

# A model study of ozone in the eastern Mediterranean free troposphere during MINOS (August 2001)

G. J. Roelofs<sup>1</sup>, H. A. Scheeren<sup>1,3</sup>, J. Heland<sup>2</sup>, H. Ziereis<sup>2</sup>, and J. Lelieveld<sup>3</sup>

<sup>1</sup>Institute for Marine and Atmospheric Research, Utrecht University, P.O.Box 80005, 3508 TA Utrecht, The Netherlands

<sup>2</sup>Institute for Atmospheric Physics, Deutsches Zentrum für Luft- und Raumfahrt, Oberpfaffenhofen, Germany

<sup>3</sup>Max Planck Institute for Chemistry, Mainz, Germany

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**Abstract.** A coupled tropospheric chemistry-climate model is used to analyze tropospheric ozone distributions observed during the MINOS campaign in the eastern Mediterranean region (August, 2001). Modeled ozone profiles are generally in good agreement with the observations. Our analysis shows that the atmospheric dynamics in the region are strongly influenced by the occurrence of an upper tropospheric anti-cyclone, associated with the Asian summer monsoon and centered over the Tibetan Plateau. The anti-cyclone affects the chemical composition of the upper troposphere, where ozone concentrations of about 50 ppbv were measured, through advection of boundary layer air from South-East Asia. A layer between 4–6 km thickness was present beneath, containing up to 120 ppbv of ozone with substantial contributions by transport from the stratosphere and through lightning  $\text{NO}_x$ . Additionally, pollutant ozone from North America was mixed in. Ozone in the lower troposphere originated mainly from the European continent. The stratospheric influence may be overestimated due to too strong vertical diffusion associated with the relatively coarse vertical resolution. The estimated tropospheric ozone column over the eastern Mediterranean is  $\sim 50$  DU in summer, to which ozone from recent stratospheric origin contributes about 30%, ozone from lightning 13%, and from South-East Asia, North America and Europe about 7%, 8% and 14%, respectively, adding to a long-term hemispheric background of 25% of the column.

of pollution transports into the region and cloud-free conditions enable efficient photochemical activity producing relatively high concentrations, e.g., of ozone and oxidized organics (Kouvarakis et al., 2000). The objective of MINOS was to observe and understand the chemical composition of tropospheric air in the Mediterranean region in terms of atmospheric transport and chemistry. In MINOS ground-based and aircraft-based measurements of atmospheric ozone, CO, higher hydrocarbons, nitrogen oxides and aerosols were performed. An overview of the MINOS results is presented in Lelieveld et al. (2002) while more specific aspects of the MINOS campaign are presented in this issue.

This model study focuses on the distribution of ozone in the Mediterranean region during MINOS, with an emphasis on the free troposphere. We simulated the photochemistry and transport for the summer of 2001 with a coupled tropospheric chemistry-climate model. The model is described in Sect. 2. In Sect. 3 we evaluate the model performance by comparing measured and modeled ozone profiles, and we analyze governing transports by means of backward trajectory calculations. In Sect. 4 we present the simulated ozone distribution over the eastern Mediterranean region and briefly discuss the governing atmospheric dynamics affecting the region. In Sect. 5 the modeled ozone distribution is analyzed in terms of contributions from the major ozone precursor source regions. Conclusions are presented in Sect. 6.

## 1 Introduction

The MINOS measurement campaign (Mediterranean INTensive Oxidant Study) was conducted from Crete in the eastern Mediterranean region during July/August 2001. Earlier measurements and model studies indicate that the combination

Correspondence to: G. J. Roelofs  
(G.J.Roelofs@phys.uu.nl)

## 2 Model description

The general circulation model (GCM) used in this study is the European Centre Hamburg model version 4 (ECHAM4), with a horizontal resolution of about  $1.8^\circ \times 1.8^\circ$  and a time step of 900 s (T63). The model distinguishes 19 hybrid  $\sigma$ -p layers between the surface and the top level at 10 hPa. Average pressure levels relevant for the troposphere and lower stratosphere are 995, 980, 950, 908, 846, 770, 680, 590, 495,

405, 320, 250, 190, 140, 100 and 73 hPa referring to approximate altitudes of 0.03, 0.14, 0.38, 0.77, 1.4, 2.1, 3.1, 4.2, 5.4, 6.8, 8.3, 10, 12, 13.8, 15.7 and 18 km above the surface. Tracer transport is calculated with a semi-Lagrangian advection scheme (Rasch and Williamson, 1990). Additional vertical transports are included through the parameterisation of vertical diffusion and convection. Detailed information on ECHAM is given by Roeckner et al. (1996). We developed a tropospheric chemistry scheme describing emissions of NO, CO and non-methane hydrocarbons (NMHC), dry deposition of O<sub>3</sub>, NO<sub>2</sub>, HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, wet deposition of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, while the CBM4 scheme represents higher hydrocarbon chemistry. This has been coupled to ECHAM (Roelofs and Lelieveld, 1995; 2000a; Ganzeveld et al., 1998).

Because the model does not represent typical stratospheric chemistry, ozone in the stratosphere is parameterised with results from a 2D troposphere-stratosphere chemistry model (Brühl and Crutzen, 1988). Additionally, the model applies an ozone-potential vorticity (PV) correlation in the extratropical lower stratosphere (LS) to preserve longitudinal variability of ozone associated with the meandering and breaking of the jet streams (Roelofs and Lelieveld, 2000b). The parameterisation is applied above the extra-tropical tropopause while transport and mixing in the tropopause region is simulated by the model.

The model considers a separate stratospheric ozone tracer, referred to as O<sub>3s</sub>. The concentration of O<sub>3s</sub> is equal to that of ozone in the grids where stratospheric ozone is prescribed. O<sub>3s</sub> is transported from the stratosphere into the troposphere along with the calculated air motions, where it is photochemically destroyed or removed by dry deposition. The difference between O<sub>3</sub> and O<sub>3s</sub> is a measure of ozone that originates from photochemical production, mainly in the troposphere, and is referred to as O<sub>3t</sub>. Applications and further discussion of the method are presented in Roelofs and Lelieveld (2000a) and Kentarchos and Roelofs (2003).

The simulated ozone seasonalities at the surface, in the free troposphere and in the tropopause region agree well with observations (e.g., Roelofs and Lelieveld, 2000a). The same is true for ozone distributions during specific meteorological conditions, e.g., synoptic disturbances (Roelofs and Lelieveld, 2000b; Kentarchos et al., 2001). The simulated annual and global net downward cross-tropopause flux of ozone is 590 Tg O<sub>3</sub> yr<sup>-1</sup> (Roelofs and Lelieveld, 2000a) which is within the current range of model estimates between 400 and 1400 Tg O<sub>3</sub> yr<sup>-1</sup> (Prather et al., 2001). However, it was found that the model may overestimate downward transport of stratospheric ozone in an individual intrusion because of the relatively coarse vertical resolution near the extratropical tropopause (~1.5 km) and the rather diffusive semi-Lagrangian transport scheme (Meloan et al., 2003; Roelofs et al., 2003).

