Here we provide comments and responses to the points raised by both reviewers. The updated version of the paper and the supplement (figures and tables are excluded), in both of which all changes have been highlighted, are also provided further below.

Response to Anonymous Referee #1

Comment 1: The authors state (page 9359, line 10) that the relation between meteorology and aerosol load "is not extensively studied" over the Eastern Mediterranean. I must somehow disagree. The authors cite at least four works covering this topic, but there is a number of modeling works covering the topic. So, I would rephrase the sentence, but if the authors want to keep the sentence as it is, they must provide stronger arguments for this fact.

Reply: This and the former paragraph of the introduction, focus on the aerosol modelling works over the Eastern Mediterranean (EM). The first of these two paragraphs presents the findings of pure aerosol studies (e.g. chemical composition, sources), which are indeed many in number (to the best of our knowledge they are at least nine). On the other hand, studies discussing the relation between meteorology and aerosol load are fewer (we have found only four). This was the reason the phrase 'is not extensively studied' was used.

Having said that, we understand the concern and the argument of the reviewer, and therefore we will now use the sentence: "The relation between meteorology and aerosol load over the EM is less understood, and it has been only until recently that people started studying it using atmospheric models" (pp 3, lines 30-32).

Comment 2: Also, they state (Page 9360, last paragraph): "[...] providing the first extensive evaluation of aerosol simulation performance over a wide region of the Mediterranean". I also believe that this sentence is not correct; again, a number of works have provided extensive evaluations of modeling performance over the Western and Eastern Mediterranean. This sentence is completely unnecessary in this context and should probably be removed from the manuscript.

Reply: Prior to this statement in the Introduction, all (to the best of our knowledge) aerosol modelling studies conducted for the region over the EM are cited. Most of those include comparisons with ground observations, while two of them are compared against flight measurements. Here, we should point out that the temporal and spatial (3D) coverage of the aerosol model evaluation in our study (~ 1500-2250 samples per species), is more extended than that of the previously performed comparisons. This was the reason we originally mentioned that this is the 'first extensive' study for aerosol predictions over the EM. Nevertheless, we can understand possible misinterpretations of the word 'first', which will be replaced by the word 'most' (pp 5, line 11).

Comment 3: In Page 9363, line 22, the authors comment: "All air quality predictions presented [...]", which leads to think that the modeling results are forecasted outputs. However, the WRF model is driven by a reanalysis form NCEP, and therefore regional results are not forecasted, but driven by a reanalysis. Probably the authors should change the word "predictions" in order to avoid further confusion.

Reply: The aim of this phrase was to make clear that all gaseous and aerosol model values presented in the results are the output of the regional model PMCAMx, and not from the global model GEOS-CHEM. To avoid confusion that can be caused by the word 'predictions', we will replace it with 'model results' (pp 7, line 23).

Comment 4: For the type of evaluation done in this work, having a detailed resolution for the vertical layering is an essential issue. I have doubts about the vertical resolution used. The authors

indicate that they use just 14 model layers up to 5.8 km to cover the troposphere with the 1st layer at 21 meters (Page 9365, line 18), but do not provide further information on the vertical coordinates of the model. Further discussion should be devoted to this issue in the manuscript.

Reply: We performed some preliminary tests before deciding about the vertical resolution. In these tests we found that the vertical configuration of 14 layers with the domain-averaged layer top at 21, 29, 70, 129, 169, 228, 531, 869, 1256, 1696, 2166, 3252, 4496 and 5758 m above ground level, gives reasonable profiles, covers the boundary layer height, excludes higher altitudes with minimum aerosol concentration values, and therefore does not unjustifiably increase the computational time. It should be noted that mass transfer from higher altitudes is incorporated into PMCAMx simulations through the coupling of GEOS-CHEM to PMCAMx (top conditions). The same applies for the meteorological phenomena through WRF-to-PMCAMx coupling (more information on the configuration of the three models lies in Table 1 of the main manuscript).

Following the comment of the reviewer, the whole sentence (Page 9365 , lines 16-18) now reads: "The PMCAMx simulation domain is that of the greater area of the Aegean Archipelago (Fig. 1a; 34.1 to 42.5°N, 18.4 to 29°E) with 0.056° (~ 6.2 km) horizontal grid resolution and 14 vertical layers with their domain-averaged layer top at 20.9, 29.3, 69.7, 129, 169, 228, 531, 869, 1256, 1696, 2166, 3252, 4496 and 5758 m above ground level (agl)." (pp 9, lines 3-5).

Comment 5: **In Page 9372, line 26, the authors indicate that "sulfate model performance is not consistent throughout the troposphere". The authors should elaborate on the causes of this discrepancy. Is it just a consequence of the low concentrations leading to a high value of the statistical figure considered, or is there any other cause for this vertical gradient of the error?**

Reply: Yes, we support that this inconsistency is mostly related to lower values. About 40% of the SO4 observations at altitudes > 2.2 km asl are low (below 1μg m^{-3}), and it is known that a few large deviations between low concentration values can have a significant impact on the overall performance assessment. As mentioned in the text (page 9372, line 26 and onwards), when we confine the results above Turkey (25% of the total number of data pairs over 27 to 29 ºE, correspond to altitudes from 4 to 7 km asl), then this difference becomes even more pronounced. Of course, since we focus on higher altitudes, thus air masses with non-local origin, the GEOS-CHEM model performance could have also interfered to the aloft discrepancies. Yet, a first evaluation of the model, performed for CO and O3 has shown that its performance regarding the physical and chemical processes that affect the gaseous species is adequate (Protonotariou et al., 2013; cf. list of reference in the manuscript). Another hypothesis for this discrepancy is inaccuracies in the injection heights of point sources (industries), which could pose some differential uncertainty per altitude. However, there is no data to support this hypothesis, thus it remains as a theoretical allegation.

Comment 6: **In Page 9376, line 10, the manuscript claims that "fire activity is the main deficiency in the current model application with respect to organic aerosols". This sentence has to be carefully considered. First, the authors should provide evidence for the fire activity (e.g. satellite images) in the target region during the August-September 2011 episode. Moreover, if the fires were causing under predictions in particles levels, a substantial underestimation should be also observed for black carbon (which is not observed in this study). The authors should also explore the VBS mechanism for the formation of SOA, which could be causing the underprediction of organic aerosols.**

Reply: In general, biomass burning plumes are known contributors to the organic aerosol load over the EM during summer. During the period we investigated, the aerosol load over the Aegean Sea is affected by the fire activity in the eastern Balkans and the western coastline of Black Sea, as indicated by the fire spots (cf. Fig. S2) and back-trajectory analysis from a previous study (Bezantakos et al., 2013; list of references in the main manuscript). For additional information and on the point regarding the possible errors introduced by the use of the VBS mechanism, please refer to our reply to the Comment 1 of Reviewer#2.

Although we agree with the reviewer that no model underestimation is observed with respect to the average concentration of ground Elemental Carbon (and Organic Carbon), at the same time we cannot ignore the evidence mentioned above, which strongly indicates that the aerosol over the Aegean Sea is affected by the wildfires. Moreover, we want to stress the following points regarding EC:

1. Long-range transport of pollutants is more efficient in higher altitudes due to a lack of surface deposition and stronger winds. This also occurs in our case for the fire plumes: air masses originating or passing from the fire spots shown in Fig. S2 reach the atmosphere over the Aegean Sea in layers from 400 to 4500 m (Bezantakos et al., 2013). This creates an extra OA mass being measured aloft. On the other hand, the good performance for PM10 EC is found at the ground sites (filter samples). This is consistent to the PM10 OC measurements at the ground, which are also somewhat underestimated by the model system (Table S4), but perform much better than PM1 OA in and above the PBL (as indicated by the AMS airborne measurements).
2. As shown in Fig. 6, the 6-hour averaged values of ground observations and predictions are low (≤ 1μg m^{-3}), with ~40% of their differences being above 0.2 μg m^{-3}. Similar is the average amount of the biomass burning fraction of EC measurements at Finokalia. The signal of fires on EC is most probably within the difference between observations and predictions over the Aegean Sea during summertime, as has been previously reported by Sciare et al. (2008).

It is commonly known that the accurate representation of emissions –including wildfires– in models strongly affects the quality of aerosol predictions (e.g., Heald et al., 2011). The fact that wildfires are not treated by the current modelling application, can explain the observed PM1 OA underestimation within PBL. Regarding the other types of sources, as well as the uncertainty of OA treatment within models, please refer to our reply to the Comment 1 of Reviewer#2. The main contributor to the PM1 OA underestimation (ca. 55%) of our current modelling application is the missing fire activity upwind the region of the Aegean Sea. This is a quite realistic hypothesis, given the observational evidence reported by Sciare et al. (2008) and Bougiatioti et al. (2014), as well as the modelling outputs of Bossioli et al. (2014). For more information on this issue, as well as our changes in order to address the points made by both reviewers, please refer to our reply to the Comment 1 of Reviewer#2.

Minor comments:

Abstract, line 1; Page 9360, line 26: What is exactly a "carefully designed model system"? How can a model system be designed "carefully"?

