Responses to the comments of Reviewer #1

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.

General Comments
This paper presents the results of the impacts of megacity emissions on local and regional air quality in the Eastern Mediterranean during the summer time. Although the paper presents various emission scenarios, unfortunately, it seems to me that it adds nothing new to our current understanding of the influences of anthropogenic and natural emissions on air quality and photochemistry. This is directly related to the fact that the paper presents many modeling results, but no in-depth analyses are unfolded, e.g., many figures are shown without adequate illustrations and discussions. Basically this is just another case for the sensitivity studies of the emission-air quality relationship. In addition, several numbers in the tables and statements are erroneous/inaccurate, as pointed out below. Considerable revisions are needed before it is considered for publication in ACP.

Response: The present modeling study evaluates the impacts of Istanbul and Athens anthropogenic emissions on the Eastern Mediterranean air quality, based on the 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. To our knowledge there is no other such study for the area.
We have improved the presentation and analysis of our results following all reviewer comments as will be detailed further. We have carefully repeated all simulations and calculations and modified/corrected the numbers where necessary throughout the manuscript. We have also added winter simulations to present the differences in seasonal patterns and responses.

Specific Comments

1. The regional air quality effect of emission changes is critically dependent on the meteorology. The authors draw conclusions based on a 26-day (June 20-July 15 2004) simulation study for the summertime air quality issue. This may be a little bit over stretched. Are the meteorological conditions during this simulation period representative of the summer season of that year, and even more, the summer climatology in this region? Such information should be provided in the paper, and the wording in the Abstract and Conclusions should be more specific to eliminate possible confusions.

Response: The meteorological conditions during the studied period represent the characteristics of summertime climatology in the region. We have further added winter time simulations and extended the simulation periods to cover the whole months of interest. Information on the meteorological characteristics of the region in winter and summer conditions is provided together with appropriate references to clearly state that these characteristics are representative of the general patterns in the region (section 2.2):
'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).'
In addition, in the abstract it is now mentioned: 'In the present mesoscale modeling study, the impacts of anthropogenic emissions from the Greater Istanbul Area (GIA) and the Greater Athens Area (GAA) on the air quality in GIA, GAA and the East Mediterranean are quantified for typical wintertime (December 2008) and summertime (July 2008) conditions.'
In the conclusions it is specified: 'In the present study, WRF/CMAQ modeling system, coupled with the MEGAN biogenic emissions model, has been employed to investigate the impacts of East Mediterranean megacity emissions on the air quality of the cities and of the region for typical wintertime (December 2008) and summertime (July 2008) conditions.

2. The regional effects as shown are very small (less than 3% for O3). Because of such small signals, there raises an issue—how accurate are the chemical ICs and BCs in the base case, and are their effects minimized in the simulations? Are they reconsidered when the emissions are changed, especially for the cases of S4 and S5, as these emission scenarios would definitely affect the chemical BCs and ICs (I guess that in all scenarios the CBs and ICs were the same as for S0). When the regional signals are so small, it should be cautious to reach quantitative conclusions, as the noises caused by many uncertain factors (such as meteorology and chemical BCs) could be very high relative to the signals. More discussions on the probable effects of chemical BCs and meteorology on the regional effect are necessary.

Response: We have tested the impacts of initial conditions and boundary conditions for both simulation periods. Because of the use of spin-up period of 11 days for all simulations, the initial conditions do not affect the results of the simulations. The boundary conditions, since they are applied at each time step, are more critical. We have performed additional sensitivity tests (not shown) and evaluated that a 50% change in the boundary conditions leads to around 50% changes in pollutant levels. We have included relevant comments in the middle of section 2.2 and at the end of section 3.3:

In the middle of the section 2.2: 'Thus, initial conditions of pollutants are not critical for the results since a 50% perturbation of these conditions has almost no effect on the results. On the contrary, perturbation by 50% of the boundary conditions of the pollutants leads to around 50% change in pollutant levels (tests not shown).'

At the end of section 3.3 we further comment: 'These contributions are comparable with the impact of boundary conditions for the region (discussed in section 2.2). In particular for O_3 the responses to the boundary condition perturbations (30-50%) are higher than those to the emission perturbations (3-6%), indicating the importance of long range transport for O_3 levels in the region.'

3. Model configuration and performance (Sect 2). The reader is required to read references to check out the relevant information. A paper should be a stand-alone entity. The relevant information should be at least briefly described in the paper.