In this study we use the model in a “nudged” mode, i.e., the model is forced to simulate specific meteorological conditions in July and August, 2001, by assimilating ECMWF

analyzed distributions of surface pressure, temperature, vorticity and divergence (Jeuken et al., 1996). We note that the model considers climatological emission data for ozone precursors (see Roelofs and Lelieveld, 2000a), which may not be consistent with the actual emissions during the MINOS period, in particular from unpredictable sources such as biomass burning.

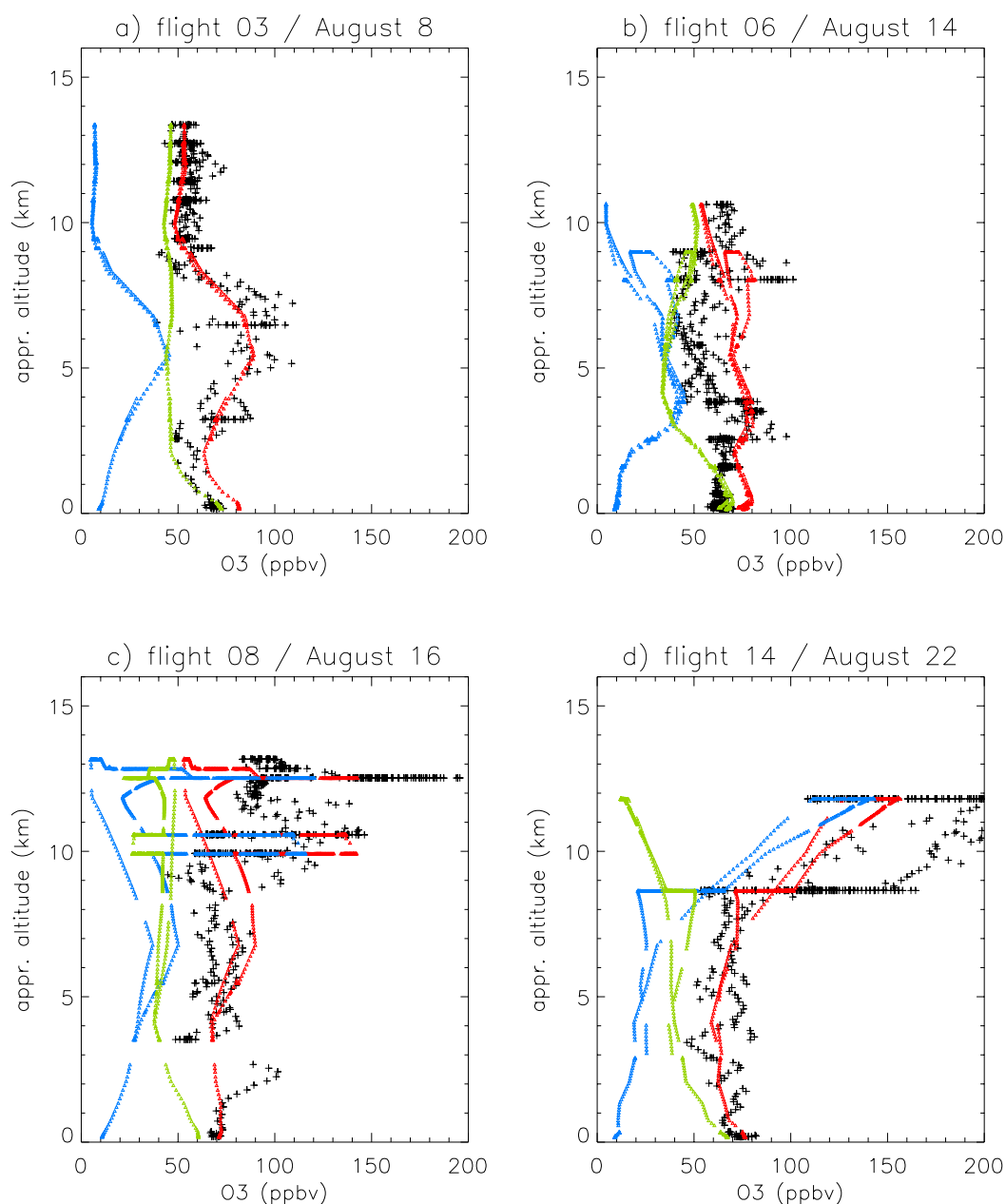
### 3 Comparison of observed and simulated ozone

MINOS encompassed fourteen measurement flights with the Falcon aircraft of the DLR (Deutsches Zentrum für Luft- und Raumfahrt, Germany), conducted from the airport of Heraklion (Crete, 35° N, 25° E). Ozone was measured by UV absorption with a modified TE (Thermo Environmental) 49 instrument with an accuracy of 5%. Detailed information about the measurement flights and data can be found in Heland et al. (2003). In this section we compare the modeled ozone profiles with those observed for four measurement flights, and analyze the profiles in terms of the actual dynamical and meteorological conditions. Figure 1 shows observed ozone concentrations with a time resolution of 12 s, for the flights on 8, 14, 16, and 22 August. Modeled concentrations are given by the red (total ozone), blue (O<sub>3s</sub>) and green (O<sub>3t</sub>) lines. The flights represent different meteorological and atmospheric chemical conditions and illustrate the associated model representativity.

#### 3.1 8 August, flight 03

During flight 03 the aircraft traveled eastwards to approximately 28° E, where it made a north-south transect of approximately 2° latitude. The aircraft was located between 10 and 14 km altitude during most of the 3-h flight, with an ascent and descent of approximately 30 min each. The results show good agreement between modeled and observed ozone concentrations in the free troposphere (Fig. 1a) and vertical ozone gradients are captured well.

Figure 2 presents 8-day backward trajectories from different altitudes in the free troposphere. These have been computed with a trajectory model made available by the British Atmospheric Data Center that uses ECMWF analyzed horizontal and vertical winds ( $u$ ,  $v$ ,  $\omega$ ) on a horizontal resolution of 2.5° × 2.5° (see <http://www.badctrj.rl.ac.uk/>). The trajectories ending above 300 hPa originate from SE Asia. The analysis presented by Scheeren et al. (2003) demonstrates that associated trace gases originate from the boundary layer in India, and are transported upward by convection into an upper tropospheric anti-cyclone centered over the Tibetan plateau. This anti-cyclone is a typical large-scale feature in the summer, extending over southern Asia and north-west Africa, and influenced by the Asian summer monsoon (ASM) (Barry and Chorly, 1987).

