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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosol chemistry above an extended Archipelago of the Eastern Mediterranean basin during strong northern winds" *by* E. Athanasopoulou et al.

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Comment 1: One of the results of model evaluation is that about half of the organic aerosol mass remains unaccounted. The authors claim that the main cause of this underestimation is the "intense" fire activity in the upwind regions, the Balkans and the Black Sea coast. First, evidence of such activity, e.g., in the form of satellite imagery, could be helpful. Second, a clarification of whether these fires are considered in the global (GEOS-Chem) modeling is necessary. Even if fire emissions were included, long-range transport in the free troposphere is not going to be well resolved in the CAMx model. Third, an estimate of the level of impact of these fires onto measured

concentrations should be made based on the fire emissions, distance travelled and atmospheric dispersion. The conditions for the given examples, especially Sciare et al. (2011) focusing on a very different region (Paris, France), may be very different from the conditions here. Organic aerosol underestimation may be due to the underestimation of the emission sources in the region. It may also be due to the underestimation of the secondary organic aerosol formation in the models. The volatility-basis set in CAMx is still under a lot of scrutiny. For these reasons, the claim that the fires are responsible for the underestimation should either be better supported or withdrawn.

Reply: Indeed our conclusion that the organic aerosols are associated with the fires is indirect. Below, we comment on each of the above-mentioned concerns and then we provide a concluding statement.

"evidence of such activity, e.g., in the form of satellite imagery, could be helpful."

- We certainly agree with the reviewer. This is why a MODIS image acquisition, showing the fire events in Turkey, south and east Europe from 29 August until 07 September 2011, is given in the Supplement (Fig. S2) and referred within main text (pp. 9374, line 14-16, in the ACPD version of the paper).

"a clarification of whether these fires are considered in the global (GEOS-Chem) modeling is necessary."

- Our current model application does not include global biomass burning emissions, because the updated emissions were not available for 2011 in the currently applied GEOS-CHEM version. This is mentioned in the Supplement (pp. 3 line 11, ACPD discussions).

"an estimate of the level of impact of these fires onto measured concentrations should be made based on the fire emissions, distance travelled and atmospheric dispersion."

- Prior to our study, Bezantakos et al. (2013) performed in-situ measurements during the same period with the one studied here, and investigated –among others– the origin

ACPD
15, C2886–C2891, 2015

of aerosol masses observed above the Aegean Sea. To this end, they calculated wind back trajectories (120-hours long) by NOAA's HYSPLIT model during 25/8-11/9/2011 over the North Aegean Sea at 400 m asl, and for selected days (1 and 4 Sept) over the south Aegean Sea at 500-4500 m asl. In all cases, air masses in the region originated from the Black Sea and/or the Eastern Balkans. Comparison between model predictions and measurements of PM concentration over the Aegean Sea when NE winds prevail shows an average difference of 1.3 μg m-3 (Table 4). When the prevailing winds have a NW direction (the air masses arriving over the Aegean basin do not seem to originate/pass from the NW fire spots, according to the same back-trajectory analysis), the difference between OA values from the model and observations is lower (0.6 μg m-3; cf. Table 4). We therefore speculate that the fires at the NNE of the Archipelago (Fig. S2) impact the atmosphere above it. The level of this impact onto OA concentrations is attempted to be estimated by our model application.

"The conditions for the given examples, especially Sciare et al. (2011) focusing on a very different region (Paris, France), may be very different from the conditions here."

- We thank the reviewer for pointing this out. The citation that should be referred here is Sciare et al. (2008): Sciare, J., Oikonomou, K., Favez, O., Liakakou, E., Markaki, Z., Cachier, H., and Mihalopoulos, N.: Long-term measurements of carbonaceous aerosols in the Eastern Mediterranean: evidence of long-range transport of biomass burning, Atmos. Chem. Phys., 8, 5551-5563, doi:10.5194/acp-8-5551-2008, 2008. According to the long-term (5-year) measurements performed at the south Aegean (Finokalia) in the frame of that study, the long-range transport of agricultural waste burning from European countries surrounding the Black Sea occurs mainly during March/April and July–September, with the latter period being the most intense. Focusing on the carbonaceous aerosol measurements in August and September, which include our period of interest, it is shown that the contribution of biomass burning to the total concentrations of OC is 30-35%. Another observational study that supports our findings is that of Bougiatioti et al. (2014) conducted at Finokalia (on the island of Crete), which in-

ACPD
15, C2886–C2891, 2015

vestigates the biomass-burning aerosol in the EM during August and September 2012. Here, all the OA mass (not only OC) was measured and complemented with HYSPLIT back-trajectory analysis and satellite images. Almost all back trajectories (shown in the Supplement) show that air masses pass from the Eastern Balkans and coastline of the Black Sea, where several fire spots are observed. During the fire events of the studied period, the contribution of organics to the total mass increased to almost 50%. Lastly, Bossioli et al. (2014)* have performed a model application over the same area and period of interest (ongoing work), after incorporating wildfire emissions, and have found that on average they contribute around 50-60% to the total PM1 OA mass. In summary, the above-mentioned findings from the same region and similar conditions to those our study can sufficiently support our model predictions.

