (O_3 -ANTHRO > 85 %), with almost zero contribution from the inflow tracer. This shows the importance of local emissions to the O_3 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 two tracers (around 50–60 % for O_3 -ANTHRO and 40–50 % for O_3 -INFLOW), suggesting that up to 50 % of the O_3 available at 2 km is being transported. The rest of the O_3 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 O_3 over the Mediterranean

O_3 concentrations at 4, 6, and 8 km in Fig. 9a–c show that the eastern part of the basin is subject to much higher O_3 values, reaching up to 100 ppbv between 6 and 8 km (see further discussion in Sect. 5). The anthropogenic contribution decreases with altitude, whereas the O_3 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 O_3 residuals plotted in panels j–l. These panels show an O_3 signature in the north eastern corner of the domain. This signature is probably related to the emitted O_3 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 O_3 precursors, like NO_x , near the fire sources were also transported with the same convective movements to the same part of the domain and eventually contributed to the production of anthropogenic O_3 in that region. Panels g–i show that 70 to 100 % of the available O_3 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, which we will discuss in the following section. The low values recorded in the residual plots in panels j–l show that the O_3 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 STE events

Figures 4 and 5 and Fig. 9a–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 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 O₃ 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 O₃-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_{vap}) measurements can be used as markers of transport from the upper troposphere–lower stratosphere (UTLS) to the troposphere: elevated O₃ and PV, as well as low Q_{vap} values, would indicate that high free-tropospheric values are due to downward transport from the UTLS (Holton et al., 1995). Here, we study PV and Q_{vap} at 4, 6, 8, and 10 km calculated from the WRF-Chem model run parameters. Figure 11 shows that, starting at 4 km, higher PV and lower Q_{vap} values start to develop to the east of the basin. At 8 and 10 km, the highest PV values (1.5 to 2 potential vorticity units (pvu); 1 pvu = 10⁻⁶ m² K kg⁻¹ s⁻¹) and the lowest Q_{vap} values (0–0.10 g kg⁻¹) are recorded to the east of the basin, in comparison with low PV values in the middle of and to the west of the basin (0.5–1) with high Q_{vap} values (0.1–0.15). The high PV/low Q_{vap} values to the east are in accordance with Figs. 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 37–39° N (panels b and d of Fig. 10), both IASI and the model suggest a stratospheric intrusion. This intrusion corresponds to PV values between 1.4 and 2 pvu at 8 km and Q_{vap} values around 0.05 g kg⁻¹. In a recent study, Zanis et al. (2014), using a 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⁻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.

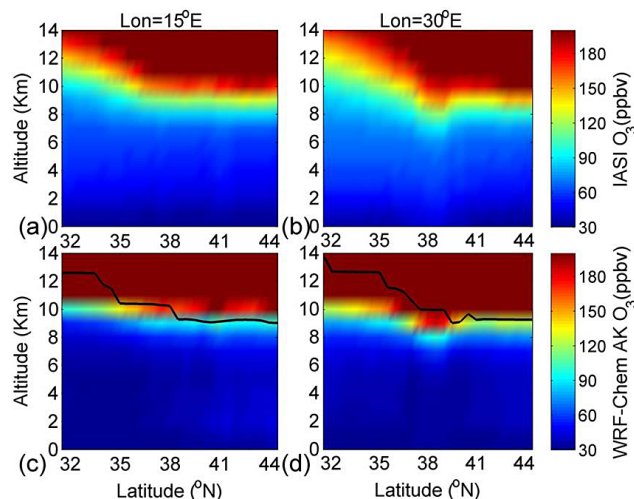


Figure 10. Mean latitude–altitude cross sections of IASI O₃ (a–b) and modeled O₃ (c–d) averaged over JJA 2010 at 15° E (left) and 30° E (right). The black line corresponds to the dynamical tropopause height.