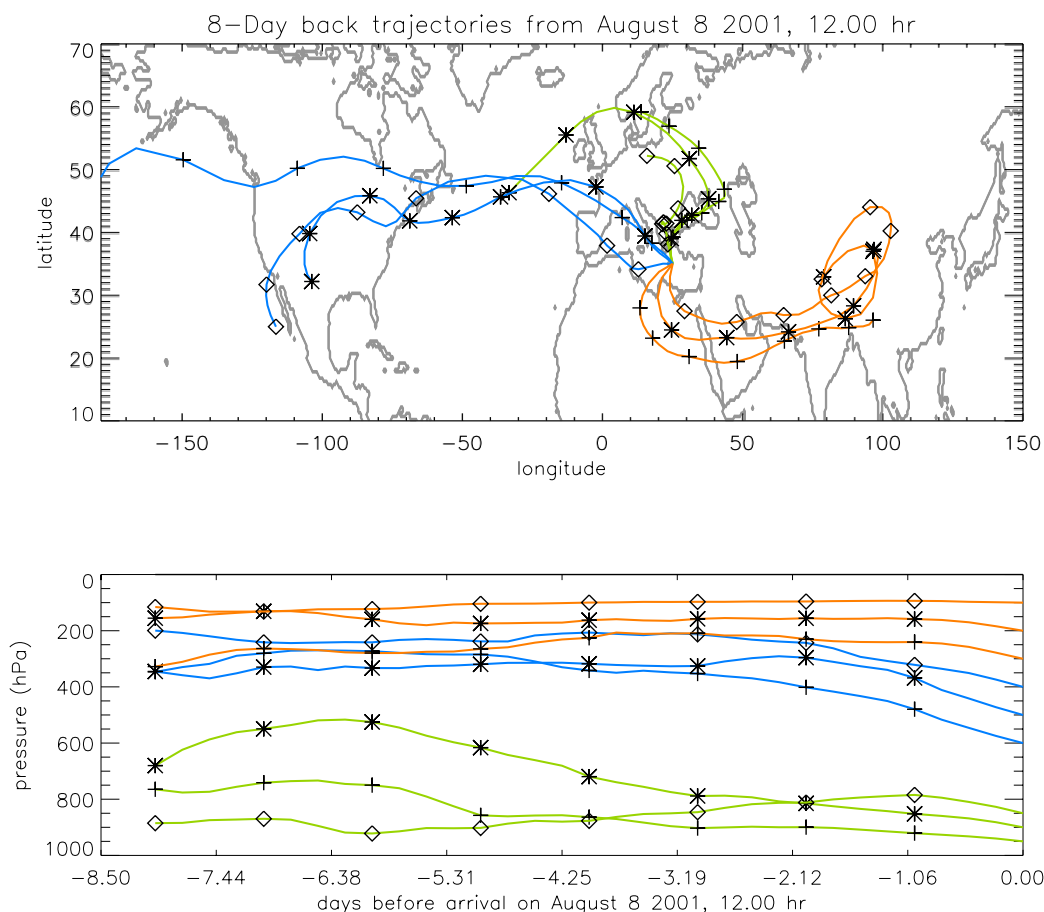


**Fig. 1.** Vertical profiles of observed ozone (black), modeled ozone (red) and contributions by O<sub>3</sub>s (blue) and O<sub>3</sub>t (green) for several MINOS flights.

Mid-tropospheric air (400–600 hPa), on the other hand, was advected from the west, being characterized by relatively high ozone levels. This air descended from the upper troposphere (UT) and the tropopause region only a few days earlier, after residing in the tropopause region for at least the 5 preceding days. Simulated O<sub>3</sub>s suggests an important influence from the stratosphere, and the high ozone content may be explained by a preceding STE event. The C-shape of the observed CO profile with  $\sim 70$  ppbv CO between 4 and 8 km altitude, and  $\sim 100$  ppbv CO in the UT (Lawrence et

al., 2003), supports this explanation. We note that CO distributions are generally reproduced well by our model (Roelofs and Lelieveld, 2000a), which was also the case for MINOS (see Scheeren et al. (2003), who compare modeled and observed CO, NO<sub>y</sub> and alkanes for MINOS).

Backward trajectories ending in the boundary layer and the lower troposphere lead across Eastern Europe, mainly Russia and the Ukraine. The model simulates a realistic ozone concentration gradient between the boundary layer and the free troposphere, although absolute concentrations



**Fig. 2.** Eight-day backward trajectories ending at different altitudes above Crete ( $35^{\circ}$  N,  $25^{\circ}$  E) on 8 August 2001.

are overestimated. We will not discuss boundary layer chemistry and transports in this study. The horizontal and vertical resolutions of the model are too coarse to accurately represent some of the relevant boundary layer characteristics in detail, e.g., height and stability or the occurrence of land-sea breeze circulations, while accurate emission estimates, e.g., for biomass burning in eastern Europe which has a significant impact on the Mediterranean boundary layer (Traub et al., 2003), are not available yet.

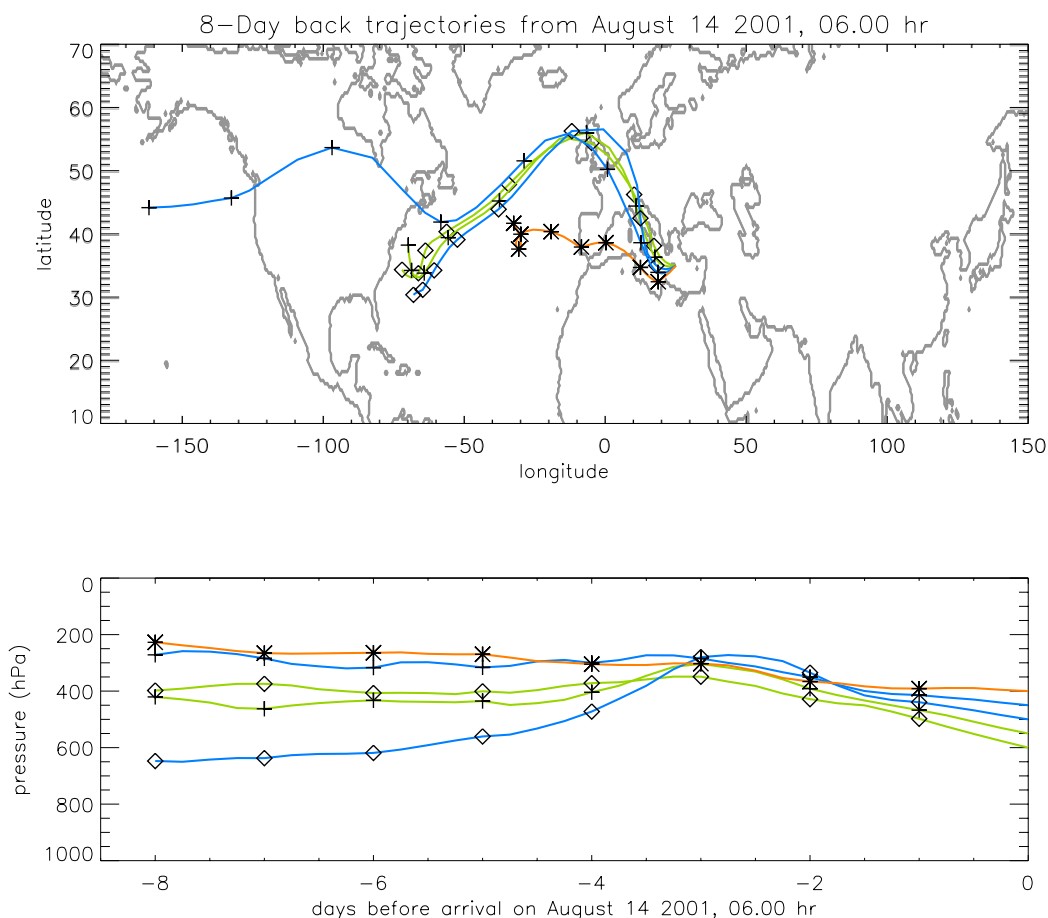
The agreement between model and measurements indicates that the photochemical contribution to tropospheric ozone (i.e.,  $O_3t$ ) in the Mediterranean area during MINOS is represented satisfactorily by the model, and that  $O_3t$  contributes 40–50 ppbv ozone throughout the free troposphere. This will be further analyzed in the next section.