Reply**:** Our model system is composed of: a) the regional model PMCAMx, which provides the aerosol mass concentrations over the greater area of the Aegean Archipelago, b) the WRF model, which provides the meteorology to the PMCAMx applications and c) the global model GEOS-CHEM, which provides the initial and boundary pollution conditions to the PMCAMx application. The coupling between the models is characterised –"carefully designed"– because certain settings are set after thorough investigation:

1. The YSU PBL scheme for the WRF application is selected in the frame of this study because it is non-local and has a better performance than other schemes as far as water vapor mixing ratio predictions are concerned (Dandou et al. 2014), which is an important input parameter for air quality studies (Tombrou et al. 2015)." This information is now included in sect. S1, pp 1, lines 9-11.
2. Given that the PMCAMx model is not provided with pre-calculated PBL depths but with fields of diffusion coefficients (Kv), it is expected that the results are strongly dependent on the latter. For that reason, the WRF code has been modified so that it directly provides Kv outputs. These fields are regarded more accurate than Kv derived by the default procedure (offline calculation of Kv considering the calculated temperature, wind speed, friction velocity etc from WRF). Moreover, Kv values are then adjusted for the heights under 100 m, which is found to benefit air quality predictions (Environ, 2011b). This information is briefly provided in the ACPD version of the paper (pp. 9365, lines 11-14).
3. The default pre-processor provided by the environ.corp in order to adjust WRF output to PMCAMx inputs has been extended to treat frictional velocity, monthly vegetation fraction, fractional land use / vegetation type, gravimetric soil moisture and soil texture type, so as to provide hourly sea-salt and dust emission fields, as analytically described in Athanasopoulou et al (2008, 2009), which are cited in Table 1 of the manuscript.
4. The previous study which coupled GEOS-CHEM to a regional air quality model (UAM-V) over our area of interest (Tombrou et al., 2009) has shown the importance of a nested GEOS-CHEM application in order to provide initial and boundary gaseous concentrations to UAM-V. This method is also applied in the current study (Table 1). This information is now included also within sect. S1 pp1, lines 29-31, as: "A previous study focusing on the same area of interest (Tombrou et al., 2009) has shown the importance of a nested GEOS-CHEM application in order to provide initial and boundary gaseous concentrations to a regional air quality model during summertime. Thus, …".
5. "Detailed coupling of gases and aerosols between the PMCAMx and GEOS-CHEM chemical transport models (CTM) is carefully designed and applied here for the first time in order to capture more efficiently the airflows over the Aegean basin" (pp. 9360, lines 25-27). In particular, it involves 63 chemical species. Modifications to the model were necessary not only for the chemical speciation of some species (e.g., sea-salt mass of GEOS-CHEM should be broken down to Na, Cl, Br etc), but also for their size distribution (e.g., total sulfates of GEOS-CHEM should be broken down to the size bins of PMCAMx). Sea-salt and dust species treated by GEOS-CHEM are chemically resolved to the species treated in PMCAMx, following Athanasopoulou et al. (2008) and Kandler et al. (2007), respectively (cf. Table 2). Moreover, primary and secondary organic mass of GEOS-CHEM (e.g., Ketones, Limonene, Terpenes, and their oxidation & aerosol products) were processed so as to match with different gaseous species (e.g., monoterpenes, sesquiterpenes) and with the VBS treatment of PMCAMx (anthropogenic and biogenic oxidized and aerosol species of different volatilities). Also, in order to assess the relative contribution of the different OA precursors to the total SOA transported from outside the PMCAMx modeling domain (GEOS-CHEM BCs), each of the five lumped SOA species treated by the volatility basis set (VBS) scheme in PMCAMx is coupled to each unique oxidative product treated by GEOS-CHEM (instead to that of the uniform distribution of their mixture, Sect. 4.3). All this information is incorporated in Table 2 and is briefly described in page 9365, lines 1-8 in the ACPD version of the paper.

After this comment, we will include the above information within the main text or supplement, while the phrase 'carefully designed' will be replaced by '**comprehensive'**, in order not to confuse the reader.

Page 9363, line 14: please change "nitrogen oxide" to "nitrogen oxides"

Reply**:** The change has been made (pp. 7 line 14).

Figures 2 and 6 are hard to read; the quality of the figures must be improved before publication.

Reply: we have improved the quality of these and the rest of the figures shown in the manuscript. Those will be separately uploaded together with the final version, following the rules of ACP.

Response to Anonymous Referee #2

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 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 investigates 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.

"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 ≤ 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 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).

In order to address the point made by the reviewer and better link these conclusions with the points listed above, we have modified the relevant text as following:

a) In the Abstract (pp 1 line 14-17): "The latter is most likely related to the intense fire activity at the eastern Balkan area and the Black Sea coastline, which is not represented in the current model application."

b) Sect. 4.3.4 Pp. 9376 lines 9-11 (ACPD version of the paper): "Regarding the sensitivity of OA concentration performance, most of the applied model scenarios (changes in road transport, maritime and industrial emissions) showed either insignificant changes in the organic aerosol predictions, or (when boundary concentrations were increased) unrealistic OA concentration results. These findings further support that fire activity is the main deficiency in the current model application with respect to organic aerosols. In addition and unlike previous findings in the area of study..."

c) pp 16, lines 8-11: "The main reasons for such underestimations are the poor model representation of SOA, as well as the lack of additional sources and sinks of OA. Regarding the former, the VBS mechanism in PMCAMx has been shown to be competent enough to predict realistic levels of PM1 OA over the south Aegean Archipelago (Fountoukis et al., 2011; 2014). With respect to the sources and sinks**,** the most probable reason for the OA underestimation…".

d) Pp 18, lines 25-28: "Wind also affects the quality of organic aerosol predictions, but only regarding direction. In particular, observation and model values show an average difference of 1.3 μg m^{-3} under NE winds, while this difference is lower (0.6 μg m^{-3}) under NW winds. This is again attributed to fire plumes, which are mainly transported from NE, but are not represented in the current model application**.**"

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." (pp. 5, lines 7-11)

Aerosol chemistry above an extended Archipelago of the Eastern Mediterranean basin during strong northern winds

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Abstract

Detailed aerosol chemical predictions by a comprehensive model system (i.e. PMCAMx, WRF, GEOS-CHEM), along with airborne and ground-based observations, are presented and analyzed over a wide domain covering the Aegean Archipelago. The studied period is ten

successive days ~~during the summer~~ of 2011, characterized by strong northern winds, which is the most frequently prevailing ~~wind conditions~~ synoptic pattern during summer~~(Etesian regime~~). The submicron aerosol load in the lower troposphere above the Archipelago ~~(< 2.2 km altitude)~~ is homogenously enriched in sulfate (average modeled and measured submicron sulfate of 5.5 and 5.8 μg m^{-3}, respectively), followed by organics (2.3 and 4.4 μg m^{-3}) and ammonium (1.5 and 1.7 μg m^{-3}). Aerosol concentrations smoothly decline aloft, reaching lower values (< 1 μg m^{-3}) above 4.2 km altitude. The evaluation criteria rate ~~Model performance is found good (according the selected evaluation criteria) for~~the model results for sulfate, ammonium, chloride, elemental carbon, organic carbon and total PM_{10} mass concentrations as 'good', indicating a satisfactory representation of the aerosol chemistry and precursors. Higher model discrepancies are confined to the highest (e.g. peak sulfate values) and lowest ends (e.g. nitrate) of the airborne aerosol mass size distribution, as well as in airborne organic aerosol concentrations (model underestimation ~~around~~ ca. 50%). The latter is most ~~probably~~ likely related to the intense fire activity ~~upwind the Archipelago (i.e.~~at the eastern Balkan area and the Black Sea coastline~~)~~, which is not represented in the current model application. ~~Overall~~The investigation of the effect of local variables on model performance revealed that~~,~~ ~~the model system shows~~ the best agreement between predictions and ~~with~~ observations occurs ~~under~~ during ~~strong~~ high ~~northeastern~~ winds from the northeast, as well as for the area confined above~~over~~ the Archipelago and up to 2.2 km altitude. The ~~activation of the chemical~~ atmospheric ageing of biogenic particles is suggested to be ~~used~~ activated in ~~for~~ the aerosol chemistry module, when treating organics in a sufficient nitrogen and sulfate-rich environment, such as that over the Aegean basin. More than 70% of the predicted aerosol mass over the Aegean Archipelago during a representative Etesian episode is related to transport of aerosols and their precursors from outside the modeling domain.

