Atmos. Chem. Phys. Discuss., 9, C6375–C6384, 2009
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Atmospheric Chemistry and Physics Discussions

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

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Received and published: 30 October 2009

We thank Anonymous Referee #1 for thorough review and comments.

(Referee #1) 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.

(Answer) Some of the VOC react with NO3, O3, and other species in the real atmosphere and simulations. However, they exclusively react with OH in the reaction tube because concentration of generated OH is much higher than other reactants. Therefore, interference by reactions with other reactants can be ignored. This explanation

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will be added after description of the experimental setup in section 3.

(Referee #1) Page 5, section 2.3: Information on model initial condition and spin-up period is helpful.

(Answer) The default datasets provided with CMAQ are used as initial concentrations in all domains and boundary concentrations in East Asia domain. Simulations are started one month before the observation campaign as a spin-up period to eliminate influence of initial concentrations. This explanation will be added.

(Referee #1) 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.

(Answer) The description was a bit inappropriate. An observation campaign has been conducted from August 21 to 29, not to 27. However, OH reactivity and VOC concentrations were measured during daytime of August 21, 22, 23, 26 and 27. Wind direction was consistently southerly but changed to north-westerly only on August 23. In order to avoid influences of different wind directions, data obtained on during daytime of August 21, 22, 26 and 27 are used. The original description will be corrected and explanation will be added.

(Referee #1) 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.

(Answer) The answer to this comment is the same as the first comment. Concentration of generated OH is high and reactions with other species including O3 and subsequent OH production can be ignored.

(Referee #1) 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.

ACPD

9, C6375–C6384, 2009

(Answer) The rate coefficient for the NO2+OH reaction has large uncertainty. Sadanaga et al. (2004) mentioned discrepancy in it among major databases and its importance for evaluation of OH reactivity. Then, Sadanaga et al. (2005) measured the rate coefficient for the NO2+OH reaction under the atmospheric pressure. This value is used in this study. These explanations and two references will be added, but detailed discussion will be left to these references.

(Referee #1) 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 HOx and OH reactivity in New York and noted that predicted OH concentrations published in many 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.

(Answer) Detailed analyses of uncertainties in the measurement are out of the target of this study. Yoshino et al. (2006) has concluded that missing sinks which were derived from the same instrumental setup cannot be explained by uncertainties. They showed clear seasonal dependence in which missing sinks became negligible in winter. It implies that missing sinks are related to photochemical activities, not to systematic uncertainties. In addition, influences of missing sinks must be evaluated even if some uncertainties are contained. They can be recognized as one of uncertainties in simulation results caused by uncertainties in measurements as well as missing sinks which really exist in the atmosphere. They are within the scope of this study. These descriptions will be added. We recognized that Ren et al. (2003) just mentioned that predicted OH concentrations, not reactivity, published in many studies were within the combined uncertainty factor of 1.5. The value 1.5 was not derived from their study and they did

ACPD
9, C6375–C6384, 2009

not indicate that this value is universal for OH reactivity.

(Referee #1) 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.

(Answer) O3 has no emission and scaling factors are applied only to boundary concentration. This explanation will be added. Other species have emissions and scaling factors were applied to emissions and boundary conceentrations.

(Referee #1) 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.

(Answer) The description was not correct for scaling factors applied to NO and NO2. The same scaling factors determined from NOx (NO+NO2) are applied to NO and NO2 to keep ratios of NO and NO2 in NOx emissions. This explanation will be added and NOx will be added in Fig. 4. NO is sensitive to various external factors because NO concentration and its fraction in NOx are low throughout the target period. Relatively small scaling factors determined by NOx are not enough to match NO concentration. In addition, NO is largely affected by O3 in the NO+O3 reaction. This explanation will be also added.

(Referee #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-

ACPD

9, C6375–C6384, 2009

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.

(Answer) The Supplementary material has been prepared to show ratios of other remaining species which are not included in Fig.10 and Fig.13 to make easier to understand reasons. In addition to oxidation by OH, SO42- is produced via the aqueous reaction of SO2 and H2O2, NO3- is produced via oxidation of NO2 to NO3 and N2O5 by O3 and the subsequent heterogeneous reaction with H2O, and ASOA and BSOA are produced via oxidation of precursors by O3 and NO3. H2O2 and NO3 as well as O3 increase in all cases, but SO42-, NO3- ASOA and BSOA decrease. Therefore, oxidation by OH is more influential than reactions with other species in the three cases. NO2 is mainly produced in the NO+O3 reaction, and is oxidized by OH. Production is enhanced by increased O3 and oxidation is suppressed by decreased OH. But in fact, NO2 decreases in the chg-RCHO case and increase only slightly in the chg-DCB1 and chg-PROD2 cases. Peroxy acyl radicals are major products in the RCHO+OH reaction, and they are converted to peroxy acyl nitrates via the reaction with NO2. Their production appears to compensate increase of NO2 especially in the chg-RCHO case. These explanations will be added.

(Referee #1) 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 explanation. 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.