### 3.2 14 August, flight 06

On flight 06 on 14 August the aircraft flew approximately  $2^{\circ}$  latitude northward from Crete and back. Both parts of the 4-hour flight consisted of a swift ascent to about 10 km altitude and a descent in intervals to the boundary layer. Ozone

concentrations between 40 and 70 ppbv were observed, with peaks up to 100 ppbv between 2 and 3 km and between 8 and 9 km altitude (see Fig. 1b). The latter peak can be explained by the vicinity of the tropopause and the lower stratosphere. It is captured by the model, but ozone levels are underestimated. This may be due to an inaccurate representation of the tropopause height associated with the relatively coarse vertical resolution around the tropopause ( $\sim 1.5$  km). The observed ozone maximum at 2–3 km altitude is not fully reproduced by the model. Observed concentrations of organic trace species in this air mass also significantly exceed background values (De Gouw et al., Inter-comparison between airborne measurements of methanol, acetonitrile and acetone using two differently configured PTR-MS instruments, manuscript in preparation), precluding a stratospheric origin.

The simulated  $O_3s$  profile maximizes between 3 and 5 km altitude while the  $O_3t$  profile has a minimum. According to the backward trajectory analysis shown in Fig. 3, the sampled air originates partly from the UT where ozone-rich conditions prevail, and partly from the sub-tropical Atlantic middle and low troposphere (3–7 km) where ozone concentrations are relatively low. The latter trajectory is consistent with



**Fig. 3.** As Fig. 2 but for 14 August 2001.

a 15-year climatological study of STE with a Lagrangian model in which the sub-tropical western North-Atlantic area is shown to be a region with relatively strong transport of lower tropospheric air into the UTLS (Sprenger and Wernli, 2003). The transport routes originating from the upper and from the lower troposphere are part of synoptic disturbances travelling across the Atlantic Ocean to Europe, following the wave-like path shown in Fig. 3. Modeled ozone concentrations between 4 and 8 km altitude are at the high end of the observed range for this flight, probably due to the relatively diffusive semi-Lagrangian transport scheme applied in our model and the coarse vertical resolution around the tropopause as mentioned above.

### 3.3 16 August, flight 08

During flight 08 on 16 August the aircraft flew in north-westerly direction to approximately 38° N, 20° E. Most of the 3-h flight was upper tropospheric, but contrary to flight 03 the sampled air contained relatively much ozone (Fig. 1c). The simulated  $O_3$ s suggests a stratospheric origin for this. The model simulates higher ozone levels at 12–14 km alti-

tude, close to the tropopause, although lower than observed. The magnitude of the ozone peak at 10–11 km altitude, also characterized by a large contribution from the stratosphere, is captured well by the model.

Ozone in the mid-troposphere is overestimated by 10–15 ppbv, representing about 2–3 Dobson Units (DU;  $1 \text{ DU} = 2.69 \times 10^{16} \text{ molecules O}_3 \text{ cm}^{-2}$ ), which may again be due to the overestimation of downward cross-tropopause ozone transports. A lower tropospheric ozone maximum is observed at 2–3 km altitude. Such peaks above the boundary layer are typical for the influence by shallow convection, e.g., in land-sea breezes and orographic flows that carry pollutants into a reservoir layer (Millan et al., 1997). Backward trajectories (not shown) indicate that the air was advected from the west across southern France, northern Italy and Greece at an altitude between 600 and 750 hPa (2–4 km altitude). It is possible that as a result of shallow convection the air mass has been affected by boundary layer pollution, which also explains the relatively high concentrations of organic trace species observed in this air mass, up to  $\sim 3$  ppb acetone,  $\sim 5$  ppb methanol, and 700 ppt acetaldehyde (De Gouw et al., manuscript in preparation), but this has not been simulated

**Table 1.** Ozone precursor source regions considered in the sensitivity simulations

source region	coordinates <sup>a</sup>
India	1° S–33° N, 63° E–89° E
SE Asia	1° S–33° N, 90° E–125° E
North America	27° N–75° N, 150° W–27° W
Western Europe	33° N–75° N, 8° W–15° E
Eastern Europe	33° N–75° N, 15° E–35° E
Africa	33° S–33° N, 18° W–50° E

<sup>a</sup> Sensitivity simulations only refer to land-surface emissions.

by the model in which convection is a highly parameterized, sub-grid scale process.

### 3.4 22 August, flight 14

During flight 14 on 22 August the aircraft flew from Sardinia (8.6° E, 40.5° N) to Crete. The altitude during the 3-h flight was partly 9 km and mostly 12 km. In contrast with the flights presented thus far, a more gradual ozone increase with height was measured on this flight (Fig. 1d). The model results indicate that this ozone increase is associated with stratospheric influence, while the contribution from photochemical production in the troposphere decreases with altitude. In the next section it is shown that the UT ASM anti-cyclone briefly retreated eastward from the region during this period. Although the vertical profile is simulated realistically, peak ozone concentrations between 9 km (> 100 ppbv) and 12 km altitude (> 150 ppbv) are not fully reproduced by the model. According to the model both peaks are associated with relatively strong stratospheric influence, which is corroborated by the fact that measured CO is generally below 80 ppbv and negatively correlated with ozone (not shown here; see Scheeren et al., 2003).

## 4 Simulated ozone distribution

Figure 4 shows time-altitude plots of simulated ozone between 19 July and 30 August 2001 (days 200–240) above Crete. Also shown are the contributions from ozone of stratospheric origin ( $O_{3s}$ ) and from photochemical formation in the troposphere ( $O_{3t}$ ). For clarity we note that the MINOS flights 3, 6, 8 and 14 which are discussed in the previous section correspond with days 218, 224, 226 and 232.

