Responses to the comments of Reviewer #4

We would like to thank all three reviewers for their comments and for motivating us to significantly improve our study as outlined below:
The present modeling study evaluates the impacts of Istanbul and Athens anthropogenic emissions on the Eastern Mediterranean air quality, based on recently developed emission inventories, background levels, chemical regimes and transport, as well as quantifying the potential impacts of country-based emission mitigation options on the major pollutant levels in the region. The meteorological conditions during the studied period represent the characteristics of summertime and wintertime climatology in the region. Wintertime simulations have been added in order to provide information on the seasonality of the impacts of emissions in the region. This addition is important since although ozone exceedences in the studied region are of concern mainly in summer, particulate matter exceedences largely occur in winter. To our knowledge there is no other such study for the area.
To enable the evaluation of the model performance in particular for the wintertime simulations, we have changed the simulation year to 2008 when data are available. Meteorological characteristics are similar in the two summer periods (2008 for the revised paper and 2004 for the ACPD paper). However, air circulation patterns and temperatures in winter are different from those in summer.
We also thank the reviewers for attracting our attention to the miscalculations regarding the NMVOC/NOx molar ratios reported in the ACPD paper. We have now corrected these ratios throughout the manuscript. This has largely increased the consistency in the discussion.
Finally, we have improved the mitigation scenarios using that developed by the IIASA group for the CityZen project. The new Figure 1 shows the extended areas and the model grids characterized as urban and rural for the discussion of the results.
The results are now presented in a standalone paper with thorough discussion supported by additional material in the supplement. To accommodate the wintertime simulations, the word ‘summertime’ has been removed from the title of the paper.
Our results point out that mitigation can be efficient for pollutants that are mostly of primary origin like CO and $PM_{2.5}$ but the system is more complex for secondary pollutants and in particular for O_3 due to the non linear behavior of the chemistry of O_3-NOx-NMVOC system as documented in the discussion.

We provide here below point-by-point replies to the reviewer comments.

Comments

One of the questions raised by current research on the impact of Megacities on chemical composition is, whether the fact that emissions are strongly concentrated on a small domain changes the fate of primary pollutants and the build-up of secondary pollutants. Thus the question of non-linearity of photo-chemical processes in the atmosphere is posed. The paper by Im and Kanakidou asks this question by performing model calculations of a decentralization scenario, in which megacity emissions for Istanbul and Athens are distributed over larger areas.
Other scenarios, in which these emissions, or emissions in the whole Eastern Mediterranean modeling domain are switched off, or in which biogenic emissions are also altered, are also simulated with a mesoscale modeling system. This paper could

give interesting answers to the questions outlined above, but it needs substantial improvement in several respects.

Response: We thank the reviewer for so clearly pointing out this strong point of our study. We have added a summary sentence in the abstract on this issue:
'During winter the concentration of the NO_x emissions in the hot spot regions is shown to enhance their impact on the domain mean levels of NO_x and HNO_3 whereas this is not the case for summertime emissions. For $PM_{2.5}$ no significant differences are computed.'

1) The local air quality impact can a priori not be determined with a 30 km resolution model. If authors do so, then they need to carefully argue, that they are correct, i.e. that their central grid cell for a Megacity represents a kind of average air quality. A comparison with higher resolution runs would be helpful, even if these runs are not used for further analysis of long range transport. The expression "Urban core" for a 30 km grid cell is misleading Not only primary pollutants are concerned, but also the titration effect of NO on ozone.

Responses: We agree that the 30 km resolution of our model grid does not allow to simulate 'urban core' chemistry. Thus we have replaced the 'urban core' by 'urban' or 'urban center' throughout the manuscript. Several studies have shown the sensitivity of model results and performance to grid resolution (Thunis et al., 2001; Queen and Zhang, 2008, Jimenez et al., 2005). They indicate that the 30 km resolution used in the present study may not capture the small scale features in the cities and particularly the local impacts evaluation may be highly uncertain. The present study aims to provide information on the impact of the emissions from the urban and rural areas of the studied cities to the East Mediterranean. There is no more reference to local impact but to regional impacts and impact in the cities extended areas. Relevant comment has been put in section 2 in order to attract the attention of the reader to the uncertainties associated with the model resolution.