(Answer) It is difficult to identify reasons for increase of ambient OH because concen-

ACPD

9, C6375–C6384, 2009

trations of a lot of species change especially in the chg-ARO2 case as shown in Fig. S2. Therefore, I am sorry but the original sentence “Products from photochemical reactions of OLE2 and ARO2 seem to contribute to the increase in ambient OH” is currently the best answer. Changes of SO42- can be explained clearly by changes of OH and H2O2. The situation is much complicated for NO2 and NO3-. In the chg-ALK5 case, production of NO2 via the NO+O3 reaction is enhanced by increased O3, and conversion of NO2 to NO3- is suppressed by decreased OH. Therefore, NO2 increases but production of organic nitrates diminishes increase of NO2. On the other hand, in the chg-OLE2 and chg-ARO2 cases, conversion of NO2 to NO3- is enhanced by increased OH. However, NO3- decreases in the chg-OLE2 case because influence of production of peroxy acyl nitrates is larger than conversion to NO3-. BSOA is also produced via oxidation of precursors by OH and O3. O3 increase only slightly and OH decreases in the ALK5 case. As a result, TRP1, which is a precursor of BSOA, increases while BSOA increases significantly. Therefore, increase of ASOA appears to be main reasons for significant increase of BSOA.

(Referee #1) 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.

(Answer) Concentrations of individual VOC species reflect strength of emissions from specific sources. They can be used as fingerprints of sources. As shown in Fig.4, ratios of simulated to measured concentrations vary among species. Based on discrepancy between simulated to measured concentrations of individual species groups, overestimated or underestimated VOC sources may be able to be identified. Coupled analyses with the receptor modelling are also desirable. However, databases are not enough to conduct such detailed analyses. Data on VOC emission profiles of vari-

ACPD

9, C6375–C6384, 2009

ous sources as well as ambient concentrations of individual VOC species are scarce in Japan. More measurement data at different places and periods are needed to be collected to contribute to a thorough improvement of the emission inventory. This idea will be added.

(Referee #1) 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.

(Answer) It may have caused confusion. The total value shown as "Measured" in Fig.7 is surely directly measured OH reactivity which corresponds to measured OH reactivity shown in Fig.2. However, contribution of species groups except for missing sinks in measured OH reactivity is obtained from measured concentrations of species and their reaction rate coefficients. OH reactivity of missing sinks in measured OH reactivity is obtained by subtracting sum of OH reactivity of species groups from directly measured OH reactivity. This explanation will be added in the title of Fig.7.

(Referee #1) Figure 5 It is more appropriate to present AVOC, BVOC and OVOC in ppbC rather than ppb.

(Answer) In the simulation, individual VOC species are speciated into surrogate groups as shown in Table 1. Some of surrogate groups contain species which have different number of carbon atoms. Therefore, it is difficult to convert ppb which is used in the simulation to ppbC.

ACPD

9, C6375–C6384, 2009

(Referee #1) 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".

(Answer) I will follow the comment.

(Referee #1) Page 4, line 18: 4 x 4km. Need a space between 4 and km.

(Answer) I will follow the comment.

(Referee #1) 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.

(Answer) I will follow the comment.

(Referee #1) 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".

(Answer) I will follow the comment.

(Referee #1) 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".

(Answer) I will follow the comment.

(Referee #1) Page 10, line 21: The authors may consider deleting the following sen-

ACPD

9, C6375–C6384, 2009

tence since reasons are provided in subsequent sentences: “Possible reasons will be discussed later”.

(Answer) I will follow the comment.

Reference Sadanaga, Y., Yoshino, A., Kato, S., Yoshioka, A., Watanabe, K., Miyakawa, Y., Hayashi, I., Ichikawa, M., Matsumoto, J., Nishiyama, A., Akiyama, N., Kanaya, Y. and Kajii, Y.: The importance of NO2 and volatile organic compounds in the urban air from the viewpoint of the OH reactivity, Geophys. Res. Lett., 31, L08102, doi:10.1029/2004GL019661, 2004. Sadanaga, Y., Kondo, S., Hashimoto, K. and, Kajii, Y.: Measurement of the rate coefficient for the OH + NO2 reaction under the atmospheric pressure: Its humidity dependence, Chem. Phys. Lett., 419, 474-478, 2005.

Please also note the Supplement to this comment.

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

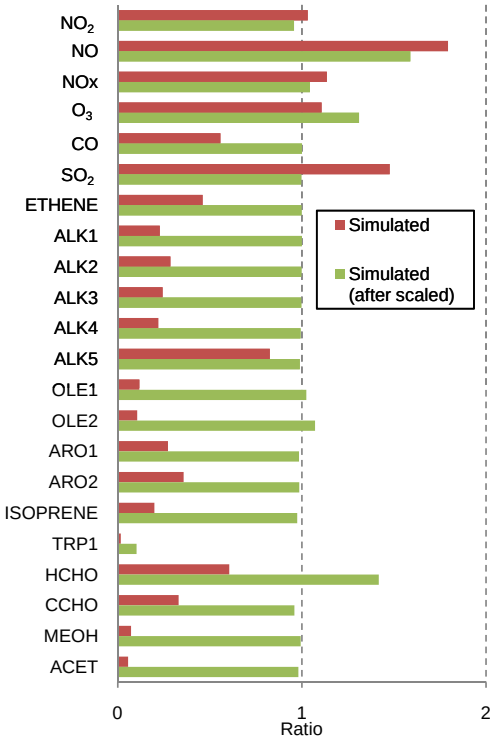

Fig. 1. Corrected Fig. 4

ACPD
9, C6375–C6384, 2009