The UT, between approximately 9 and 16 km, is characterized by ozone levels between 45 and 55 ppbv, while ozone levels in the lower troposphere are generally between 70 and 90 ppbv. Relatively high ozone concentrations are simulated between 3 and 9 km altitude almost throughout the 40 days considered here. The ozone variability at these altitudes is mainly associated with ozone of stratospheric ori-

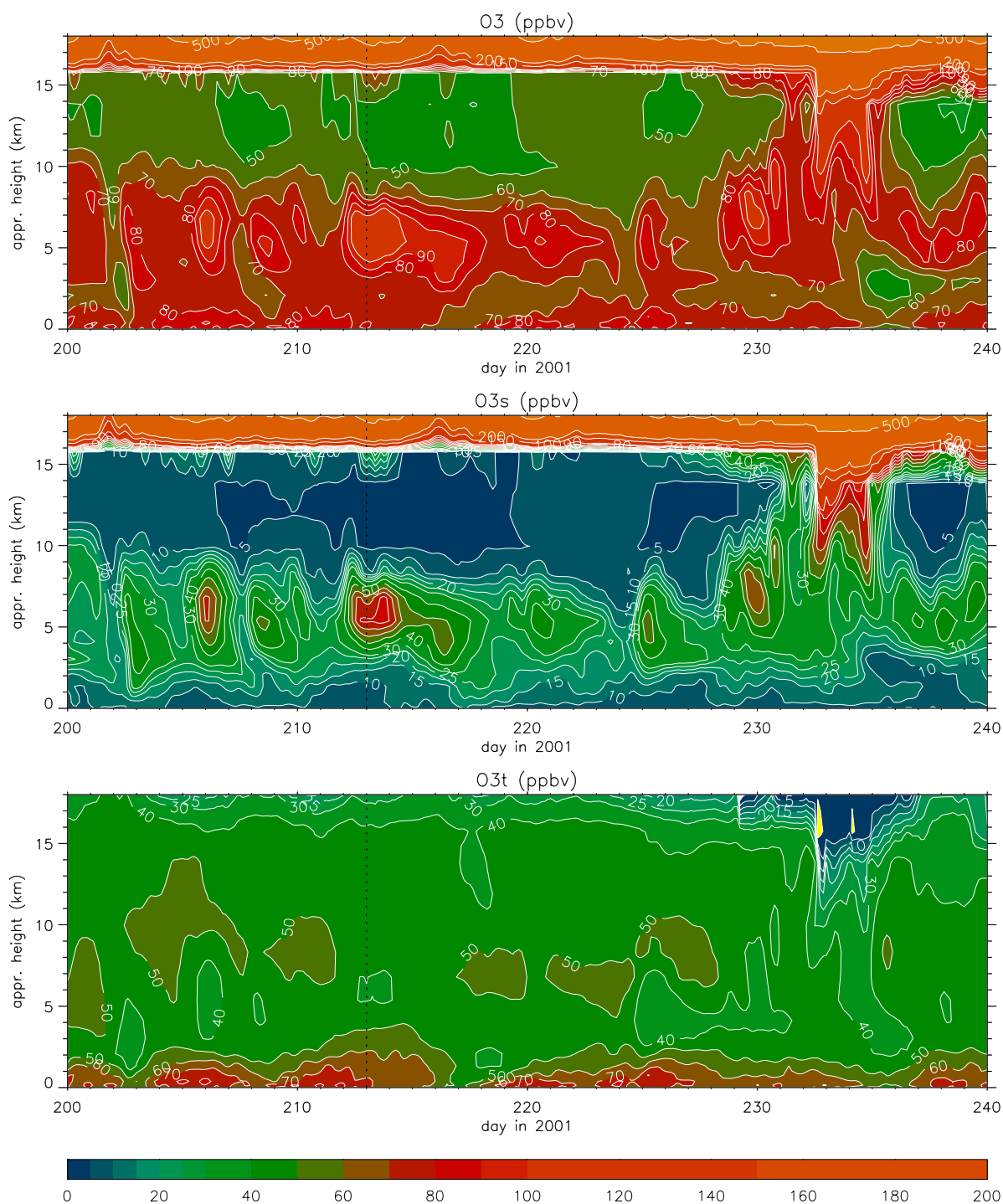
gin ( $O_{3s}$ ), while ozone concentrations from photochemical origin ( $O_{3t}$ ) are less variable, between 45 and 55 ppbv, as shown in Figs. 4b and c. The calculated contribution of  $O_{3s}$  to tropospheric ozone in this layer generally exceeds 30% and sometimes even 60%, directly associated with synoptic systems that travel from the North-Atlantic to Europe, while  $O_{3s}$  contributions below 10% are simulated above and below this layer.

The typical summer conditions in the eastern Mediterranean atmosphere are illustrated in Fig. 5, which shows a latitude-height distribution of the potential temperature along 25° E for 8 August (day 218). Below the UT, under the influence of the ASM anti-cyclone, a more stable layer exists with a relatively steep potential temperature gradient, between 9° and 6° km<sup>-1</sup>. This layer connects the lower stratosphere at high latitudes and the middle troposphere at lower latitudes. Enclosed between two less stable air masses (i.e., the ASM anti-cyclone and the lower troposphere) and almost parallel to the isentropes, this layer acts as a funnel through which extra-tropical UTLS air is efficiently transported south-, east- and downward. This is illustrated by the potential vorticity distribution (PV; 1 PV unit=10<sup>-6</sup> K m<sup>2</sup> kg<sup>-1</sup> s<sup>-1</sup>) also displayed in Fig. 5, which shows a characteristic high-PV tongue of air in the stable layer. The tropopause height, defined as the 2 PVU level, is approximately 15–16 km altitude above Crete. The situation described here is briefly interrupted between days 232 and 236 when the UT anti-cyclone retreated eastward for a few days. This resulted in a lower tropopause height over the eastern Mediterranean region and higher ozone levels, of 80–200 ppbv, between 10 and 15 km altitude.

Ozone from in-situ photochemical formation ( $O_{3t}$ ) is 40–60 ppbv in the free troposphere (Fig. 4c). In addition to the stratospheric contribution discussed above, other ozone or ozone precursor source regions are found to significantly contribute to the tropospheric ozone column over the eastern Mediterranean. This is analyzed further in the next section.

