

Interactive comment on “Sensitivity analyses of OH missing sinks over Tokyo metropolitan area in the summer of 2007” by S. Chatani et al.

Anonymous Referee #1

Received and published: 14 September 2009

General comments:

The study focused on the comparison of measured OH reactivity in Tokyo to calculated values. Reactivity calculated using measured ambient NO, NO₂, CO, SO₂, O₃, and speciated VOC concentrations and published reaction rates was about 30% lower than measured value. Reactivity calculated using model predicted ambient concentrations and reaction rates was significantly lower than the measured value since predicted concentrations were much lower than observed ambient data. When scaling factors were used to increase predicted ambient concentrations, calculated reactivity was in much better agreement but still lower than the observed value. The difference between the measured and predicted reactivity is termed as the missing sinks. Model sensitivity studies were conducted to evaluate the impact of the missing sinks on air quality. This is

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a potentially useful study on the evaluation of three dimensional air quality model using OH reactivity and merits publication. However several issues need to be addressed before publication.

Specific comments:

1. Section 2

Page 5, line 7-9: Table 1 shows relationships between the species measured in the observation campaign and the SAPRC99 species which react with OH. Since some of the VOC (ETHENE, OLE1, OLE2, ISOPRENE, TRP1) also reacts with NO₃ and O₃, the statement needs to be clarified.

Page 5, section 2.3: Information on model initial condition and spin-up period is helpful.

2. Section 3

Page 5, line 19-20: Observation campaign was conducted from August 21 to 27. However, data obtained only on August 21, 22, 26, 27 are used in the study. Reason for not including all data is needed.

Page 5, line 22-24: Some alkenes are known to produce OH by their reactions with O₃. Readers will benefit from a discussion of the effect of such OH production on the measurement of OH reactivity.

Page 6, line 1-2: Rate constant for NO₂ + OH was measured and used in the study. It would be beneficial to readers to know the measured value and any comparison with published data.

Page 6, line 3-5: It appears that calculated OH reactivity was lower than observed value by a factor of about 1.3. Measurements of OH reactivity, concentrations of chemical species that affect OH, as well as published rate constants contain uncertainties. Ren et. al. (Atmospheric Environment, 37, 3627–3637, 2003), measured HO_x and OH reactivity in New York and noted that predicted OH concentrations published in many

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studies were within the combined uncertainty factor of 1.5 while for others predicted OH differed from observed data by more than the uncertainty factor. Is it possible to develop a combined uncertainty factor for OH reactivity for this study? The existence of the missing sink needs to be supported by taking into consideration such uncertainties.

3. Section 4

Page 6, line 30-32: Figure 4 contains secondary species such as O₃ for which there are no emissions. It will help readers to identify chemical species for which scaling factors were applied.

Page 7, line 5-8: HCHO is produced by many chemical reactions and the production of O₃ is also affected by VOC. Thus, ratios of these two species are not expected to be 1.0 as explained in the article. However, the ratio of simulated and measured NO is close to 1.75 in Figure 4 (before scaling); thus a scaling factor of about 0.57 was used. After scaling, the ratio of simulated and measured NO is still about 1.6; reasons for this high value should be clearly explained.

4. Section 5.1

Page 9, line 27-31: Chg-RCHO decreased NO₂ while chg-DCB1 and chg-PROD2 increased NO₂ (Figure 10). Reason for such changes needs explanation. Aerosol NO₃- possibly came from HNO₃ formed via daytime chemistry of NO₂ + OH. It will help readers to explain why NO₃- decreased in all three cases while NO₂ increased in some cases. Reaction of H₂O₂ with SO₂ is more important than the reaction of SO₂ with OH for aerosol SO₄²⁻. The reason for changes in aerosol SO₄²⁻ should be further explained by accounting both H₂O₂ and OH. Daytime BSOA is produced via reactions of biogenic compounds with OH and O₃. Predicted OH decreased while ozone increased; thus a more detailed explanation is needed to explain BSOA changes.

Page 10, line 24-32 and page 11, line 1-5: Chg-ALK5 increased NO₂ while chg-OL2 and chg-ARO2 decreased NO₂ (Figure 13). Reason for such changes needs expla-

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nation. Reasons for changes in aerosol SO₄²⁻ and aerosol NO₃⁻ need further explanation. Reason for the increases in BSOA is given as the increase in organic mass due to ASOA. Predicted OH and O₃ changed which also affected the production of BSOA; more detail explanation is needed. OH decreased with Chg-ALK5 while it increased with chg-OL2 and chg-ARO2; reasons for the increases in OH with chg-OLE2 and chg-ARO2 need further explanation.

5. Summary

Page 11, line 18-23: Emissions appear to be significantly under-estimated and the use of scaling factors enhances the simulated OH reactivity much closer to measured reactivity. Additional measurements are always helpful. The author may recommend the steps that can be taken to improve existing emissions inventory for Tokyo based on the results presented in the article and then state the specific measurements activities that are needed in the future to further improve the emissions inventory.

6. Figures

Figure 2 and 7 Measured and calculated total OH reactivity are presented in Figure 2. Calculated OH reactivity was obtained from measured concentrations and reaction rate coefficients of the measured species on August 21. Measured and simulated OH reactivity of species groups are presented in Figure 7. It appears that measured OH reactivity in Figure 7 was obtained from measured concentrations and reaction rate coefficients while simulated OH reactivity was obtained from simulated concentrations and reaction rate coefficients. A better terminology is needed to differentiate measured, calculated, and simulated reactivity since it appears that “calculated” total OH reactivity presented in Figure 2 may be the “measured” OH reactivity in Figure 7. If that is not the case, it should be clarified.

Figure 5 It is more appropriate to present AVOC, BVOC and OVOC in ppbC rather than ppb.

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Technical corrections:

Page 4, line 5: The authors may consider re-writing the following sentence “The below describes how to perform simulations” as “Details of the simulation are described below”.

Page 4, line 18: 4 x 4km. Need a space between 4 and km.

Page 7, line 13-14: The authors may consider re-writing the following sentence “Application of scaling factors makes their concentrations closer to the measured ones” as “Application of scaling factors makes their concentrations closer to the measured values”. Similar sentences exist throughout the article.

Page 8, line 16-17: The authors may consider re-writing the following sentence “Coincidence may be achieved between measured and simulated OH reactivity if simulated concentrations of HCHO could be agreed with the measured ones” as “Better agreement may be achieved between measured and simulated OH reactivity if simulated concentrations of HCHO could be agreed with the measured values”.

Page 9, line 19-22: The authors may consider re-writing the following sentences “The OH reactivity is expected to increase by 3.0 s^{-1} , however, the fact is that the OH reactivity increases by more than 3.0 s^{-1} because increased RCHO, DCB1 and PROD2 form species which react with OH in subsequent reactions.” as “The OH reactivity increased by more than 3.0 s^{-1} because increased RCHO, DCB1 and PROD2 form species which react with OH in subsequent reactions”.

Page 10, line 21: The authors may consider deleting the following sentence since reasons are provided in subsequent sentences: “Possible reasons will be discussed later”.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 18479, 2009.

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