Comments on "Summertime impacts of Eastern Mediterranean megacity emissions on air quality" by U. Im and M. Kanakidou

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, i.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.

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.
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.
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.
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.
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 Athen 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 difference 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.

6. P26667 line 3, P26670 lines 25-29, and Table 2. I can not 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.
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.
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).
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.
10. Table 2, add NOx concentrations.

Technical

Label Athens and Istanbul in Fig 2.

References

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