## 5 Regional contributions to tropospheric ozone during MINOS

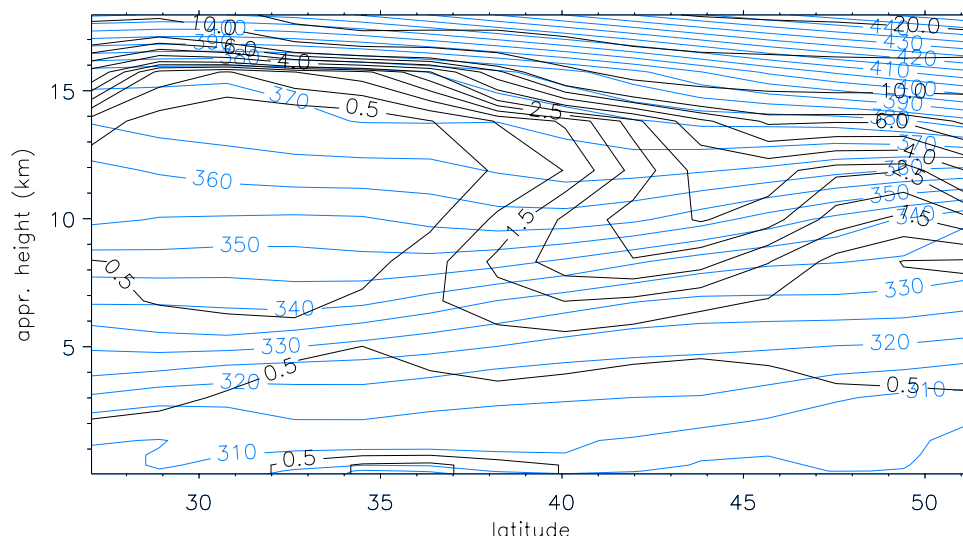
We performed a series of sensitivity runs in which anthropogenic and natural emissions of NO<sub>x</sub>, CO and NMHC were omitted for the regions listed in Table 1. In another simulation NO<sub>x</sub> emissions from lightning, which may contribute significantly to tropospheric ozone (e.g., Lelieveld and Dentener, 2000), were omitted. We note that lightning emissions are parameterized according to Price and Rind (1992), and that the simulated annual global NO<sub>x</sub> source by lightning is 5 Tg N yr<sup>-1</sup>. A specific contribution is calculated as the difference between the control simulation, i.e., with all emissions considered, and a sensitivity run. All simulations started on 1 January 2001, allowing a mixing throughout the NH of the chemical effects due to the emission changes.



**Fig. 4.** Simulated time-altitude distributions (ppbv) of (a) ozone, (b) O<sub>3s</sub>, and (c) O<sub>3t</sub> over Crete (35° N, 25° E) during MINOS. The dotted line refers to 1 August at 00:00h.

It must be noted that the decrease of the ozone production due to the ozone precursor emission reductions in the sensitivity simulations may be partly offset by an increase of the ozone production efficiency per NO<sub>x</sub> molecule. Changes in

the calculated photodissociation rates, for which the model ozone serves as input, may have an additional effect. Additionally, we performed a simulation that only considered the ozone precursor emissions from the regions listed in Table 1,



**Fig. 5.** Simulated time-latitude distributions for 25° E of potential temperature (K, blue) and potential vorticity (PV units, black) for noon time on 8 August 2001.

from lightning and the ozone source from the stratosphere. The difference between this and the control simulation represents the amount of  $O_3t$  that can not be assigned to the source regions considered, and which we will refer to as “background residual”. To minimize the effect of the chemical compensation effects the regional and residual contributions were scaled so that their sum equals  $O_3t$  from the control simulation. The scaling factor varies between about 1.10 in the UT to 1.25 in the boundary layer.

Figure 6 shows the calculated contributions to ozone from each of the regions and from lightning. Again the tropospheric layering over the eastern Mediterranean region is illustrated, with the SE Asian contribution in the UT, the North American and, albeit relatively small, African contribution in the middle troposphere, and the western and eastern European contributions in the lower troposphere.

The ozone precursor emissions from India and SE Asia together contribute up to 25 ppbv of ozone in the UT. This contributes 30–50% to  $O_3t$ . Around 22 August (day 232) the SE Asian contribution diminishes for a few days due to a weakening of the anti-cyclonic influence in the region.

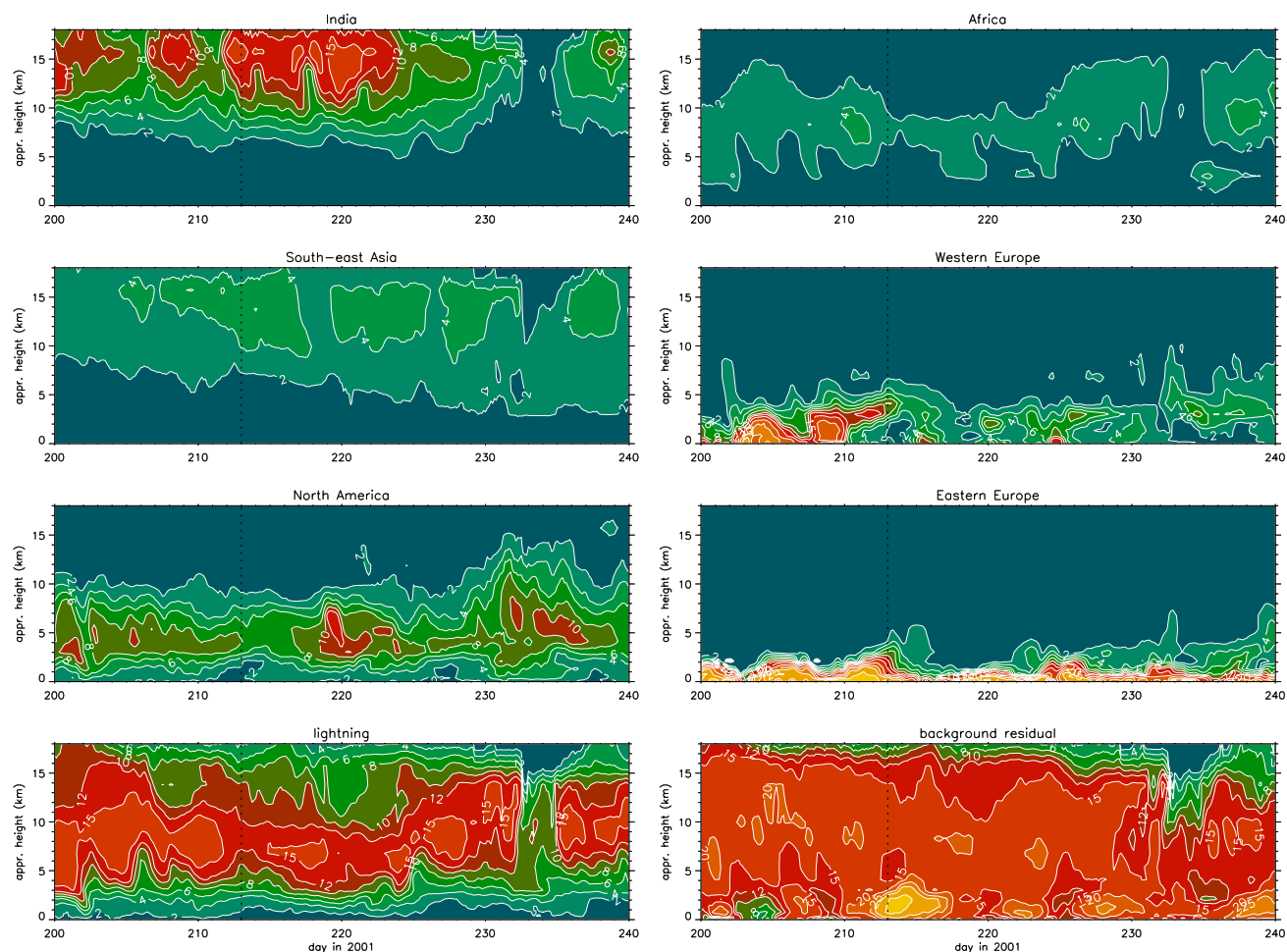
The main contributions to ozone in the mid-troposphere, apart from  $O_3s$  discussed in Sect. 4, are from North America and from lightning. The North American contribution ranges between 6 and 12 ppbv. The maximum in North American ozone between days 219 and 222 is associated with a synoptic disturbance that also causes a peak in  $O_3s$  on day 220 (Fig. 4b). The role of synoptic disturbances as a mechanism for cross-Atlantic transport of North American pollution has been discussed by Stohl and Trickl (1999), and our model results indicate that similar transports occurred during MINOS. Note that when the ASM anti-cyclone retreats, between days 231 and 236, the North American contribution