Response: Section 2 now provides a stand-alone description of the model configuration and emissions (section 2.1). This is supported by i) Table S1 in the supplementary material that summarizes the sectoral contributions to the anthropogenic emissions of the major pollutants in GIA and GAA for winter and summer, ii) Table 1 that summarizes the anthropogenic and biogenic emissions in GIA, GAA and the model domain for winter and summer and iii) Table S2 that provides country-based emission mitigation factors applied for the mitigation scenario. Section 2.3 outlines the observations used for the model evaluation. It is supported by Table S3 that provides information on the sites of the observations and the pollutants that have been measured. As earlier mentioned, we have changed the simulation year from 2004 to 2008 in order to have sufficient observational data to evaluate our model results, particularly for the winter period since year 2004 is lacking observations in most areas of interest. The new section 3.1 presents detailed model evaluation for the winter and summer simulations including aerosol chemical composition.

4. Table 1. I am not able to figure out the NMVOC/NOx ratio numbers listed in the table (1.4, 1.7, 74.2, 76.0) in light of the NMVOC and NOx emission rates provided. These ratios appear to be less than 1.0 in Istanbul and less than 2.0 in Athens in my calculations. In addition, it is stated (p26664, lines11-12) that "only small changes in the NMVOC/NOx molar emission ratios are calculated when biogenic emissions are taken into account". This is contradictive to the fact that the biogenic NMVOCs account for more than one third of the anthropogenic counterpart in Athens, and contradictive to the statement in P 26670 line 20.

Response: We thank the reviewer for the careful reading of the paper and for pointing us this error. We have found miscalculations in these ratios and corrected them throughout the text.

5. P26666 lines 15-19. If the higher O3 levels in Athens relative to Istanbul are due to the elevated background O3 in Athens, then why the O3 level in the Athens rural area (60 ppb) is slightly lower than that in the Istanbul rural area (65 ppb)? Suppose it does, how the 5ppb difference in the background levels accounts for the ~ 30 ppb differences in the two urban areas? Certainly this is not the correct answer. The authors need to do additional analyses to give right explanations in terms of emissions, transport and O3-NOx-VOC nonlinear chemistry. The authors use the CO/NOx ratio as a support for their explanation. Is the CO/NOx ratio really a good indicator for O3 production? I really doubt it.

Response: All simulations have been repeated for the year 2008 due to the observational data availability for model evaluation. These results are reported in the new Table 4 (earlier Table 2). This table shows higher O_3 levels in GAA (Urban, Rural and Extended area) compared to the corresponding regions in GIA for both seasons. The higher O_3 levels in Athens than in Istanbul are due to the elevated background of O_3 in the Athens extended area resulting from higher temperatures and solar fluxes, regional influences and long range transport. They also reflect differences in the NMVOC reactivity between the two cities. To further analyze these patterns the reactivity of NMVOC mixture with respect to OH has been computed as the sum of the products of the rate of reaction of each NMVOC with OH and its computed concentration for all NMVOCs considered in the model. This has been compared to the product of the rate of NO_2 reaction with OH with the computed NO_2 concentration. It is found that in Athens rural areas the NMVOC reactivity is by 10% to 80% higher compared to Istanbul rural areas in winter and summer, respectively. This translates to 2 to 3 times higher ratio of $k_{OH^\cdot}$ [NMVOC]/ $k_{OH^\cdot}[NO_2]$ in Athens than in Istanbul rural areas, showing the larger potential of Athens atmosphere to produce O_3. Similar conclusions can be drawn when also accounting for the CO reactivity with respect to OH. These comments have been added in the second paragraph of section 3.2.

6. P26667 line 3, P26670 lines 25-29, and Table 2. I cannot understand that concentration rations of NMVOC/NOx in Istanbul and Athens differ by nearly a factor of 50, since the ratios in the emissions differ by no more than a factor of 3! These numbers are erroneous. Recheck these numbers, together with those in Table 1.

Response: As above mentioned, the NMVOC/NO_x molar ratios have been recalculated and corrected throughout the text. As reported in the new Table 4, they vary between 1 and 9.1.

7. P26668 lines 3-7. This is interesting. A figure showing the change of the radical concentrations (OH, HO2 or RO2) will be helpful. In principle, OH in general serves as the catalyst in the OH-initiated VOC oxidation, which means that the ultimate OH level is not affected by the addition of VOC. This maybe has something to do with the chemical mechanism used in CMAQ. Some discussions on the mechanism (particularly the biogenic VOC oxidation processes initiated by OH) and the effects of VOC oxidations on OH and other radical levels will add insights to the effect of biogenic VOCs on PM formation.

Response: We have now provided information in the manuscript on the responses of OH and HO_2 in sections 3.3 and 3.4.1. Two extra panels have been added in Figure 6 showing the response of OH levels to the 'no biogenics' scenario. As expected, the wintertime impact of biogenic emissions is small since these emissions are weak in winter. In both seasons, the changes in OH due to the biogenic emissions maximize over land.