6 Discussion and conclusions

Six years of tropospheric O₃ observations provided by the IASI mission above the Mediterranean are shown. Tropospheric [0–8] km O₃ columns show a consistent seasonal behavior over the period 2008–2013, with pronounced maxima in summer and 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-year recurrent O₃ summer maxima in July to the east of the basin. Since IASI has a lower sensitivity in the lower troposphere and above the sea, the anthropogenic emission contribution to the boundary layer O₃ is not well captured by the instrument. However, IASI is able to detect high tropospheric O₃ values in the free to upper troposphere, where its sensitivity is the highest, 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 O₃ from anthropogenic sources in the domain (O₃-ANTHRO) and O₃ from inflow at the domain boundaries and stratosphere (O₃-INFLOW). Our results show that transport plays an essential role in the O₃ budget over the Mediterranean troposphere and that summer O₃ maxima over the region are especially recorded in the eastern part of the basin. Even though high local anthropogenic emissions are responsible for 60–100 % of O₃ in the boundary layer (surface–2 km), as demonstrated by the anthropogenic O₃ tracer of the WRF-Chem model, O₃ is mainly transported above 2 km. Kalabokas et al. (2007, 2013) showed that the highest ozone concentrations in the lower troposphere are associated with large-scale subsidence of ozone-rich air masses from the upper troposphere. However, Zanis et al. (2014), using model simulations, reported that long-distance transport and local

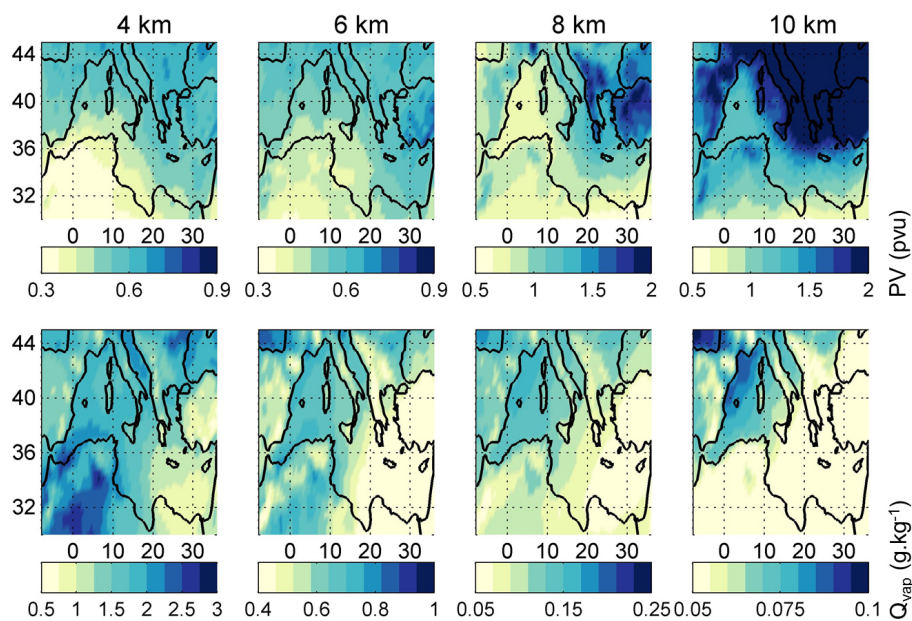


Figure 11. WRF-Chem (a) potential vorticity (PV) at 4, 6, 8, and 10 km over the Mediterranean region for JJA 2010 and (b) the water vapor mixing ratio (Q_{vap}) for the same vertical levels and time period.

photochemical processes dominate at the low troposphere. In this study and in the free troposphere, WRF-Chem shows that vertical and lateral transport of O_3 (represented by the $\text{O}_3\text{-INFLOW}$ tracer) 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 interannual O_3 variability significantly drives 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_{vap}) over the same region. This result is in agreement with many previous studies (e.g., Butkovic et al., 1990; 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., 2014; 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 demonstrates the importance of quantifying and analyzing O_3 and its sources at different altitudes in the atmosphere. Quantification of long-term trends and distinguishing between the different sources are crucial. This

should be possible with observations and model runs over longer timescales with additional tracers to identify all O_3 sources.

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