1 Introduction

The geographical characteristics, specific atmospheric conditions, large range of natural and anthropogenic sources in the Mediterranean basin, create a complex environmental situation contributing to the aerosol load. The major motivations for characterizing aerosols in the Mediterranean are their subsequent climate forcing (Nabat et al., 2014), as well as relevant air quality and health issues (Rodríguez et al., 2002; Medina et al., 2004). During summertime, regional circulation phenomena and increased photochemistry, favor the accumulation and

secondary formation of atmospheric aerosols (Millan et al., 1997; Rodríguez et al., 2002; Pey et al., 2013). The atmosphere over the Aegean Archipelago (also referred as the Aegean Sea), part of the Eastern Mediterranean (EM), is frequently affected by strong northern winds during the warm period. These winds are often bound to the Etesian flow (Maheras, 1986; Kotroni et al., 2001; Tylris and Lelieveld, 2013; Anagnostopoulou et al., 2014), which is the most common synoptic situation over the Aegean Sea (AS) during summer, transporting dry and cool air masses downwind southern Russia, Ukraine, central/eastern Europe, the Balkan states and Turkey (Vrekoussis et al., 2005; Bryant et al., 2006; Sciare et al., 2008). The emissions from biomass burning and important urban and industrial centers situated in these regions, combined with the intense photochemical ageing of the arriving plumes and the decreased deposition of species in marine environment makes the atmosphere above the AS a favorable area for aerosol investigation particularly during regional-range transport phenomena observed in summer.

Previous aerosol modeling studies covering the AS (Lazaridis et al., 2005; Fountoukis et al., 2011; Im et al., 2012) have shown the predominance of non sea-salt sulfate in the fine aerosol mode, in agreement with previous ground-based observations (Mihalopoulos et al., 1997; Bardouki et al., 2003; Kanakidou et al., 2011), unlike anywhere else in Europe. Together with the high degree of oxidation of the organic matter (Hildebrandt et al., 2010), these findings are both consistent with the atmospheric conditions stated above. In addition, the important role of natural aerosol sources (sea-salt production and long-range transported dust plumes) has been investigated, not only on the total PM_{10} mass levels (particulate matter with aerodynamic diameter < 10 μm) and on model performance, but also on the gas-aerosol interactions towards the modification of inorganic aerosol composition (Kallos et al., 2007; Astitha and Kallos, 2008, Athanasopoulou et al., 2008; Im, 2013). Another common output of model applications over this Archipelago is the exogenous influence (short-, medium- and long-range transport) on aerosol chemical composition, PM_{10} concentration levels (European limit exceedances) and regional climate, in comparison with the contribution of local sources (Lazaridis et al., 2005; Kallos et al., 2007; Im and Kanakidou, 2012).

The relation between meteorology and aerosol load over the EM is less and only recently understood, and it has been only until recently that people started studying it using atmospheric models. ~~.is not yet extensively studied over the EM. Recently,~~ Im et al. (2012) and Megaritis et al. (2013) have studied the influence of temperature increases up to 5 K on the chemical composition of the aerosol particles. Their results are contradictory for sulfate

(negative and positive changes in mass concentrations, respectively), but they are in agreement for nitrate (decrease in mass concentrations) and organics (increase in mass concentrations). Inversely, the effect of aerosols on regional climate has been investigated by Solomos et al. (2011) and Kallos et al. (2014), who showed that the properties of atmospheric particles can modify the cloud structure and precipitation during a heavy rainfall event over the EM. Given the complexity of the aerosol mixture in the Mediterranean basin, further studies on the chemical characterization and size distribution of the aerosol mass will elucidate the interactions between airborne particles, meteorology and climate in the region.

A satisfactory representation of aerosol chemical species by model applications is a challenging task. Predictions over the AS from the aforementioned studies have been evaluated against concurrent or past measurements (Chabas and Lefevre, 2000; Kouvarakis et al., 2001; Smolik et al., 2003; Eleftheriadis et al., 2006; Gerasopoulos et al., 2006; 2007; Sciare et al., 2003; 2008; Koulouri et al., 2008; Pikridas et al., 2010; Im et al., 2012). Comparisons showed a moderate to large underestimation of the simulated PM_{10} (Lazaridis et al., 2005; Im and Kanakidou, 2012) or organic mass concentration (Fountoukis et al., 2011), despite that inorganic species are well-represented (Astitha and Kallos, 2008; Athanasopoulou et al., 2008; Fountoukis et al., 2011). Improved model performance for precipitation is achieved when cloud condensation nuclei activation of aerosols is included (Kallos et al., 2014).

Most of the above modeling studies focus on the surface representation of aerosols and are compared against ground-based observational data from the station of Finokalia in Crete Island (south AS). A few modeling studies that investigated the vertical profiles of dust and sea-salt aerosols found that particles over the EM did not elevate higher than two kilometers (Astitha and Kallos, 2008; Solomos et al., 2011). The latter study, which was compared against airborne measurements conducted near the Israeli coast, showed a good correlation between modeled and airborne measurements of aerosol mass concentrations. An earlier airborne experiment over the Aegean Archipelago (not bound to a regional model application), showed that the atmosphere 3.5 km above sea level (asl) is almost completely depleted of particles during Etesians (Formenti et al., 2002). This study also confirmed that additional quantities of aged aerosols from fossil fuel combustion and forest fires are transported southward. Recently, four clustered airborne campaigns performed during a ten-day period of strong northern winds (including Etesians), provided among others a unique dataset including measurements of the chemical composition of submicron particles above

the AS and western Turkey. The first results from these measurements are selectively presented in Bezantakos et al. (2013) and Tombrou et al. (2013; 2015).

The present study provides predictions of the size distribution and the chemical composition of aerosol particles observed over the wider region of the Aegean Archipelago during the same 10-day period (August - September 2011), taking full advantage of the aforementioned airborne dataset and supportive ground-based aerosol observations. In order to capture more efficiently the airflows over the Aegean basin, ~~A~~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~~, in order to capture more efficiently the airflows over the Aegean basin~~. Outputs from the PMCAMx model are compared against the complete set of experimental aerosol data, providing the ~~first~~ most extensive evaluation of aerosol simulation performances over a wide region of the Mediterranean basin. The large number of prediction-observation pairs enables the investigation of the parameters that significantly affect aerosol model performance. An inter-comparison among different scenarios is performed with respect to the airborne observations, in order to improve predictions of the organic aerosol fraction in the marine environment. This combined use of CTMs and monitoring data, which is emphasized by the latest European air quality directive, is taking advantage of the capabilities of the applied model system. The current model applications presented here complement the newly existing aerosol dataset regarding the origin and chemical ageing of the organic matter (primary, oxygenated, anthropogenic and biogenic), the chemical composition and particle size distribution and the role of non-local sources of air pollution on the mass of each aerosol species under different paths of northern transport.

2 Experimental Data

2.1 Airborne measurements

Airborne data from four EUFAR (http://www.eufar.net/) campaigns (i.e. AEGEAN-GAME, ACEMED, CarbonExp and CIMS) are utilized in this study. The measurements were conducted using the UK BAe-146-301 Atmospheric Research Aircraft, which was operated through the Facility for Airborne Atmospheric Measurements (FAAM, http://www.faam.ac.uk/). Nine flights were performed between 31 August and 09 September 2011 (cf. Fig. 1). In all flights, the aircraft took off from and landed at the airport of Chania (NW Crete). Five of the flights passed over the AS (1, 2, 4, and 7 September), one oriented

towards Thessaloniki passing over Athens (8 September), while for the rest the aircraft flew over the western coast of Turkey up to the SW coast of the Black Sea. With the exception of the last flight on 8 September, all flights were performed from 08:00 to 15:00 UTC. Flight paths in the Greek airspace were at altitudes up to 5 km asl, while those over Turkey were above 2 and up to 7.6 km asl.

The airborne measurements during these campaigns provided, among other atmospheric parameters, the chemical composition of aerosols. High-time resolution measurements of the sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Cl^-) and organic (OA) content of the sub-micron particles (PM_1) were performed by an airborne compact Time-of-Flight Aerosol Mass Spectrometer (cToF-AMS) (Canagaratna et al., 2007; Morgan et al., 2010). Aerosol mass concentrations are reported at ambient temperature and pressure (i.e. a conversion from standard temperature and pressure to ambient conditions has been applied). In common with other AMS measurements, these measurements nominally represent the submicron, non-refractory component of the aerosols, therefore do not include any sulfate, nitrate or chloride associated with sea salt or dust particles. The collection efficiency (CE) was estimated based on the parameterisation described by Middlebrook et al. (2012), which was close to unity based on the acidic nature of the particles. Because no on-board validation of this chemical data was available (no other composition data was obtained and the possible presence of sea salt particles would confound a comparison with the particle sizing instruments), it is prudent to assign an uncertainty of ca. 30-35% to the AMS measurements, as suggested by Bahreini et al. (2009).

Wind speed and direction, air temperature and water vapor mixing ratio were also available and here used for model evaluation (Sect. 4.1). More information on the flights, instrumentation and measured data during this period can be found in Bezantakos et al. (2013) and Tombrou et al. (2015).

2.2 Ground measurements

Ground-based measurements of the chemical composition and physical properties of the particles in the region were conducted at two remote stations located at Vigla (39°58'N, 25°04'E, 420 m asl) on the island of Lemnos and Finokalia, (35°20' N, 25°40' E, 150 m asl) on the island of Crete, between 29.08 and 09.09.2011. Both sites are far from major cities and local anthropogenic sources (Fig. 1a). To determine the aerosol chemical composition observed at Vigla and Finokalia, particles were collected every 1, 6 or 8 hour using PM_{10} and

PM_1 samplers. The ground aerosol data used in this study are the PM_{10} elemental (EC) and organic carbon (OC) (6 h samples), the PM_1 SO_4^{2-} (hourly samples) and the total PM_{10} mass (8 h samples).