It is now commented in section 3.3: 'In particular, the computed increase in the 'NoBiog' case can be attributed to the increase in the domain-mean hydroxyl radical (OH) levels by 1% in winter and 25% in summer (Figures 6e, f), with the largest changes in OH levels computed to occur over land where the emissions take place. Similar conclusions on the role of biogenic emissions and the $PM_{2.5}$ behavior have been pointed out by Im et al. (2012) who investigated the response of $PM_{2.5}$ chemical composition and levels to air temperature increases in the region. The impact of biogenic emissions in winter is negligible. These results agree with the findings from Kiendler-Scharr et al. (2009) that reported decreased aerosol concentrations with increasing isoprene levels, showing that the high reactivity of isoprene with OH leads to suppression of new particle formation. However, although the role of biogenic NMVOC in limiting oxidant levels is established, the magnitude of their effect on OH under low NO_x and high NMVOC conditions remains unknown since recent observations indicate significant OH recycling mechanism under such conditions (Hofzumahaus et al., 2009; Lelieveld et al., 2009).'

Further in Section 3.4.1 (impact of megacities on gases): 'Therefore, in the absence of anthropogenic emissions, NMVOC oxidation in the urban core is enhanced, produces hydroperoxy (HO_2) radicals (an HO_2 increase of 80% in GIA and 30% in GAA) and finally forms O_3.'

8. P26668 lines 25-27 – P26669 lines 1-3. The statements on the effect of the emission reduction on O3 production are not clear, and I am not sure if the NMVOC oxidation would be enhanced in the absence of the anthropogenic emissions in the urban areas. The essence of the emissions on O3 formation in the urban areas is the competition of NOx and NMVOC for OH. There are some classic articles in illustrating O3-VOC-NOx chemistry and the dependence of O3 production on NMVOCs and NOx, such as Sillman et al. (1990), Sillman (1999), Kleinman et al., (1997), Daum et al. (2000), and Lei et al. (2007).

Response: Discussion in section 3.2 has been significantly improved. References to the Finlayson-Pitts and Pitts (2000) textbook and to Lei et al. (2007) have been added. As a follow up of our reply to point 5 of the reviewer, the monthly mean NMVOC reactivities with regard to OH radical have been plotted as a function of the corresponding NO_2 reactivities with regard to OH. Thus, the values for GIA and GAA urban and rural areas for summer and winter and for the 'base' and the 'NoIstAth' cases are shown in a new Figure 5 that is added that is discussed in sections 3.2 and 3.4. This figure clearly shows that Athens has a higher NMVOC reactivity than Istanbul, while Istanbul experiences higher NO_2 levels and NO_2 reactivity than Athens in consistence with the emission patterns shown in Table 1. Overall, for the base case Istanbul has a lower $k_{OH^\cdot}$ [NMVOC]/ $k_{OH^\cdot}[NO_2]$ than Athens (almost half) that combined with the high NO_2 levels in Istanbul favors HNO_3 formation than O_3 formation in Istanbul more than in Athens. When Athens and Istanbul anthropogenic emissions are omitted in the 'NoIstAth' case, the NMVOC reactivity is higher than that of NO_2 in Athens for both seasons whereas in Istanbul this is the case only in summer. In both cities NO_2 levels remain reasonably high (Table S4) to support O_3 formation. Relevant discussion is added in sections 3.2 and 3.4.

9. P266670 lines 19-29. First re-examine the NMVCO/NOx ratios in the concentrations and emissions, which I believe, as pointed out above, are not correct. Add the NMVOC and NOx entries in Table 3 for verification. Second, the authors conclude that the O3 chemistry is VOC-limited in Istanbul through the result of increasing O3 when the anthropogenic emissions are masked. Although I believe the conclusion is right (largely based on the low NMVOC/NOx ratios in the emissions), the analysis is not—the O3 increase in the absence of the anthropogenic emissions is not an indication of the VOC-limited chemistry, which you need to do the sensitivity studies of changing VOC and NOx emissions separately to reach the conclusion.

Response: NMVOC, NOx and NMVOC to NOx molar ratios in the emissions are now correctly reported in Table 1 (earlier Table 2), distinguishing the anthropogenic from the biogenic emissions and the GIA, GAA and domain emissions, both for winter and summer. NMVOC/NOx molar ratios vary between 0.4 and 2.1 for the anthropogenic emissions and between 18 and 65 for the biogenic emissions. NMVOC and NOx concentrations have been added in the new Table 4 that also reports the molar ratios in the concentrations (for summer and winter). The discussion has been modified following all relevant reviewer comments to accommodate both winter and summer simulations (section 3.4.1). (See also replies to earlier points raised by the reviewer).

10. Table 2, add NOx concentrations.

Response: We have added NMVOC and NOx concentrations in the new Table 4.

Label Athens and Istanbul in Fig 2.

Response: This Figure is now Figure 1 and the labels have added as suggested.