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Atmospheric Chemistry and Physics Discussions

Interactive comment on "

The impact of temperature changes on summer time ozone and its' precursors in the Eastern Mediterranean" *by* U. Im et al.

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REPLIES TO REVIEWER #2

We thank the reviewer for the careful reading and the valuable comments that helped improving our paper. All suggested English and typographic corrections are incorporated in the revised version of the manuscript. Below we present how we address the specific comments of the reviewer.

Reply to the comment on P4356, L22: The first paragraph of the introduction has been

rewritten as provided in the replies to the reviewer #1.

Reply to the comment on P4356, L25: Since this part of the introduction has been changed following the comments of both reviewers, discussion on aerosols does not fit anymore to the revised text.

Reply to the comments on P4359, L3: References for WRF-ARW and CMAQ models are provided in the materials and methods section (sub-sections 2.1 and 2.3, respectively).

Reply to the comment on P4359, L19; P4369, L2: Additional information on the model vertical extent and layers is provided together with information on the PBL heights in the model. It is now clearly stated that: The sentence is modified as following: "The lowest level is 8 meters high and the domain top extends to $\sim$16 km. The model layer thickness increases from surface to the model upper boundary. PBL heights are calculated with the Meteorology-Chemistry Interface Processor (MCIP: Otte and Pleim, 2010) and the PBL top is generally within the first 27 vertical layers. The 27th layer corresponds to a height of about 3 km. The remaining 3 layers are very coarse and their width extends from around 3 km from surface to 16 km." We further mention in section 2.3, second paragraph: 'that the PBL varies spatially and temporally (hourly) as presented in Fig. S1 (provided in the replies to the reviewer #1)."

Reply to the comment on P4361, L19: Soil emissions of nitrogen oxide (NO) are taken into account in this study.

Reply to the comment on P4362, L6: Although TM4-ECPL references are already included in the ACPD paper, to satisfy the reviewer additional information is provided. Precisely, we clarify that TM4-ECPL originates from the TM4 model (VanNoije et al., 2004) of which emissions, chemistry and carbonaceous aerosol modules have been modified as described in detail by Myriokefalitakis et al. (2008, 2010, 2011) and references therein. TM4-ECPL model is able to simulate gas phase chemistry coupled with the major primary and secondary aerosol components including sulfate, nitrate

and organic aerosols."

Reference added: Van Noije, T. P. C., van Eskes, H. J., van Weele, M., and van Velthoven, P. F. J.: Implications of the enhanced Brewer-Dobson circulation in European Centre for Medium-Range Weather Forecasts reanalysis ERA-40 for the stratosphere-troposphere exchange of ozone in global chemistry transport models, J. Geophys. Res. 109, D19308, doi:10.1029/2004JD004586, 2004. Other references have already been provided in our discussion paper.

Reply to the comment on P4362, L21: "The horizontal and vertical resolution of the CMAQ model is identical to that of the WRF model." This is now clearly stated at the end of the 1st paragraph of section 2.3.

Reply to the comment on P4363, L5-8: The discussion at the end of section 2.3 on the evaluation of the contribution of individual process to the levels of the trace gases is modified for simplicity following the comments of the reviewers: "The weighted contributions of each process on O3, NOx and VOC levels have been estimated using Eq. 1, where PCi is the individual contribution of the process i and %PCi is the relative contribution of that process to the sum of the contributions from all the processes (Goncalves et al., 2009).

In the present study, we evaluate the contributions of the major atmospheric processes (i): HTRA, VTRA, DDEP, and CHEM that determine O3 mixing ratios."

Reply to the comment on P4363, L17: "A spin-up period of 11 days has been used for all the simulations, starting from 20th of June, 2004" as now explicitly mentioned in the first paragraph of section 2.4.

Reply to the comments on P4364, L10; P4372, L1; P4373, L5; P4376, L11: Indeed, scenario S6 has significantly different meteorology than the other scenarios. This is now mentioned in the text and supported by Table S1 to be included in the supplementary material: "Indeed, although there are no computed changes in soil properties

(temperature and moisture), deposition velocities and wind speeds in scenarios S0 to S5, these parameters change in scenario S6 (Table S1). The MEGAN module takes into account the air temperature and the incoming radiation. In scenarios S0 to S5, only the 2 meter temperatures input to the MEGAN module have been modified. However in S6, the whole meteorology is computed after perturbing the air temperatures, thus also impacting the radiation. Therefore, both parameters affect biogenic emissions. In addition, CMAQ internally recalculates the precipitating and non-precipitating cloud fractions using the ambient air temperature, which leads to changes in cloud cover and relative humidity in each scenario (Table S1) that affect the photodissociation rates and wet removal of atmospheric trace constituents." Further at the end of the 5th paragraph of section 3.3, it is now added: "The computed changes in S6 are also due to the differences in meteorological variables, such as wind, soil properties and deposition velocities that modify transport and deposition patterns (Table S1)."

Reply to the comment on P4365, L11-13: "These stations have been attributed to the model grid boxes. Further, observations from stations located in the same model grid have been first averaged to better represent the conditions in that grid and then compared with the model results"

Reply to the comment on P4366, L27-28: This part is removed from the revised text following the comments of both reviewers.

Reply to the comment on P4367, L4: The correlations between hourly model results and observations have been calculated, reported in the revised Table 2 and discussed in the text: "As seen in Table 2, hourly variations are not captured as good as the daily variations."