OC and EC concentrations on the collected samples were measured with a Sunset lab instrument (Sunset Laboratory Inc.; OR, USA) implemented with the EUSAAR-2 protocol (Cavalli et al., 2010). ~~Punches of 2 cm^2 from each filter were also analyzed by Ion Chromatography for the major anions and cations.~~ Analytical procedures ~~as well as uncertainty~~ and detection limits of the methods are reported in detail by Paraskevopoulou et al. (2014). Finally, measurements of anions in PM_1 were performed at Finokalia using a Particle-into-Liquid-Sampler (PILS) (Orsini et al., 2003) running at 15.5LPM and coupled with an Ion Chromatograph (IC). More information on the PILS-IC settings used here are available in Sciare et al. (2011).

Wind speed, wind direction, as well as the concentrations of ozone (O_3) and nitrogen oxides (NO_x: $NO+NO_2$) measured at the Finokalia station are also used herein (cf. Sect. 4.1).

3 Methodology

3.1 Model framework

The model system used in this study is comprised of the regional aerosol model PMCAMx, the regional meteorological model WRF/ARW (hereafter referred as WRF, Skamarock et al., 2008) and the global chemistry transport model GEOS-CHEM (Bey et al., 2001), following the methodology described by Tombrou et al. (2009). The ~~main characteristics~~setup of the model~~s are~~ is given in Table 1 and Sect. S1. All air quality ~~predictions~~ model results presented in this study correspond to the PMCAMx runs.

PMCAMx is the research version of a former version (v.4) of the publicly available 3D, Eulerian chemical transport model CAMx (Environ, 2003). Aerosols therein, are represented by a detailed chemical composition: potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), NH_4^+, sodium (Na^+), SO_4^{2-}, NO_3, Cl^-, water (H_2O), EC, reactive and inert primary organic aerosols (APO and POA, respectively), oxidized APO (AOO) and secondary organic aerosols of anthropogenic (ASOA) and biogenic (BSOA) origin. All these species are distributed over ten discrete and internally mixed size sections, in the diameter range 0.04 to 40 μm (cut-off diameters: 0.04, 0.08, 0.1, 0.3, 0.6, 1.2, 2.5, 5, 10, 20, 40 μm). This chemical and size treatment results in 400 aerosol model components in total.

The aerosol related dynamical processes considered in PMCAMx include primary emissions, new particle formation by nucleation, condensation, evaporation, wet and dry deposition, coagulation and chemistry. The incorporated chemical modules are shown in Table 1. The ageing rate constants for primary and secondary organic aerosols (both anthropogenic and biogenic) are 4×10^{-11} and 1×10^{-11} cm^3 mol^{-1} s^{-1}, respectively (Murphy et al., 2011).

3.2 Model coupling

In the frame of this study, the two chemical models are coupled offline, so that GEOS-CHEM provides concentrations for a series of species at the boundaries (lateral and top; BCs) of the PMCAMx domain for each hour of the simulation period. A three-dimensional initialization field (29 August 2011, 00:00 Local Standard Time; LST) is also extracted from GEOS-CHEM and used by PMCAMx. Differences in the chemistry and spatial resolution used by the two models demanded a chemical and three-dimensional matching between the two models with respect to the gas and aerosol fields. The chemical linking between the two air quality models (Table 2) involves 41 gaseous species (20 of which are VOCs) and 63 aerosol species (SO_4^{2-}, NO_3^-, NH_4^+, APO, ASOA, BSOA, EC, Na^+, Cl^-, Mg^{2+}, Ca^{2+} and other, distributed over the size bins treated by PMCAMx). A conversion factor of 2.1 was used to calculate total organic aerosols (OA) from the OC GEOS-CHEM outputs, which value is suitable for non-urban areas (Turpin and Lim, 2001) and has already been reported in the literature for OA over Crete (Sciare et al., 2005; Hildbrandt et al., 2010). In order to assess the relative contribution of the different OA precursors to the total SOA transported from outside the PMCAMx modeling domain (GEOS-CHEM BCs), each of the five lumped SOA species treated by the volatility basis set (VBS) scheme in PMCAMx is coupled to each unique oxidative product treated by GEOS-CHEM (instead to that of the uniform distribution of their mixture, Sect. 4.3). Sea-salt and dust species treated by GEOS-CHEM are chemically resolved to the PMCAMx species following Athanasopoulou et al. (2008) and Kandler et al. (2007), respectively (cf. Table 2).

The hourly meteorological fields provided offline by the WRF to the PMCAMx, include horizontal wind speed, temperature, diffusion coefficients (K_v), pressure and water vapor, cloud optical depth, cloud and precipitated water. K_v values are calculated directly during the WRF run, and are then adjusted for the heights under 100 m, which is found to benefit air quality predictions (Environ, 2011b). Minimum K_v value is set to 0.1 m^2 s^{-1}.

3.3 Simulations setup

The PMCAMx simulation domain is the greater area of the Aegean Archipelago (Fig. 1a; 34.1 to 42.5°N, 18.4 to 29°E) with 0.056° (~ 6.2 km) horizontal grid resolution and 14 vertical layers with their domain-averaged layer top at 20.9, 29.3, 69.7, 129, 169, 228, 531, 869, 1256, 1696, 2166, 3252, 4496 and 5758 m above ground level (agl).~~5.8 km vertical extent (14 layers, first layer top at 21 m above ground level; agl).~~ The simulations are realized during the period from 29 August to 09 September 2011, so that they are directly comparable with measurements. Model outputs are extracted on hourly basis. The first two days are used as a spin-up.

Emissions from the anthropogenic, agricultural activities and forests used by the PMCAMx model for the area of Greece are based on a National database provided by the Ministry of Environment for the year 2002. The emission rates for the area of Turkey are retrieved from the EMEP emission dataset (http://www.ceip.at/webdab-emission-database/officially-reported-emission-data/). Analytical information on the setup for the WRF and GEOS-CHEM simulations, as well as on the emissions treated by the chemical models is given in the Supplement (Sect. S1).

The standard model application that provides the base-case outputs follows the modeling configuration described so far. The first applied scenario aims at investigating the exogenous aerosol fraction over the Aegean Archipelago (trans-boundary pollution). This is captured by the coupling between PMCAMx and GEOS-CHEM models and was identified through a combination of two simulations: the standard run (i.e. BCs provided by GEOS-CHEM) and a scenario with constant, minimum BCs (scenario 1). The different contribution to aerosol levels from sources in Greece and the Turkish area (covered by the simulation domain) is calculated by switching off the emissions from Turkey in scenario 1 (scenario 2) (Sect. 4.2 to 4.4).

To assess the sensitivity of organic aerosol simulation performance, a series of model scenarios was performed. Here, results on the OA sensitivity to their ageing process are presented, following previous model studies (Tsimpidi et al., 2010, Fountoukis et al., 2011): one scenario with the BSOA ageing switched off (scenario 3) and another with the ASOA ageing constant multiplied by four (scenario 4) (Sect. 4.3).

The sensitivity of simulated aerosol mass loading on modeled meteorology is also examined. Apart from the standard model setup, where WRF uses the YSU planetary boundary layer

(PBL) parameterization (Table 1), two additional PMCAMx simulations were performed using WRF inputs from an application with the Bougeault–Lacarrère (BOULAC) PBL parameterization scheme (Bougeault and Lacarrère, 1989) (scenario 5) and with Quasi-Normal Scale Elimination (QNSE) (Sukoriansky et al. 2005) (scenario 6). This selection was based on wind speed differences between seven different PBL schemes (Dandou et al., 2014) (Sect. 4.2 to 4.3).

In order to compare predicted versus measured nitrate aerosol fractions (i.e. using the AMS data), a sea-salt aerosols free case was applied (scenario 7) (Sect. 4.5). A summary of all model applications is given in Table 3.

3.4 Model evaluation statistics

Aerosol predictions are compared against AMS measurements using the statistical measures of Mean Bias (MB) and Error (ME), Mean Fractional Bias (MFB) and Error (MFE), Normalized Mean Bias (NMB) and Error (NME), Root Mean Square Error (RMSE), and correlation coefficient (r and r^2). The formulas of these indices are given in Table S2. The airborne observational data that fall within a computational cell during a model time step (hour) are averaged, in order to be directly comparable with the model outputs.

In order to estimate which parameters systematically affect the model discrepancies, a multiple linear regression was used for each aerosol species among the model biases and basic, local variables (e.g. co-ordinates, day/flight, time, wind speed and wind direction). Based on the regression results, paired samples were created between the model biases and each parameter that significantly affects them (e.g. the model biases and the observed wind speeds were paired and formed one sample).

