

Interactive comment on “Impact of a new condensed toluene mechanism on air quality model predictions in the US” by G. Sarwar et al.

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General comments: This manuscript describes the sensitivities of ozone and several PM species to CB05 and CB05 with a new toluene mechanism for western and eastern US. The impact of the new mechanism on RRF and OPE is discussed as well. Since aromatic chemistry is important to ozone and secondary PM formation, this work is an important step and relevant to this journal. The manuscript is generally well written on a scientific base. However, the authors should make at least moderate revisions before it can be considered for publication.

Response: We appreciate the reviewer thoughtful comments to improve the paper. We have carefully reviewed each comment and revised the paper accordingly.

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Specific Comment: Section 2.1, line 27. Why two different years were selected for the simulations for eastern US and western US? Since the two domains give readers a big picture of whole continental US. It will be more interesting to see model result for the two model domains over same time period. Will your conclusions change if you run July 2001 for western US or July 2002 for eastern US?

Response: While we have used two different time periods for the western and eastern US domains, we do not expect our findings to change if we run July 2001 for western US or July 2002 for eastern US. We have added following text in section 2.1:

While the modeling time periods used for the western and eastern US domains are different, findings presented herein are not likely to change if same time period is used for the both domains.

Specific Comment: Section 3.2. In the second paragraph of this section, the authors show day-to-day variation of the increases in daily 8-hr maximum O₃ in 6 cities. However, the description in the text is rather simple and the information I get from this paragraph is no more than that from the first paragraph. For this part, I would expect to see more detailed explanation to the day-to-day variation in at least one city in each model domain. For example, in Los Angeles, why the change in 8-hr O₃ is about 6.5 ppb in day 7 while in day 24, the change is less than 0.5? What's the difference between these two days? This additional information will provide more insights into how the new mechanism will impact on air quality under different conditions.

Response: We have added following text in section 3.2:

While the day-to-day variation in toluene emissions is relatively small, the variation in meteorology affects toluene concentrations and subsequent atmospheric chemistry. Generally, greater toluene levels produce greater increases in ozone.

Specific Comment: Section 3.4. OPE is defined as the slope of a regression between O₃ and NO_z. So the correlation coefficient between O₃ and NO_z is critical. I guess

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at both Los Angeles and Chicago, the correlation coefficient should be low which will make the OPE value less meaningful. So please provide the correlation coefficients where OPE values are discussed. With new mechanism, the OPE value is slightly lower at LA and keeps same at Chicago. But if we look at figure 4(b) and figure 5(b), monthly mean NO_z at both LA and Chicago are increased by about 25% while monthly mean daily 8-h O₃ are increased by less than 2.5% at both sites when new mechanism is used. So that suggests the OPE is actually lower at both sites. I would recommend the authors to replace Figure 4a,b with same plots using mean NO_z from 10:00am-5:00pm. If the new plots are very different to the original ones, this will also indicate that the impact on NO_z is different during daytime than during nighttime.

Response: We have provided correlation coefficients for both LA and Chicago areas. The correlation coefficient is 0.90 in LA and 0.79 in Chicago. It should be noted that OPE values are calculated for multiple grid-cells using only data pairs when O₃/NO_x > 46; this effectively filters for aged air mass.

As suggested, we have replaced Figure 4(a), (b) with a similar Figure prepared using mean NO_z from 10:00 am-5:00 pm. Results did not change substantially (revised Figure 4 attached).

Specific Comment: Section 3.7. The predictions for PM species from base mechanism vary spatially (e.g. western domain vs. eastern domain), so does the difference between the two mechanisms. A discussion/explanation with respect to these spatial variations should make this section more complete and provide more insights. O₃ problem usually only exists during summer time. But PM problem could be more significant during winter month especially in western US, like California. Do the authors have any ideas with regard to the impact of the new mechanism on PM predictions during winter time?