Reply to the comment on P4368, L5: The last sentence of the fourth paragraph of section 3.1 is rewritten as following: "This can be attributed to higher NMVOC emissions and in general, faster thermal reactions in the troposphere, since most of them show positive temperature dependence. Due to warmer temperatures, this results in more

and faster reacting organic compounds in the atmosphere and leads to more intensive chemical activity over Athens."

Reply to the comment on P4368, L10: This discussion on CO/NOx ratio has been changed to accommodate the comments of both reviewers: "The model calculated molar CO/NOx ratios are compared with the observations from measurement networks at IST, ATH and THES. The CO/NOx ratio is an indicator of emission composition and air mass ageing. Due to the short lifetime of NOx compared to CO, low CO/NOx ratios indicate high contribution by local emissions whereas high ratios point to important contribution of transported air masses. The distribution of CO/NOx molar ratios at surface, computed for simulation S0 and averaged over the simulation period, is depicted in Fig. 5f. The model calculated CO/NOx ratios increase from below 50 in the large agglomerations to above 150 downwind, due to influence from the surrounding region, which is consistent with the observed pattern."

Reply to the comment on P4369, L13: We agree with the reviewer and his/her comment has been inserted in the revised manuscript: "VTRA leads to the mixing of the air masses from the surface with above through turbulence and convection. VTRA transports high O3 from above downwards, and surface emissions and precursors (NOx and NMVOCs) upwards."

Reply for the comment on P4372, L7: CMAQ calculates a correction factor to the clear-sky photo dissociation rates based on the cloud cover. As presented in Table S1 (please see above), the cloud cover changes in each scenario, which in return has an effect on the dissociation rates. Therefore, increase in temperature leads both to faster thermal reactions and higher photo dissociation rates, resulting in more intense chemistry. This is clearly stated in the revised manuscript.

Reply for the comment on P4372, L25: The spatial variability of the 15-days mean of the simulated VOC/NOx ratios at the lowest model layer is shown in Fig. 5e. Domain mean VOC/NOx ratios are calculated and discussed as indicators of the overall

chemical limitations in the region.

Reply to the comment on P4373, L16: The sentence is rewritten as following: "The O3 mixing ratios are very similar ($\sim$72 ppb) around 4000 meters at all stations, indicating a high free-tropospheric O3 background over the entire region."

Reply to the comment on P4375, L23: Indeed, the horizontal resolution of the model (30 km x 30 km) imposes limitations in the model ability to simulate the sharp gradients in the emissions between the urban centers and the surrounding rural locations. As a consequence, urban center modeled emissions might be underestimated whereas those in the surrounding location overestimated. This is expected to result in an underestimation of O3 titration by NOx in the urban centers and an overestimation in the close-by surrounding regions.

Tables and figures

'Concentrations' have been replaced by 'mixing ratios' in Table 4 and throughout the revised manuscript where necessary.

Figures 2, 5 and 9 are redrawn for clarity.

Vertical axis is added in Figure 6.

The caption of Figure 8 already mentions 'for the simulation period of 15 days'.

The caption of Figure 9 is rephrased as following: Spatial differences between simulations S5 and S0 (S5-S0; left panel) and between simulations S6 and S0 (S6-S0; right panel) averaged over the 15-day simulation period in: a,b) isoprene emissions; c,d) surface ozone; e,f) surface molar VOC/NOx ratios and g,h) surface PAN.

In the caption of Figure 10, it is stated "...for the simulation period of 15 days."

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 4355, 2011.

Table S1. Comparison of deposition velocity of ozone, soil temperature, soil moisture and wind speed at FIN and the domain-averaged cloud fractions for the different scenarios.

	S0	S1	S2	S3	S4	S5	S6
Deposition velocity ($m\ s^{-1}$)	0.00255	0.00255	0.00255	0.00255	0.00255	0.00255	0.00260
Soil temperature (K)	290.844	290.844	290.844	290.844	290.844	290.844	293.698
Soil moisture ($m^3\ m^{-3}$)	0.2180	0.2180	0.2180	0.2180	0.2180	0.2180	0.2175
Wind speed ($m\ s^{-1}$)	3.04	3.04	3.04	3.04	3.04	3.04	2.93
Precip. cloud cover (%)	0.003	0.003	0.003	0.003	0.003	0.003	0.005
Non-precip. cloud clover (%)	0.011	0.002	2.68E-4	3.67E-5	2.45E-6	4.81E-8	0.012

Fig. 1. Table S1

Table 2. Comparison of model calculated (S0) surface hourly and daily mean isoprene and ozone mixing ratios with observations for the station groups.

		Hourly Variation					Daily Variation				
Parameters	Species	IST	ATH1	ATH2	THES	FIN	IST	ATH1	ATH2	THES	FIN
Correlation	Isoprene	-	-	-	-	-	-	-	-	-	0.5
	Ozone	0.4	0.3	0.3	0.7	0.3	0.9	0.8	0.9	0.5	0.4
Mean Normalized Bias (%)	Isoprene	-	-	-	-	-	-	-	-	-	90.7
	Ozone	61	11	18	9	48	6.1	12.2	13.5	7.1	47.5
Index of Agreement	Isoprene	-	-	-	-	-	-	-	-	-	0.3
	Ozone	0.6	0.5	0.6	0.8	0.4	0.9	0.7	0.7	0.6	0.4

Fig. 2. Table 2