Each of these paired samples were sub-divided in two samples, on the basis of thresholds considering the model performance; i.e. the threshold is set for the parameter value where performance goals are met (or not) for the ~75% of the predicted values of the one (or the other) sub-sample. In particular, the threshold regarding altitude is estimated to be at 2.2 km, close to the PBL height over the domain. Other thresholds set for the paired samples are the longitude of 27º that separates the Aegean Sea from Turkey, the zero degree winds that divide NW from NE sectors and the wind speed of 9 m s^{-1}. The statistical hypothesis tests (F- and t-tests) confirmed that for all cases the two sub-samples were significantly different from each other. This procedure specified under which conditions (e.g. wind speed values and

direction) aerosol model performance over the AS is systematically good or poor and is presented in Sect. 4.2 to 4.4.

4 Results and discussion

The following sections analyze the model results with respect to the measurements. In parallel, measurement findings are supported by the capabilities of the current model system. Model outputs are thoroughly evaluated against airborne AMS and ground-based observations. MFB and MFE were selected as the most appropriate metrics to summarize aerosol model (PMCAMx) performance (Boylan and Russell, 2006). The calculated values are compared against the proposed goals and criteria for each aerosol species (Table S2), in order to characterize model performance as good (the level of accuracy that is considered to be close to the best a model can be expected to achieve) or average (the level of accuracy that is considered to be acceptable for modeling applications). When the standards are not met for one or more species, the model skills (with regard to these species) are characterized as poor, and the reasons for the model discrepancies are further investigated.

The WRF model was evaluated following the model-evaluation benchmarks suggested by Tesche et al. (2001) and Emery et al. (2001). In particular, Mean Absolute Gross Error (MAGE), MB, RMSE and Index of Agreement (IA) are compared against the proposed benchmark values (Table S2).

4.1 Meteorology and gas-phase chemistry

Strong northerly winds dominated during the simulated period, as also shown by Tombrou et al. (2015). In most cases, both the predicted and the observed winds were NE and NW, which seems to depend on the latitude. Nevertheless, local surface winds observed at the site of Finokalia exhibit a strong western component (Fig. S1a). This pattern is attributed to the effect of local topography, while predictions reflect a representative value of a grid cell (an area of ~38 km^2), mainly covered by sea.

An overall good agreement is found between the airborne measured and simulated values over the Archipelago, as far as humidity, air temperature and wind direction are concerned (cf. Table S3). Regarding wind speed, model performance is weaker (2 out of the 3 proposed benchmarks are reached, as shown in Table S2). The predicted mean value (8.0 m s^{-1}) along all flight tracks is in good agreement with the measured one (8.4 m s^{-1}; Table S3). More specifically, the average (maximum) predicted value was 9.0 (16.5) and 7.5 (19.5) m s^{-1} upon

the flight tracks below and above 2.2 km asl, respectively. The corresponding measured wind speeds were 9.7 (22.4) and 7.8 (24.1) m s^{-1}. As far as the surface-wind speed (at 10 m agl) is concerned, the 9-day average (minimum to maximum) surface wind speed predictions at Finokalia were 7.5 (3.0 to 10.7) m s^{-1}, while the respective measurements were 6.8 (1.1 to 9.1) m s^{-1}. The different scale between point measurements and model results, which represent volume averages, contributes to this divergence.

On 4 and 7 September 2011 were typical Etesian days with strong-channeled northeasterly surface winds (> 15 m s^{-1}) over the Archipelago (Tyrlis and Lelieveld, 2012). Under such conditions, the afternoon marine atmospheric boundary layer was around 1000, 700 and 500 m in the north, SW and SE Aegean, respectively, successfully represented by the PBL schemes used in this study (Tombrou et al., 2015; Dandou et al., 2014).

Gas-phase comparisons between PMCAMx and ground concentration measurements do not exhibit any significant inconsistencies. The 12-day average (minimum to maximum) NO_x and O_3 predictions at Finokalia were 0.4 (0.1 to 2.8) and 62 (42 to 72) ppbv, while the respective measurements were 0.5 (0 to 1.4) and 66 (41 to 89) ppbv. The temporal correlation between predictions and measurements is also good, i.e. NME of the hourly data series is 55 and 10%, respectively (Fig. S1b and c).

Overall, the aerosol model performance during the studied period is independent of any systematic and important meteorological and/or gaseous inconsistencies.

4.2 Sulfate aerosols (PM_1 SO_4)

Model evaluation. Figure 2a shows all available prediction-observation pairs of the airborne PM_1 SO_4 in the greater area of the Archipelago. The average profile of airborne sulfate is rather homogeneous up to 2.2 km asl and shows average modeled (measured) concentration of 5.8 (5.5) μg m^{-3}. Concentrations smoothly decline aloft, reaching lower values (< 1 μg m^{-3}) above 4.2 km. The high uniformity and content in the vertical is a first indication that the low troposphere above the AS is a receptor of distant industrial plumes and medium-range sources, especially under strong NE winds (Fig. S1a). This also explains the higher sulfate concentration values in the lower troposphere above the AS (modeled: 5 μg m^{-3} and measured: 4.7 μg m^{-3}) than above Turkey (are 3.6 and 3.7 μg m^{-3}, respectively).

The average model performance statistics have satisfactory values with 77% of the data pairs being within the 2:1 and 1:2 lines (Table S3). The MFB and MFE, when compared with the

goals, rate the sulfate model system performance as good, with only 15% of the MFE values calculated for each data pair being outside the criteria lines.

The good model performance is also supported by checking each ground data pairs. Figure 3 shows all predictions of PM_1 SO_4 against the respective available (PILS-IC) measurements from ground level, while Table S4 embeds the average ground statistics. The average modeled (measured) concentration is 5.9 (6.4) μg m^{-3}, representative of the aforementioned domain-wide average within the PBL over the Archipelago. Most of MFE values meet the criteria with few outliers observed (14% of the cases). Evidently, there is no clear diurnal cycle of sulfate during the studied period (Fig. 3). This is attributed to the lack of strong local sulfur dioxide (SO_2) sources (Pikridas et al., 2010), as well as to the continuous dispersion of the overflying plumes, during their transport over the sea.

Sulfate is the dominant species of the atmospheric aerosols, as indicated both by observations and predictions. This is in line with the majority of earlier long term observations and campaigns in the region (Sciare et al., 2008; Pikridas et al., 2010; Im et al., 2012). PM_1 SO_4 production is related to its gaseous precursors (SO_2) mostly emitted from the industrialized areas in the Balkans, Turkey and E. Europe (Sciare et al., 2003a, b; Pikridas et al., 2010), which is converted to sulfuric acid (H_2SO_4) that has low vapor pressure and nucleates or condenses mainly in the aerosol fine mode (Mihalopoulos et al., 2007). The satisfactory comparison between model predictions and spatially divergent observations of sulfate over the greater area of the AS proves the good representation of its sources and processes in the applied model system.

Exogenous influences. Confidence in this model system allows the provision of supplementary information on the role of sulfur transport from outside the PMCAMx domain, not provided by the measurements. The origin of sulfate from the hot spot regions upwind the Archipelago is tracked by the calculation of the transported mass to the total PM_1 SO_4 predictions (standard run – scenario 1, light red shaded area in Fig. 3). It is found that a notable part of area-wide episodic events is attributed by about 85% to trans-boundary transport of sulfate particles and its gaseous precursor during most of the studied period. The spatial distribution of daily mean sulfate concentrations over the domain of interest together with the contribution of the trans-boundary transport (standard run – scenario 1, iso-lines) is given for a representative Etesian day (Fig. 4a). The exact origin of SO_4, determined by back-trajectory calculations (Bezantakos et al., 2013), is the Eastern Europe and the wider Black Sea region. The remaining 10 – 15% SO_4 of PM_1 is equally formed by sulfur emissions in the

western continental part of Greece and sources in the Turkish area of the domain (scenario 2-scenario 1, not shown).

A different pattern is observed on 31 August 2011, when the observed winds at Finokalia change to NW (Fig. S1a). The concentration map of this episode indicates that the air parcels passing over continental Greece (Athens and Peloponnese) head towards the south AS (Fig. 4b). During that day, trans-boundary pollution in the area is less important compared to the rest of the studied period. In particular, the submicron sulfate over the south AS (Finokalia) is equally shaped by the local (domain-wide) and by the exogenous sources, with the 80% of the former originating from the Greek territory (scenario 2-scenario 1; not shown). Interestingly, the peak values (~10 μg m^{-3}) at Finokalia observed during the sulfur transport from Greek power plants towards the south AS (Fig. 3) are lower than those related to the transport from the Balkans and from further NE (~12 μg m^{-3}). Model inconsistencies during this plume transport (Fig. 3) are related to the strong gradient from near source to background, which is not accurately resolved and captured by the model's grid resolution. The exogenous influence on SO_4 concentrations in the N. Aegean remains high (70%) on 31 August and originates from the continental area between the Black and the Caspian Sea (Bezantakos et al., 2013).