2) Model build-up performance should be briefly summarized and not only cited. For example are primary OA values correctly modeled taking into account volatility of POA emissions, is secondary OA build-up correctly modeled. The authors are expert in this field!

Response: We have now added detailed model evaluation for the winter and summer simulations including gaseous pollutants and PM_{10} and $PM_{2.5}$ levels and aerosol chemical compositions. We have changed the simulation year from 2004 to 2008 in order to have more complete observation data to evaluate our model results, particularly for winter period since year 2004 lacked observations in most areas of interest. The model evaluation is now described in a new section 3.1 that is supported by Tables 2 and 3 that provide statistical information on the comparison of simulated and observed levels of pollutants, including aerosol chemical composition in Istanbul, Athens and Finokalia both for summer and winter.

In particular, for the carbonaceous aerosols (OC and EC), the OC to EC ratios are also reported in this table as deduced from the observations and from the model calculations in order to provide hint on the secondary organic aerosol simulations. Comparison of both concentrations of OC and EC and the OC/EC ratios in GIA for winter and summer shows very good agreement between model and observations in particular when accounting for the standard deviation in the concentrations. These ratios are similar to those of the emissions indicating the dominance of primary carbonaceous particles in both seasons. For GAA the comparison is not as good as for GIA since during summer model comparison to the observations in Athens shows about 3 times higher EC and OC with OC/EC ratio almost double than modeled. These are indications of a possible underestimate of carbonaceous aerosol primary emissions in the model as well as of the buildup of secondary organic aerosol from the oxidation of intermediate volatility organics that is not accounted in the actual version of the mesoscale model. At FKL the model seems to perform reasonably when accounting for the standard deviation in the observations and the model results. Relevant discussion has been added in section 3.1.

3) Major differences between the impact of Athens and Istanbul should be much better worked out. Apparently, this has to do with the chemical regime, the absolute magnitude of emissions. Also the transport regime seems to be different, plumes often seem to be more pronounced for the case of Athens, is this due also to a more stable transport regime?

Response: We have now further elaborated the discussion of our results:

i) We compare anthropogenic (and biogenic) emissions from the Athens and Istanbul and those from the domain (Table 1 and relevant discussion) as well as the sectoral distribution of the emissions in the two cities for various pollutants (Table S1 and relevant discussion) (detailed reply to comment 4 of reviewer #3)

ii) We discuss the major transport regimes for the simulation periods that are 'typical' summer and winter months for the region (detailed reply to comment 1 of reviewer 1)

iii) We have also compared the chemical regimes in the studied regions. For this, we have calculated the reactivity of the NMVOC mixture with regard to the OH radical in GIA and GAA and compared it to the reactivity of NO2 with regard to OH (reaction forming HNO_3). (also detailed replies to points 5 and 6 of reviewer #1)

4) The time period for the analysis is very short (2 weeks), no information about meteorological conditions is given. Is this period meant to represent climatological or at least typical conditions in terms of air transport regimes and chemical composition? The computational costs for the model runs with low resolution should are not high even for 8 scenarios, so longer periods could easily be simulated.

Response: We agree with the review that the 20 days was a relatively short time – it has been chosen like that to avoid changes in the meteorological conditions. For the revised version of the manuscript in order to complement the study and address several of the concerns of reviewers we have performed both summer and winter time simulations. The addition of winter simulations enables more complete investigation of the responses of gaseous and particulate species since experimental data shows that while gaseous species are more critical during summer, PM pollution largely occurs during winter in our region.

In order to have appropriate observational data for model evaluation the simulated periods were in 2008. Thus, we re-run all simulations (the mitigation scenarios improved as explained in our replies to reviewer 3) for the entire months of July 2008 and December 2008 with an 11-days of spin-up time (in November and June respectively). We now explicitly state that the meteorological conditions during these two months in 2008 were representative of the summer and winter periods in the region.