*Bossioli E., Tombrou M., Kalogiros J., Allan J., Bacak A., Bezantakos S., Biskos G., Coe H., Jones B.T., Kouvarakis G.N., Mihalopoulos N., Percival C.J. Simulation of physical and chemical processes of polluted air masses during the Aegean-Game airborne campaign using WRF-Chem model, C O M E C A P 2 0 1 4 e-book of proceedings ISBN: 978-960-524-430-9 Vol 1 Page | 155

“Organic aerosol underestimation may be due to the underestimation of the emission sources in the region.”

- We agree with the reviewer. This is why we have performed a series of sensitivity tests regarding OA performance: increases in emissions from road transport, maritime and industrial emissions. These scenarios showed insignificant changes in the organic aerosol predictions. Furthermore, we also increased boundary concentrations from GEOS-CHEM (bcs scenario), but this time unrealistically high OA concentration predictions occurred (cf. pp. 9376 lines 6-9 in the ACPD version of the manuscript). Although we cannot exclude some uncertainty in the emission inventory as well as in GEOS-CHEM OA performance, these were not found –through the bcs scenario- as the important reasons for the OA underestimation by the current model application.

ACPD
15, C2886–C2891, 2015

"It may also be due to the underestimation of the secondary organic aerosol formation in the models. The volatility-basis set in CAMx is still under a lot of scrutiny."

- Previous PMCAMx applications over Europe (including Finokalia) using the VBS scheme for SOA formation, have been shown to be satisfactory with respect to OA performance (Fountoukis et al., 2011, 2014). These applications neglect the chemical aging of biogenic SOA (bSOA): they assume that the chemical aging reactions of biogenic SOA do not result in a net increase of the bSOA concentration. Having said that, however, we agree with the reviewer that this configuration (scenario 3) underestimated SOA formation for our model application/period of interest (Fig. 2b: green dashed line) and changed the model skills for organics from average to poor. On the contrary, the activation of the BSOA chemical ageing in the VBS module (standard run) increases the total OA mass predictions by 50 to 80% in the atmosphere over the Aegean Sea during the whole simulation period. The reason that BSOA are likely to undergo atmospheric ageing lies in the sufficient quantities of anthropogenic nitrogen and sulfur pollutants in the atmosphere over the AS (NOx = 1 to 2 ppb, mean molar ratio NH4+/SO4 $\leq$ 2), which facilitates BSOA oxidation (pp 9376 lines 11-22, in the ACPD version of the paper). We also tested the sensitivity of SOA formation on ASOA ageing in the VBS scheme (scenario 4), but this had a minor effect on performance metrics (pp 9376 line 23 – pp 9377 line 2, in the ACPD version of the paper). A limitation of the one-dimensional VBS approach –as this in the PMCAMx model– is that species with similar volatilities can have different properties and reactivities (Donahue et al., 2012). To cope with this deficiency, a two-dimensional VBS scheme is developed, which uses the degree of oxidation as a second coordinate (Donahue et al., 2011). However, when tested against measurements in Europe it was found that the simple one-dimensional scheme had as good a performance as any of the more complex two dimensional VBS schemes. This is probably due to uncertainties in our understanding of SOA evolution in the atmosphere (Murphy et al., 2012). Lastly, in case a chemical process –like VBS– would have caused OM underestimations, then OC comparisons at both ground locations would have also been poor, which is not the case. Based on a prior VBS setup

ACPD
15, C2886–C2891, 2015

within the PMCAMx model that has shown good OA performance, and after conducting our own investigation on this, we concluded that the current model application with respect to OA treatment is optimized.

Overall, based on the evidence described above these conclusions are safe to draw, claiming that the fire activity, not taken into account by the current model application, is the main cause of OA underestimation (around 54%). This finding provides a challenge for future model development (pp. 9382 lines 2-6, in the ACPD version of the paper).

Comment 2: The claims to be the first aerosol analysis and the first carefully designed modeling study to capture the airflows over the Aegean are not sufficiently proven and probably unnecessary.

Reply: We thank the reviewer for pointing this out. However, we believe there is a misunderstanding here. Our claim is that to the best of our knowledge this study is the first to: a) couple the regional model PMCAMx to the global model GEOS-CHEM b) provide an extensive spatio-temporal analysis of the aerosol over the EM, using both observations and model predictions, thereby providing one of the most extensive model evaluations in the region to date. To make that more clear, we proceed to certain modifications in the text. In particular: a) we removed the phrase 'for the first time' from the abstract (in the ACPD version of the paper) and b) we will modify the relevant sentence in the Introduction section as follows: "In order to capture more efficiently the airflows over the Aegean basin, a comprehensive coupling of gases and aerosols between the PMCAMx and GEOS-CHEM chemical transport models (CTM) is performed and applied here for the first time."

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 9355, 2015.