Response: We have included a discussion of the spatial variation of the predictions for PM species from base mechanism as well as the difference between the two mecha-

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nisms. We have also included a discussion on the possible impact of the new mechanism on PM predictions in winter and revised text in section 3.7 as follows:

Monthly mean anthropogenic SOA, biogenic SOA, and in-cloud SOA with CB05-Base and their percent increases between the two mechanisms are shown in Figure 9. Predicted anthropogenic SOA concentrations are greater in eastern US than those in western US. Concentrations over 0.05 ug m⁻³ are predicted over most areas in the eastern US while such levels are predicted only over smaller areas in western US. More anthropogenic VOCs are emitted in eastern US than in western US; consequently SOA derived from these precursors are greater in eastern US. CB05-TU increases anthropogenic SOA by more than 2% in northwestern US, Los Angeles, and northeastern US. Carlton et al. (2010) describes SOA formation mechanisms in CMAQv4.7. In CMAQ, benzene, toluene, and xylene (precursors to anthropogenic SOA) react with OH to produce organic peroxy radicals. These organic peroxy radicals react with NO to produce semi-volatile organic compounds and HO₂ to produce non-volatile SOA. Semi-volatile organic compounds produced via the NO reaction pathway can partition to form SOA. Semi-volatile organic compounds can also form non-volatile oligomers through particle phase-reactions. While the CB05-TU produces more organic peroxy radicals via reactions of VOCs with enhanced OH, increases in SOA via the NO reaction pathway are small since NO also decrease with CB05-TU. Since HO₂ increases with CB05-TU, SOA produced via the HO₂ reaction pathway becomes more important and consequently anthropogenic SOA increases. CB05-TU increases anthropogenic SOA in areas with high levels of anthropogenic SOA precursors and toluene.

Monthly mean biogenic SOA concentrations exceeding 0.4 ug m⁻³ are predicted over the southeastern US while such values are predicted only over a small area covering northern California and southern Oregon. Biogenic SOA precursors are emitted mostly in southeastern US; consequently SOA derived from these precursors are high in southeastern US. CB05-TU increases biogenic SOA by more than 1.0% over a wide area in the southeastern US while increases in western US are generally lower

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than 1.0% and occurs only over small areas. In CMAQ, isoprene, monoterpene, and sesquiterpene are precursors to biogenic SOA. For SOA production from isoprene, only reaction with OH is considered. For SOA production from monoterpene, reactions with OH, O₃, O(3P), and NO₃ are considered. For SOA production from sesquiterpene, reactions with OH, O₃, and NO₃ are considered. These reactions produce semi-volatile organic compounds which partition to form SOA. The semi-volatile organic compounds can also form oligomers through particle phase-reactions. Acid enhanced isoprene SOA is also accounted in the mechanism. Since oxidants increase with CB05-TU, biogenic SOA also increases. Although percent increases in biogenic SOA and anthropogenic SOA are similar, absolute increases of biogenic SOA are much larger. CB05-TU increases biogenic SOA in areas with high levels of biogenic SOA precursors and toluene.

Monthly mean in-cloud SOA concentrations of greater than 0.2 $\mu\text{g m}^{-3}$ are predicted over a large portion of the eastern US while in-cloud SOA concentrations in the western US are generally lower than 0.2 $\mu\text{g m}^{-3}$ and are predicted only over small isolated areas. In-cloud SOA precursors and cloudiness are more frequent in eastern US, thus in-cloud SOA concentrations are higher in eastern US. CB05-TU increases in-cloud SOA by more than 12% over much of the northeastern US while it increases in-cloud SOA by more than 12% only over small isolated areas in western US. Aqueous-phase oxidation of glyoxal and methylglyoxal by OH produce in-cloud SOA (Carlton et al., 2008 and Carlton et al., 2010). Glyoxal is not a chemical species in CB05; therefore only methylglyoxal is used for in-cloud SOA production (Carlton et al., 2010). CB05-TU enhances both methylglyoxal and OH; thus in-cloud SOA increases. CB05-TU increases in-cloud SOA in areas of frequent cloud occurrence and high levels of in-cloud SOA precursors and toluene.

The relative contributions of anthropogenic, biogenic, and in-cloud SOA to total SOA with CB05-TU are compared to those with CB05-Base. The relative contribution of anthropogenic SOA with each mechanism ranges up to 54% in the western US and

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39% in the eastern US. The spatial distribution of the relative contribution of anthropogenic SOA is similar with each mechanism in each domain (the largest difference is 4% in each domain). The relative contribution of biogenic SOA with each mechanism ranges up to 88% in the western US and 80% in the eastern US. The largest difference of the relative contribution of biogenic SOA was 7% in the western and 4% in the eastern US. The highest relative contribution of in-cloud SOA increased from 69% with CB05-Base to 75% with CB05-TU in the western US and from 46% with CB05-Base to 52% with CB05-TU in the eastern US. Thus, the relative contribution of anthropogenic, biogenic, and in-cloud SOA to total SOA did not substantially change between the two mechanisms.