Model performance issues. The high spatial and temporal resolution of airborne measurements, allows for an extended diagnostic evaluation and may help to better address poor model system performance over the EM. Increased model discrepancies are mostly attributable to the lower and the higher ends of airborne PM_1 SO_4 concentrations distribution (minimum and maximum observed values shown in Fig. 2a). Poor model performance for lower aerosol concentrations is explained below, although being typical for aerosol concentrations below 2 μg m^{-3} (Boylan and Russell, 2006). The largest model underestimations occur mainly at the area of Chania, where measurements frequently exceed 14 μg m^{-3}. Measurements during take-offs and landings are contaminated by local airport emissions, while predictions cannot ideally reproduce concentrated plumes, but are representative of a much wider area (~38 km^2) and time scales (1 h). Indeed, sulfate model predictions in the greater area of Chania (6 to 10 μg m^{-3}) are much closer to previous measurements (7 to 9 μg m^{-3}) in a nearby, suburban area (Kopanakis et al., 2012). The maximum sulfate aerosol concentration (23.4 μg m^{-3}) is observed in the lower troposphere (~1.7 km) over Athens (02 September 2011, around 10:00 UTC). Here, the model under-prediction (4.6 μg m^{-3}), is intensified by the narrow shape of Athens pollution plume

(relatively to the size of the model grid size), as well as by the spatial and temporal changes in actual conditions and fuels used for transportation in the greater Athens area, that are not captured in emission inventories.

For more in-depth examinations regarding model system skills for sulfate predictions, MFE for airborne data are broken down for those parameters significantly affecting model performance (Table 4). As shown in this table, sulfate model performance is not consistent throughout the troposphere: it meets the goals at altitudes lower than 2.2 km asl, but is poor at higher altitudes. This is more pronounced over Turkey (25% of the total number of data pairs over 27 to 29 ºE, correspond to altitudes from 4 to 7 km asl) and it is because a few large deviations between low concentration values (below 1 μg m^{-3}) can have a significant impact on the overall performance assessment.

The other two parameters affecting sulfate model skills are related to the wind conditions. Good model performance is observed under strong (> 9 m s^{-1}) NE winds above the Archipelago (local measurements along the flight tracks), that are typical of an Etesian pattern (Tombrou et al., 2015). Under NW and/or winds of lower intensity, sulfate predictions are still acceptable. The sensitivity of sulfate on the simulated wind is further examined by scenarios 5 (BOULAC PBL scheme) and 6 (QNSE PBL scheme), providing the lowest and strongest wind speeds respectively, below 2.2 km altitude. The average value inside the PBL layer ranges between 5.3 and 5.8 μg m^{-3}, for an average wind speed variation from 8.6 (BOULAC) to 9.8 (QNSE) m s^{-1} (below 2.2 km altitude) among the runs. Changes among concentration fields are anti-correlated with the wind fields, due to the higher dispersion of pollution that is associated with stronger winds. The aerosol model skills are rather insensitive to these variations, although scenario 6 exhibited the lowest MFB and MFE values (12.9 and 56.3%, respectively) and the highest correlation with measurements (r^2 = 0.4). Lastly, sulfate predictions showed a similar performance for all days (flights), independently of the time of day and latitude.

4.3 Organic aerosols (PM_1 OA and PM_{10} OC)

Model evaluation. Experimentally determined concentrations of the organic fraction of the submicron particles over the AS (Fig. 2b) are much lower than sulfate. In particular, the average measured concentration below 2.2 km asl is 4.2 μg m^{-3}, with peaks ranging from 7 to 11 μg m^{-3}. Similar findings have been previously observed in the AMS measurements at Finokalia (Hildebrandt et al., 2010; Pikridas et al., 2010).

Measurements of organic compounds over the Archipelago below 2.2 km altitude are moderately underestimated by this model system (average predicted PM_1 OA value is 2.3 μg m^{-3}), which is consistent with findings reported by many modeling studies (e.g. Zhang et al., 2014 and references therein). Also, the comparison of GEOS-CHEM results with integrated global airborne observations resulted in the underestimation of the median OA concentrations in 13 of the 17 aircraft campaigns over central Europe, north America and western Africa (Heald et al., 2011). The main reasons for such underestimations are the poor model representation of SOA, as well as the lack of additional sources and sinks of OA. Regarding the former, the VBS mechanism in PMCAMx has been shown to be competent enough to predict realistic levels of PM_1 OA over the south Aegean Archipelago (Fountoukis et al., 2011; 2014). With respect to the sources and sinks, ~~T~~the most probable reason for the OA underestimation found in this study is the missing representation of fire emissions for the current model application. Biomass burning plumes may enter the free troposphere and be advected over very long distances, especially under strong winds. Back trajectory calculations from 400 to 4500 m asl (Bezantakos et al., 2013) show that the air masses arriving over the Archipelago during the studied period, originate from (or pass over) the eastern Balkan area and the west coastline of the Black Sea, where several fire spots are located during (and prior to) the study period (Fig. S2). The regional ("diffuse") biomass burning influence on OA concentrations over the AS is found to reach up to 50% (Sciare et al., 2008~~11~~; Bougiatioti et al., 2014), a value which is similar to the underestimation of the OA mass by the current application (i.e. around 54%).

The calculated organic aerosol model skills in the PBL show an acceptable performance, with the 58% of the model predictions meeting the performance criteria (Table S3). Also, PBL model predictions are better correlated to the observed aerosol distribution for organics (r^2 = 0.6) than for sulfate (r^2 = 0.3). This can be explained by the fact that the injection heights of the sulfuric compounds emitted from the industry range from 0 to 1 km agl (e.g. Mailler et al., 2013), whereas the large oxygenated fraction of organics in the AS troposphere creates a more homogeneous field.

Modeled organic concentrations (PM_{10} OA) are divided here by a factor of 2.1, to extract the organic carbon mass concentrations over non-urban areas (see explanation in Sect. 3.2), which can be compared to ground PM_{10} OC measurements. Model performance is good (Fig. 5 and Table S4), with the 41 % (82 %) of the model predictions meeting the performance goals (criteria). The average PM_{10} OC concentration values are similar over the north and

south AS (2.3 and 2.9 μg m^{-3}, respectively), indicating the absence of major local OA sources, which can also explain the smaller range of their spatial variability.

OA analysis. The experimental data obtained during this study cannot separate SOA from OA, their biogenic from their anthropogenic part, as well as the fine from the coarse organic PM_{10} fraction. Model outputs are used to help untangle these contributions cf. Fig. 5). Similar predictions over both measurement sites, suggest again the large spatial homogeneity of organic particles over the Archipelago. Up to 40% of PM_{10} organics are located between 1 and 10 μm (which is slightly higher compared to the 25% experimentally determined at Finokalia by Sciare et al., 2003a), the 75% of which is coarse ($PM_{2.5-10}$). Submicron OA over the AS are mainly secondary (95%) and originate primarily (80%) from biogenic sources, which is explained in the next paragraph. Most of these results are consistent with previous studies covering the region of the AS (Hildebrandt et al., 2010; Athanasopoulou et al., 2013), and are explained by the aged nature of the OA over the sea, especially during the summer period.

Exogenous influences. Organic aerosol mass and gaseous (VOC) precursors from the Balkans and further north, shapes more than 90% of their total concentration levels over the AS during the Etesian event (Fig. 4c). The effect of organic-rich plumes from continental Greece during the non-Etesian event (with prevailing NW winds, Fig. 4d), as well as the domain-wide photochemistry, decrease slightly the role of exogenous sources (now 70% on average) over the whole region of the AS. Examining the different chemical constituents of the transported SOA and precursors (34 to 41 gaseous and 4 to 11 aerosol paired species as listed in Table 2) in the studied domain, shows that the exogenous organic mass is primarily originating from isoprene (mean NE boundary concentration values of 1 to 2 μg m^{-3}), while aromatics are 2 to 6 times lower. The rest transported organic species (a-pinene, myrcene, sesquiterpenes etc) are insignificant.

Model performance issues. Regarding the sensitivity of OA concentration performance, most of the applied model scenarios (changes in road transport, maritime and industrial emissions) showed either insignificant changes in the organic aerosol predictions, or (when boundary concentrations were increased) unrealistic OA concentration results. These findings further support that fire activity is the main deficiency in the current model application with respect to organic aerosols. In addition and unlike previous findings in the area of study (Fountoukis et al., 2011), our results indicate that the activation of the BSOA chemical ageing (standard run) leads to a significant improvement of the OA levels over the Aegean Sea (continuous

green line in Fig. 2b). In particular, the BSOA oxidation in the Aegean troposphere increases by 50 to 80% the total OA mass predictions 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 (NO_x = 1 to 2 ppb, mean molar ratio $NH_4^+/SO_4 \leq 2$), which facilitates BSOA oxidation (Zhao et al., 2013, and references therein). As a consequence, deactivating BSOA ageing (scenario 3, dotted green line in Fig. 2b) changed the model skills for organics from average to poor (average predicted value from scenario 3 is 0.7 μg m^{-3} for the atmosphere up to 2.2 km asl over the AS).

The sensitivity of model results on ASOA ageing was limited to 5% both for the average OA concentration predictions and chemical composition (standard run-scenario 4). In particular, the faster rate of the oxidation of anthropogenic SOA resulted in a minor increase (up to 10%) of the predicted OA during the whole simulation period of scenario 4. Such a different model response to BSOA/ASOA changes stems from the isoprene/aromatics concentration ratio from GEOS-CHEM, which takes the average value of 9/1 over the Aegean. Scenario 4 had a positive though minor effect on performance metrics.