extends throughout the depth of the troposphere, which increases its contribution to the tropospheric ozone column by  $\sim 50\%$ . It appears that the presence of the ASM anti-cyclone over the eastern Mediterranean limits the vertical dispersion of North American pollution in the free troposphere, thereby suppressing associated ozone production.

Ozone from lightning  $NO_x$  also maximizes in the mid-troposphere, possibly associated with convection in synoptic systems. We estimate that lightning  $NO_x$  contributes up to 35% of  $O_3t$  at this altitude. At altitudes dominated by the ASM anti-cyclone the contribution by lightning is also relatively large, 6–10 ppbv ozone or 15–25% of the  $O_3t$ . Here, lightning ozone is associated with the monsoon convection south of the Tibetan plateau, which also transports SE Asian boundary layer air into the UT anti-cyclone. Finally, ozone precursor emissions from Africa have a relatively small influence, 2–4 ppbv, on ozone in the mid-troposphere.

The effect of eastern European precursor emissions is limited to altitudes below 3 km, with contributions up to 55 ppbv at the surface. Ozone concentrations from western European precursor emissions are smaller but their contribution extends further upward, up to 5 km altitude. The results clearly illustrate that the stable mid-tropospheric layer suppresses mixing between the boundary layer and the free troposphere so that European pollution does not significantly affect free tropospheric ozone. However, it is possible that shallow convection plays a role. On days 226–227 a small maximum of western European ozone occurs at 3 km altitude, corresponding with the lower tropospheric ozone maximum measured on flight 08 and discussed in Sect. 3. As mentioned above, the small-scale plumes are not resolved adequately by the model.



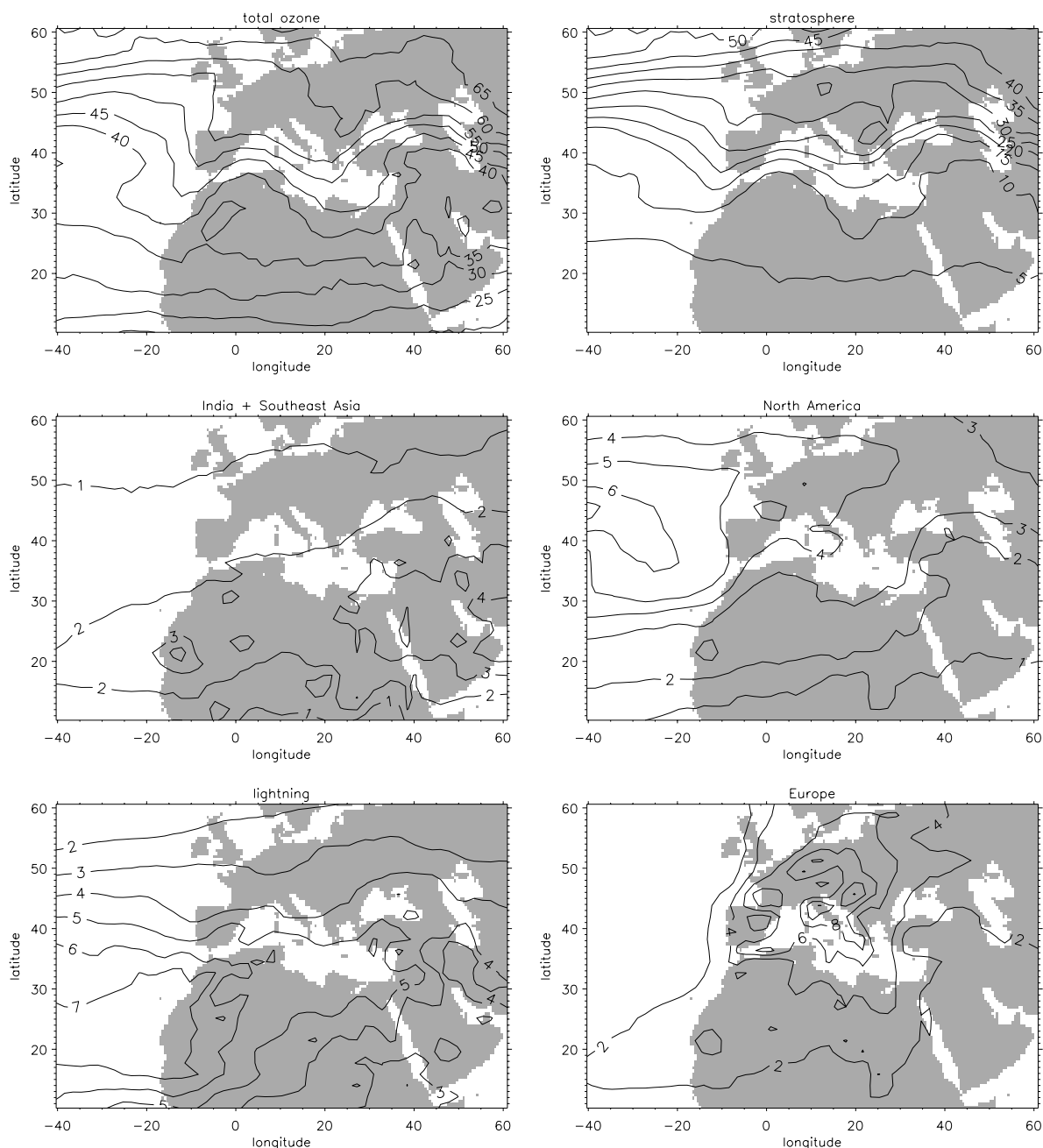


**Fig. 6.** Simulated time-altitude distributions (ppbv) of photochemically produced ozone due to emissions from (a) India, (b) SE Asia, (c) North America, (d) lightning, (e) Africa, (f) western Europe, (g) eastern Europe, and (h) background residual. The dotted line refers to 1 August at 00:00.