It is now stated in section 2.2.:
'All simulations have been conducted for two 42-day periods; from November 20, 2008 to December 31, 2008 representing winter and from June 20 to July 31, 2008 representing summer. The first 11 days in both simulation periods have been considered as spin-up period and not evaluated in the analyses. The summer period is dominated by northerlies, the so-called 'Etesian' that are characteristic summertime circulation patterns in the studied area over the East Mediterranean area whereas the winter simulation period is characterized by higher frequency of southerly and western winds (Kanakidou et al., 2011). These transport patterns affect also the studied sites of Istanbul (Im et al., 2008), Athens (Kallos et al., 2007) and Finokalia (Gerasopoulos et al., 2005). The summer period also experiences stronger winds compared to winter due to the existence of Etesian winds in the region leading to transport of pollutants to longer distances (Im et al., 2011). The studied periods are also selected based on the availability of observations of gaseous and aerosols chemical composition for the evaluation of the model performance.'

5) A specific question is on the VOC/NOx ratio for Athens, which decreases, when Athens emissions are switched off. This is astonishing and should be better explained. One would expect that the rural background with large BVOC emissions and longer lifetimes of VOC's as compared to NOx favor a larger background NMVOC/NOx ratio than the urban one.

Response: As explained in the replies to the other reviewers, we are grateful to the reviewers for their careful reading and for attracting our attention to the miscalculations in the NMVOC/NOx molar ratios that have been now corrected in the Tables and throughout the text. As shown in Table 5 (for winter) and Table 6 (for summer) switching off anthropogenic emissions over the studied cities or over the entire domain increases the NMVOC/NOx molar ratios as expected.

6) How much do emissions from Istanbul and Athens contribute to average pollutant levels as compared to their contribution to total emissions in the domain, i.e. does their concentration on a small spatial scale change this contribution?

Response: To address this question we compare the contribution of the anthropogenic emissions of NO_x from Istanbul and Athens to the anthropogenic emissions in the model domain (Table 1) and the respective impacts on the domain mean concentrations (Tables 5 and 6). It seems that in winter the Istanbul and Athens concentrated emissions are ~13% of the domain anthropogenic emissions. Their impacts of concentrated emissions on the domain mean levels of NO_x and HNO_3 (secondary pollutant formed during NOx oxidation) compared to the impact of the regional emissions are ~22% and ~67%, i.e. significantly larger than the expected based on the share in the emissions. In summer the emissions contribution is ~14% and the respective impacts ~13% and ~ 14% of the regional emissions impact. On the contrary, very small gain in the impacts on PM2.5 domain mean is calculated when PM2.5 emissions are concentrated in the cities. The emissions share is ~12% in winter and ~12.5% in summer and the impacts share is ~11.5% in winter and ~10.5% in summer. Relevant discussion has been added in section 3.4 and the abstract (text mentioned in the beginning of the replies to the reviewer).

7) The authors should better present the spatial changes in pollutants induced by the decentralization scenario, for example as a function of distance from the megacity (and keeping in mind the transport regime). There are some obvious effects, like impact on primary pollutants and ozone titration. But the interesting effects are those dealing with the non-linearity in atmospheric chemistry. For example, how much more (or less) secondary species are formed from more diluted emissions, and how can this be explained with current theory (or the one included in the model). This is the sense in my view of running this highly idealized decentralization scenario.
These questions would need to be answered before acceptation of the paper. All in all the study could lead to an interesting paper, but a more "careful" analysis and presentation would be needed.

Response: Motivated by reviewer #1 we now use a mitigation scenario developed by the IIASA group in the frame of the CITYZEN project. This new simulation (Mitig scenario) is now presented in section 3.5, Figures 8 and 9 and Table S5, instead of the highly idealized decentralization scenario. Discussion on transport patterns and chemical regimes, including the competition between NMVOC and NO_2 for OH, has been extended as detailed in the above provided replies as well as the replies to the other reviewers.