The calculated statistics for the paired sampling for airborne organics (Table 4) showed results similar to sulfate. In particular, unlike previous comparative results (Heald et al., 2011), it is found here that the differences between modeled and observed OA concentrations are not consistent throughout the troposphere. The poor model performance in the upper atmosphere and especially in the area above Turkey (elevated flight paths, low concentration values, as described in the previous section), deteriorates the overall organic model performance.

Wind also affects the quality of organic aerosol predictions, but only regarding direction. In particular, observation and ~~prediction~~ model values show an average difference of 1.3 μg m^{-3} under NE winds, while this difference is lower (0.6 μg m^{-3}) under NW winds. This is again attributed to fire plumes, which are mainly transported from NE, but are not represented in the current model application. The day, time of day, latitude and wind speed do not affect organic aerosol model performance. The latter is also confirmed by scenarios 5 and 6 (MFE = 72 to 80%), although scenario 5, which was based on slightly lower winds (i.e. lower dispersion), produced slightly higher concentration values having the subsequent (though minor) reduced model bias.

4.4 Ammonium aerosols (PM_1 NH_4)

The hourly variation of airborne ammonium concentration predictions is consistent with the observations (Fig. 2c). Apart from the expected and already discussed inconsistencies in the observed peak values, performance issues are tied with sulfate inconsistencies (e.g. during 04 September 11). This is related to the fact that during summer most of the ammonium is associated with the sulfate rather than the nitrate fraction.

The average predicted (observed) PBL concentration of PM_1 NH_4 is 1.6 (1.4) μg m^{-3}, which is consistent with the ground ammonium concentrations in earlier measurements at Finokalia (Kouvarakis et al., 2001; Metzger et al., 2006; Pikridas et al., 2010). Regardless of the high uncertainties in ammonia emissions usually incorporated in the photochemical models (Skjøth et al., 2011), the reproduction of the observed data by the current model system is high, i.e. the 70 % (79 %) of the MFE values meets the goals (criteria). The overall model performance for the ammonium species is good and optimized over the Archipelago and under strong winds (Table 4). The rest of the examined parameters (flight/day, time of day, altitude, latitude and wind direction) do not seem to affect model performance with respect to ammonium.

Air parcels arriving in the simulation domain are predicted to contribute ca. 70% of the average PM_1 NH_4 concentrations when originating from NE direction (Fig. 4e) and by a lower percentage (though above 50%) when originating from NW (Fig. 4f).

4.5 Nitrate and chloride aerosols (PM_1 NO_3 and Cl)

The measured non-refractory submicron nitrate concentrations below 2.2 km asl (0.2 μg m^{-3} in average) are strongly overestimated by the model system (1.9 μg m^{-3}) (as shown in Table S3). This is attributed to two distinct reasons: the sea-salt component of nitrate (standard run-scenario 7), which is not captured by the AMS measurements, accounts for the 54% of PM_1 NO_3^- predictions. Also, the average exogenous contribution from upwind (standard run-scenario 1) is ca. 1 μg m^{-3}, which is unrealistic according to current measurements. When subtracting these mass fractions from total PM_1 NO_3 predictions, the model results become more realistic. Nevertheless, it should be taken in mind, that performance issues are commonly tied to low concentrations (< 1 μg m^{-3}) cases, not only because they greatly degrade normalized model performance, but also due to the higher uncertainty of measurements.

Measured (submicron non-refractory) and modeled chloride is low (< 0.8 μg m^{-3}), because of the insignificant sea-salt content in the submicron fraction, the inability of AMS to measure sea-salt chloride, as well as its gradual displacement by nitrate and sulfate ions. Nevertheless, model performance is found good (Table S3).

4.6 Particulate elemental carbon (PM_{10} EC)

Figure 6 shows the diurnal variation of the PM_{10} EC for the ground sites of the south and north Aegean basin. Both the absolute values and their temporal evolution are well reproduced by the model. In particular, the average measured (and modeled) concentration is ca. 0.3 μg m^{-3}, and therefore the model performance is rated as good (Table S4), with a few exceptional outliers. Elemental carbon is dominated by combustion sources. Thus, it can be assumed that the fossil fuel sources are well represented by the emission datasets used by this model system.

As for sulfate, the footprint of continental Greek sources (mainly from the Athens metropolitan area) is apparent in EC concentrations at Finokalia during the prevailing NW directions (0.6 to 1.2 μg m^{-3}). During the rest of the period, EC levels fluctuate in similar levels at both sites.

The OC/EC ratio from the measured (modeled) data during this period is as high as 4.7 (4.0) and 4.0 (7.1) at the north (Vigla) and south (Finokalia) AS (Fig. 6), being at similar levels with those measured previously Finokalia (Koulouri et al., 2008; Pikridas et al., 2010; Im et al., 2012). OC/EC slopes greater than 2, suggest the significant fraction of secondary species in the organic aerosol mass in background areas, as predicted and previously discussed in section 4.3. The lower OC/EC slope at Finokalia during 31 August (1.9) is close to previous findings in urban areas (Favez et al., 2008; Theodosi et al., 2010) and is related to the higher EC levels during the urban plume transport from NW. The latter was also depicted in the spatial distribution of sulfate (Fig. 4b).

4.7 Particulate matter (PM_{10})

The average predicted total PM_{10} mass at Finokalia during the simulated period is found 30.1 μg m^{-3}. This value is very close to the average of the concurrent observations (29 μg m^{-3}), as well as to previous measurements in non-urban areas of the Mediterranean region (Rodriguez et al., 2001; Gerasopoulos et al., 2006; Lazaridis et al., 2008; Koulouri et al., 2008; Kopanakis et al., 2012). The performance skills of the model system on PM_{10} predictions are rated as good (Table S4) and the daily evolution of PM_{10} predictions is satisfactory (Fig. 7).

Atypically high PM_{10} concentration levels observed at Finokalia on 1 September suggest that the quality of sampling on this particular day might be questionable.

The combined use of measurement and modeling techniques during this period is useful for the estimation of the chemical composition and the size distribution of PM_{10} measurements at Finokalia (Fig. 7). Sulfate account for the 45% of PM_1 mass, followed by OM. The latter represents the 20% of PM_1 (2.6 μg m^{-3}), which is similar to measurements at Finokalia (Pikridas et al., 2010). The predicted submicron ammonium content at Finokalia (1.7 μg m^{-3}) is consistent either with the current airborne or with the past ground-based observations at this site (Sect. 4.4). The contribution of the rest aerosol species (Cl and EC) is minor (2%). The levels of the submicron nitrate are greatly overestimated by the model system (Sect. 4.5).

Submicron aerosol is the largest fraction of the $PM_{2.5}$ mass (76%), but accounts for the 42% of total PM_{10}. This is mostly related to the elevated coarse aerosol concentrations (14.2 μg m^{-3}), which shape the $PM_{2.5}/PM_{10}$ ratio around 54%. Previous ground-based observations over the EM have resulted in fractions ca. 50% (Kanakidou et al., 2011), further supporting the satisfactory aerosol predictions over the whole size range by this model system.

Given the similar levels of ground and airborne measurements over the AS and below 2.2 km asl (discussed in Sect. 4.2-4.5), it can be stated that the current analysis of the ground PM_{10} measurements performed by the model, is representative of the PBL above the Archipelago during strong northern winds.

5 Summary and conclusions

A recently applied model system consisting of three well-established atmospheric models (namely, PMCAMx, WRF and GEOS-CHEM), and a unique aerosol dataset collected in the EM are synergistically used in the frame of this study during a 10-day period characterized by strong northern winds (August-September, 2011). The aircraft dataset used represents a spatially diverse set of aerosol observations (covering the horizontal area of ca. 3×10^5 km^2 and extending from the sea surface to 7.5 km aloft), employed to perform the most extensive –to our knowledge– model evaluation of major aerosol chemical component concentrations over the EM to date (> 1300 observation-prediction samples per species).

The vertical resolution in the measurements allowed the exploration of the aerosol profiles above the Aegean Sea. The PBL above the Archipelago (< 2.2 km asl) is homogenously enriched in sulfate (average modeled and measured PM_1 SO_4 of 5.5 and 5.8 μg m^{-3},

respectively), followed by organics (2.3 and 4.4 μg m^{-3}) and ammonium (1.5 and 1.7 μg m^{-3}). Aerosol concentrations smoothly decline aloft reaching low values (< 1 μg m^{-3}) above 4.2 km.

Aerosol model performance within the PBL is largely within an acceptable level of accuracy (for all major chemical species except from nitrate), or even close to the best level of accuracy (sulfate, ammonium and chloride satisfy the criteria), with 50 to 80% reproduction of these standards. Comparison with the ground-based observations (356 observation-prediction samples in total) suggested an even higher model quality, with a good reproducibility of all studied species and a few outliers (< 15% outside the criteria lines).