The background residual ozone fraction in the free troposphere amounts to 15–20 ppbv. It originates from all other natural and anthropogenic precursor emissions in the northern hemisphere. In the boundary layer the residual exceeds 30 ppbv on days 206 and 214, associated with easterly transport of pollution from the Istanbul area (Turkey) (see also Traub et al., 2003). In the free troposphere, the residual is larger than the direct contribution by any of the source regions except the stratosphere. Figure 7 shows the regional distributions of the simulated tropospheric columns of ozone and the contributions associated with the stratosphere, the ASM, North America, lightning and Europe. The columns are averaged between days 200 and 225, i.e., with the UT anti-cyclone present, and integrated between the surface and 15–16 km altitude. The tropopause height decreases with increasing latitude, and the stratospheric contribution (Fig. 7b) dominates the latitudinal variability of the total tropospheric ozone column in Fig. 7a. Figures 7c–f show the contributions

from the main ozone source regions. The figures nicely illustrate how advection from different directions contributes to the ozone column in the eastern Mediterranean troposphere.

Table 2 lists the computed tropospheric ozone column above Crete and the separate contributions. The computed tropospheric ozone column above Crete is nearly 50 DU. This is, for example, very close to the globally outstanding ozone column maximum of 50–60 DU over the tropical southern Atlantic Ocean in austral spring, under influence of strong biomass burning emissions (e.g., Thompson et al., 1996). Our study indicates that the tropospheric ozone column over the eastern Mediterranean contains a substantial contribution by natural sources, with about 40% originating from the stratospheric and lightning sources together. Our estimates are subject to some uncertainty. Although ozone concentrations in the mid-troposphere, i.e., where  $O_3$ s maximizes, appear to be representative, the model may overestimate mixing of the intrusion air, especially



**Fig. 7.** Simulated regional distributions of the tropospheric column (DU) of (a) ozone, and the contributions from (b) the stratosphere, (c) India and SE Asia, (d) North America, (e) lightning, and (f) Europe, averaged between days 200 and 225.

downward into the lower troposphere and the boundary layer (Fig. 1). Therefore, the calculated contribution by stratospheric ozone is probably an upper limit, with an estimated uncertainty of several DU. The present estimate of NO emissions from lightning ranges between 3 and 13 Tg N yr<sup>-1</sup> (Prather et al., 2001), so that the actual contribution from lightning may also differ by a few DU from the model estimate. We note that Scheeren et al. (2003) suggest that, for MINOS, the model underestimates enhanced tropospheric

NO<sub>y</sub> originating from lightning. The contribution from Europe may be a lower limit because biomass burning emissions in Eastern Europe were not considered by the model (Traub et al., 2003). Additional errors are associated with other inaccuracies in the ozone precursor emission inventory, in the representation of transport and mixing processes, e.g., associated with convective clouds or synoptic disturbances, and in chemical transformation rates, but we estimate these to be relatively small.

## 6 Conclusions

We investigated the distribution and sources of free tropospheric ozone over the Mediterranean area in July and August 2001 with a coupled tropospheric chemistry-GCM. Model results were compared with aircraft measurements of ozone from the MINOS field campaign.

The model simulates three distinct ozone layers in the troposphere over the eastern Mediterranean region for the summer of 2001. The uppermost layer, between 9 km altitude and the tropopause at 15–16 km, is strongly influenced by the western branch of a large UT anti-cyclone centered over the Tibetan plateau associated with the Asian monsoon. Air pollution originating from the South and SE Asian boundary layer can thus reach the Mediterranean UT. The model simulates 40–55 ppbv ozone in this region, of which up to 20 ppbv derives from natural and anthropogenic emissions in South and SE Asia.

The anti-cyclone influences potential temperature and vorticity distributions in the UT in the region so that a stable layer is created in the mid-troposphere along which ozone-rich air from higher latitudes is efficiently transported downward and southeastward. In the Mediterranean region this appears as a layer with 65–100 ppbv ozone at 3 to 8 km altitude between the UT anti-cyclone and the boundary layer. Between 25 and 60 ppbv of ozone in this layer derives from the stratosphere. At several instances during MINOS cross-Atlantic transport of North American air adds to this mid-tropospheric ozone layer, with the largest contribution of 8–10 ppbv coinciding with the passage of synoptic disturbances around 7 August. Lightning is an additional important source of ozone to this layer, contributing 10–20 ppbv.

Lower tropospheric ozone over the eastern Mediterranean region is strongly influenced by precursor emissions from eastern Europe, remaining in the boundary layer, and from western Europe in and directly above the boundary layer. Upward mixing into the free troposphere is efficiently suppressed by the stable layer aloft. The typical layering in the region was briefly interrupted around 20 August when the influence of the UT anti-cyclone on the atmospheric layering decreased, resulting in more vigorous mixing of pollutants throughout the depth of the troposphere.

Comparison of modeled and observed ozone profiles generally shows good agreement, indicating that transport and chemistry in this period are represented adequately by the model. Some discrepancies occur that are associated with a tendency of the model to overestimate downward tracer fluxes in stratospheric intrusions, as also indicated by previous studies. The fact that shallow convection is a sub-grid scale process in the model also hampers a realistic representation of occasional concentration peaks encountered at approximately 2–3 km.

On average, the estimated tropospheric ozone column in summer over the eastern Mediterranean region is about 50 DU. Of this, ~12 DU (25%) is associated with chemically

**Table 2.** Contributions from source regions to tropospheric ozone columns during MINOS

source region	O <sub>3</sub> column (DU)	contribution to O <sub>3</sub> column (%)
stratosphere (O <sub>3</sub> s)	14.3±3.2	29
India	2.0±0.4	4
SE Asia	1.5±0.3	3
North America	3.8±0.6	8
Western Europe	3.0±1.5	6
Eastern Europe	3.8±1.5	8
Africa	1.4±0.3	3
lightning	6.5±0.7	13
residual	12.3±1.9	25
total column	48.5±3.0	

aged and well mixed air, representing typical mid-latitude summer background ozone levels of 15–20 ppbv. The contribution of ozone from stratospheric origin is about 14 DU (30%), and that from lightning NO<sub>x</sub> emissions is about 6 DU (13%), with possible uncertainties of a few DU due to inaccuracies in the representation of transport and emissions from lightning. The estimated contributions from emissions from Europe, SE Asia and North America are 6.8, 3.5 and 3.8 DU, respectively (together 29%).

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