Monthly mean aerosol sulfate, nitrate, ammonium, and total PM_{2.5} with CB05-Base and their percent increases with CB05-TU are shown in Figure 10. CB05-Base predicts relatively low aerosol sulfate (< 1.5 $\mu\text{g m}^{-3}$) over most of the western US compared to relatively high predictions (> 3.0 $\mu\text{g m}^{-3}$) over most of the eastern US. It predicts relatively high aerosol sulfate (> 6.0 $\mu\text{g m}^{-3}$) over the Ohio valley area in the eastern US while similar concentrations are not predicted in the western US. Predicted values reach up to 1.5–4.5 $\mu\text{g m}^{-3}$ only over a small area in the western US. Sulfur dioxide is emitted mostly in eastern US; consequently aerosol sulfate is high in eastern US. CB05-TU increases aerosol sulfate by 0.5–1.5% in small areas in the western US and 0.5–1.0% in small areas in the eastern US. CB05-TU increases aerosol sulfate in areas with high levels of sulfur dioxide and toluene.

Predicted mean aerosol nitrate of greater than 0.8 $\mu\text{g m}^{-3}$ are predicted only over isolated areas in the western US while similar values are predicted over a much larger area in the eastern US. CB05-TU increases aerosol nitrate by more than 2.0% in some isolated areas in the western and larger areas in the eastern US. CMAQ produces aerosol nitrate from the partitioning of HNO₃, which is produced via nighttime homogeneous and heterogeneous hydrolysis of dinitrogen pentoxide as well as daytime production via $\text{NO}_2 + \text{OH} = \text{HNO}_3$. The primary reason for the increase in aerosol nitrate

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is the enhancement of the daytime production of HNO₃.

Mean ammonium concentrations of greater than 1.2 ug m⁻³ are predicted over most of the eastern US while similar concentrations are predicted over only small areas in the western US. The spatial distribution of ammonium with CB05-Base follows to that of aerosol sulfate. CB05-TU increases ammonium over only small isolated areas in both the western and eastern US by 0.5-1.0%. Increases in ammonium concentrations with CB05-TU also follow the pattern of the increases in aerosol sulfate. CB05-Base predicts greater than 10.0 ug m⁻³ of PM_{2.5} in most areas in the eastern US while concentrations are typically lower than 5.0 ug m⁻³ for most of the western US. CB05-TU increases PM_{2.5} by 0.5-2.5% in some areas in the western and 0.5-1.0% in the northeastern US. However, increases over 1.0% occur in only a few isolated areas in the western US where predicted mean PM_{2.5} concentrations are generally lower than 5.0 ug m⁻³.

CB05-TU induced changes in predicted PM concentrations arise primarily from differences in atmospheric oxidant levels. Due to lower actinic flux and temperature in winter, atmospheric chemical reactions proceed at slower rates; consequently atmospheric oxidant levels are lower in winter than in summer. Thus, the impact of CB05-TU on secondary aerosols in winter would likely be less than described here.

Interactive comment on Geosci. Model Dev. Discuss., 3, 2291, 2010.

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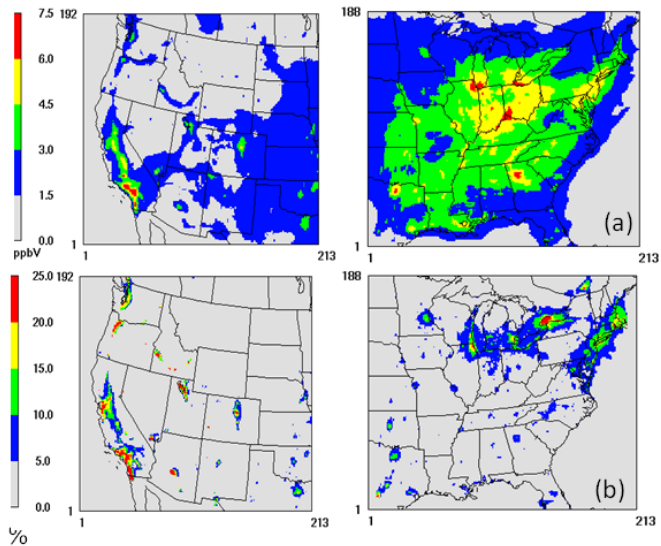


Fig. 1. Revised Figure 4