Wide and commonly found under-predictions in sulfate, elemental carbon and coarse aerosols (cf. Nopmongcol el al., 2012) are not observed in the current study. Also, in contrast to the uncertainties in ammonia emissions usually reported in air quality modeling (e.g. Skjøth et al., 2011), the observed ammonium levels are well reproduced here. These findings support that the power plants, motorways and natural aerosol sources, including agricultural activities of the surrounding area of the Archipelago and upwind are well represented and treated by this model system.

Relatively high OC/EC ratios (4 to 5) from the ground observations are successively reproduced by the PMCAMx model (OC/EC: 4 to 7), suggesting the large oxygenation rate of the organic matter above the Archipelago, nicely represented by the employed OA chemical module. The activation of the chemical ageing of BSOA in this formulation, greatly improves model performance due to the sufficient NO_x concentration and the sulfate-rich Aegean environment. On the other hand, OA predictions showed minor (or unrealistic) response to anthropogenic emissions and BCs variations. The fire activity, not taken into account by the current model application, is the main cause of OA underestimation (around 54%), which is consistent with local measurements of the fire-induced OA fraction (e.g. Bougiatioti et al., 2014). This finding serves as a challenge for future model development.

Model performance was also dependent on the altitude (below and above 2.2 km), the longitude (western and eastern than 27º E, i.e. above the AS and W. Turkey, respectively), the wind speed (above and below 9 m s^{-1}) and wind direction (NE and NW) over the studied area. The (time of) day and latitude did not affect model biases. The sensitivity of aerosol predictions on different PBL schemes showed a minor effect on aerosol concentrations (e.g. 5.3 to 5.8 μg m^{-3} and 2.1 to 2.4 μg m^{-3} for airborne sulfate and organics, respectively), and

did not change model performance. Overall, aerosol predictions within the PBL over the Archipelago under strong NE winds showed the best performance.

More than 70% of the predicted aerosol mass over the AS during the Etesians is associated with the transport of aerosols and their precursors from outside the PMCAMx modeling domain. In the case of organics, this mass originates primarily from the oxidation of isoprene. These findings underline the significance of the detailed gaseous and aerosol model coupling developed in this study, towards more accurate model predictions. The origin of the transported plume during NW winds, distinctively identified from the model simulations (Greek industrialized areas) and the daily evolution of sulfate, EC (and OC/EC) and total PM_{10}, shapes half of the total sulfate mass, the rest being attributed to the exogenous sources. Also, the observed peak in submicron sulfate during this event at Finokalia (10 μg m^{-3}) is lower than the concentrations during the Etesian flow (12 to 14 μg m^{-3}). Therefore, developing abatement strategies to reduce aerosol levels in the EM is both a national and transnational task. Key findings from the current and similar applications can provide information on the origin of air parcels and the contribution of local and exogenous sources, thus on the effective design of air policies.

A forthcoming application of the same model system aims at investigating its performance, as well as aerosol levels and interactions during recent Saharan dust intrusions in the troposphere over the Aegean Sea.

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S1 Supplementary model details

The meteorological inputs for the PMCAMx applications are provided by the WRF/ARW model (Skamarock et al. 2008) (http://www.wrf-model.org/index.php). The model is driven by the National Centers for Environmental Prediction (NCEP) operational Global Final (FNL) Analyses (1.0º×1.0º spatial resolution), in combination with Sea Surface Temperature (SST), from the Real-Time Global SST (0.5º×0.5º spatial resolution). The 25-category USGS land-use classification scheme was adopted in order to provide land-cover data. The planetary boundary layer (PBL) parameterization used is the 'first-order' closure scheme developed by the Yonsei University (YSU) (Hong et al., 2006). This scheme was selected as it is non-local and has a better performance than other schemes as far as water vapor mixing ratio predictions are concerned (Dandou et al. 2014), which is an important input parameter for air quality studies (Tombrou et al. 2015).

The WRF numerical simulations were performed using triple two-way nesting, with the first domain covering the extended area of Europe (23.0 to 77.0ºN, 14.5 to 44.5ºE) with 0.5º horizontal resolution, the second covering the extended area of Greece and Italy (29.3 to 50.2ºN, 4.8 to 32.2ºE) with 0.167º horizontal resolution and the third following the horizontal grid system as PMCAMx. In the vertical axis, 35 full sigma levels resolve the atmosphere (model top at 50hPa or 20 km), with a finer resolution near the surface.

The global model GEOS-CHEM (Bey et al., 2001; http://acmg.seas.harvard.edu/) is applied in order to cope with the transported air masses from outside the PMCAMx simulation domain. The model is driven by assimilated meteorological data from the Goddard Earth Observing System, Version 5 (GEOS-5) of the NASA Global Modeling and Assimilation Office (http://gmao.gsfc.nasa.gov). The version applied for the current study (v8-03-01) uses the SOA chemical mechanism, which includes the NOx-Ox-hydrocarbon-aerosol species module and a SOA module based on the framework proposed by Chung and Seinfeld (2002) and Henze et al. (2008). Moreover, the ISORROPIA II package for aerosol thermodynamical equilibrium is used (Fountoukis and Nenes, 2007).

A 9-month (January to September 2011) simulation of the global model is initially performed (4º latitude × 5º longitude). Three-hour boundary conditions (BCs) are calculated for May-September 2011 (allowing 5-month model spin up) around a domain centered in Europe (22 to 74º N and -20 to 45º E). A previous study over the same area of interest (Tombrou et al., 2009) has shown the importance of a nested GEOS-CHEM application in order to provide initial and boundary gaseous concentrations to a regional air quality model during summertime. ~~Then~~Thus, a nested run over this window is applied, with 0.5º (latitude) × 0.67º (longitude) horizontal resolution (Protonotariou et al., 2013). The vertical grid is composed by 47 levels up to 0.01 hPa.

S2 Emission model inputs

The PMCAMx applications are provided with hourly emissions for a series of pollutants from different source categories. Data for the area of Greece include NO_x, SO_2, NMVOC, CO, NH_3 and bulk PM_{10} emissions from several types of industries, road transport, central heating, maritime activities, railways, air traffic, agricultural activities and isoprene, terpenes, NO from forests (provided by the Ministry of Environment for the year 2002). This emission database has been refined to account for the changes related to the newer motor highway inside the Athens basin. These emissions vary against season and weekday/weekend of the week.

In the frame of this study, emission rates for the area of Turkey are retrieved from the EMEP emission dataset (http://www.ceip.at/webdab-emission-database/officially-reported-emission-data/). NO_x, SO_x, NMVOC, CO, NH_3 $PM_{2.5}$ and PM_{coarse} emissions from the 10 recommended SNAP sectors at 0.5º x 0.5º are horizontally downscaled to the model grid following the land use (eg. coarse ship emissions are equally split only to the fine cells covered by the sea). The vertical downscaling of the EMEP emissions for PMCAMx is done using the disaggregation factors proposed by Bieser et al. (2011), as described in Mailler et al. (2013). The temporal disaggregation of the EMEP emissions from the yearly totals to hourly values for a winter and a summer weekday and weekend is performed using the temporal factors extracted from Greek National emissions.

The daily emission rates from anthropogenic and natural sources of gaseous and particulate atmospheric constituents used in the PMCAMx model are given in Table S1. The emissions of most species in the two countries are in similar levels (e.g., nitrogen species are ca. 50 megaton/day). Differences (e.g. in particulate sulfate) are attributed to difference in the surface coverage between the two countries, and the fact that a significant part of Istanbul (and emission sources therein) is outside the PMCAMx simulation domain (treated as BCs by GEOS-CHEM). At this point, it should be noted that particulate sulfate is the most abundant anthropogenic emitted specie. This is in line with the significance (above 60%) of the industrial contribution in PM_{10} emissions in Athens and Istanbul reported in Kanakidou et al. (2011) and explains the predominance of sulfate in the total aerosol content in the EM (Kopanakis et al., 2012; Im et al., 2012; Tagaris et al., 2013).

Sea-salt particles, road (tire, brake, road wear and re-suspension) and soil dust emission fluxes are calculated online with meteorology, following the methodology developed and applied by Athanasopoulou et al. (2008, 2010). The size and chemical distribution of total aerosol emissions to the species and size bins used by the current PMCAMx model applications are also described therein. An update is related with the conversion of organic carbon (OC) to total organic aerosol (OA). In particular, industrial and motorway OC emissions are multiplied by a factor of 1.25 and by 1.54, respectively (Bergstrom et al., 2012; Brown et al., 2013), so that the modeled organic concentrations are directly comparable to the measured organic mass. The chemical speciation of the non-methane hydrocarbons from transportation and industry for SAPRC99 is described in Bossioli et al. (2002).

The emission databases used for the GEOS-CHEM applications are from fossil fuel burning (including ships) from the EMEP inventory for the European domain (Vestreng and Klein, 2002), biofuel emissions (Yevich and Logan, 2003), biogenic VOC emissions from vegetation based on the MEGAN model (Guenther et al., 2006) and natural sources from the oceans (Spracklen et al., 2008), volcanic activity (Chin et al., 2000) and lightning (Price and Rind, 1992). Global biomass burning emissions are not included, because the updated emissions were not available for the year 2011 in the currently applied GEOS-CHEM version.

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