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Assessing and Improving the Isoprene Oxidation Mechanism

Executive Summary

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COORDINATING RESEARCH COUNCIL, INC.

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EXECUTIVE SUMMARY

The objectives of this project were (1) to improve the representation of isoprene reactions in chemical mechanisms used in photochemical grid models (PGMs), (2) to determine the more important pathways in the isoprene chemistry, and (3) to evaluate the impact of isoprene chemistry and emissions on urban and rural ozone (O_3) formation. We addressed the objectives by reviewing recent studies on isoprene reactions, sensitivity simulations with a three-dimensional (3-D) PGM, and additional sensitivity simulations with a box model. We studied the Carbon Bond version 6, revision 2 (CB6r2) mechanism, the Statewide Air Pollution Research Center 2007 Toxics and Isoprene (S07TIC) mechanism, and a modified CB6r2 mechanism with increased hydroxyl radical (OH) production (CB6r2OH mechanism). For the latter mechanism, the increased OH production comes from the isomerization of the radical (ISO2) formed by OH addition to isoprene and represents the upper limit to OH production by this path suggested in recent literature.

The 3-D simulations focused on central California using the meteorological conditions of July, 2007. Ozone model performance evaluation was conducted for this period, and all three mechanisms gave acceptable performance for maximum daily average 8-hour (MDA8) O_3 relative to measurements (normalized mean bias < $\pm$5%; normalized mean error < 20%). The other 3-D simulations were done with the same meteorology but with emissions projected to 2017. The emissions for the box model were drawn from the 2017 inventory, and the four-day simulations include the wide range of chemical conditions in an air parcel passing through rural, then urban, and then again rural areas. With the box model, we calculated sensitivities to formation of all the products from the isoprene chemistry in the CB6r2, CB6r2OH and S07TIC mechanisms. For products containing nitrogen, we defined and calculated net formation sensitivities that account for both the loss of the nitrogen-containing reactants as well as the formation of the products. This required minor modifications to the Comprehensive Air Quality Model with Extensions (CAMx) that will be included in a future release.

The 3-D O_3 results obtained with the CB6r2 and CB6r2OH mechanisms are very close, as shown in Figure ES-1 for sites at Edison (Kern County) and Cloverdale (Sonoma County). Thus, additional OH formation from the isomerization route within the isoprene chemistry has little effect on O_3 formation for the California domain. The box model results also showed little sensitivity of O_3 to OH formation from any of the routes in the isoprene chemistry of the S07TIC as well as the CB6r2 and CB6r2OH mechanisms. At the current level of OH production in these mechanisms, O_3 is quite insensitive to reasonable changes in the OH production of the isoprene reactions.

The S07TIC mechanism, however, gives MDA8 O_3 predictions larger than those of the CB6r2 mechanism in most areas of California (Figures ES-1, ES-2). We tested whether the difference in concentrations between these mechanisms exceeds the uncertainty due to uncertainties in the emissions inventory, and it does at most locations in the modeling domain. I.e., if the emission inventory for 2017 is altered within the estimated uncertainty limits and the same altered inventory is used with both mechanisms, the S07TIC mechanism will give the greater MDA8 O_3 predictions.

We calculated the sensitivity of O_3 to emissions of anthropogenic NO_x (ANO_x), volatile organic compounds (AVOC), carbon monoxide (ACO), and biogenic isoprene. Where NO_x is abundant, the sensitivities to ANO_x emissions from the CB6r2 and S07TIC mechanisms are similar and mostly negative. Where O_3 formation is NO_x-limited, the sensitivities are positive, and the S07TIC sensitivities are generally larger than the CB6r2 sensitivities (Figure ES-1). The S07TIC and CB6r2 sensitivities to AVOC emissions are either positive or very small and generally closer together than the sensitivities to ANO_x emissions. Ozone sensitivities to ACO emissions are small at all locations, with the S07TIC sensitivities usually smaller than the CB6r2 sensitivities.

An important result is that the O_3 sensitivity to isoprene emissions obtained with the CB6r2 and S07TIC mechanisms is positive at most locations, but negative at some locations, especially when NO_x availability is low (Figures ES-1, ES-2). The S07TIC sensitivity is generally greater than the CB6r2 sensitivity (more positive or less negative). Some studies with other chemical mechanisms have shown a positive sensitivity to isoprene emissions at all locations; other studies found a negative sensitivity at some locations, similar to our results. The negative sensitivity can arise from several pathways in the chemistry. The direct pathway is the loss of O_3 by reaction with isoprene or products of isoprene degradation. An indirect pathway is the nighttime reaction of isoprene and its products with the nitrate (NO_3) radical, which leads to formation of organic nitrates (ONs) and also removes O_3 because O_3 is needed to make NO_3. The other indirect pathway is the formation of ONs from daytime reactions. There appears to be a delicate balance between O_3 formation and O_3 destruction and/or suppression from the isoprene chemistry in low-NO_x environments.

We also tested whether the sensitivity of O_3 to ANO_x emissions and to isoprene emissions is significantly different between the S07TIC and CB6r2 mechanisms, considering the uncertainty in the emissions inventory. The sensitivity of O_3 to ANO_x emissions is significantly different between the mechanisms primarily in central and northern California. Also, the sensitivity of O_3 to isoprene emissions is significantly different between the mechanisms in southern California.

The July maximum MDA8 O_3 predicted for 2017 exceeds the new U.S. 8-h O_3 standard of 70 ppb across a large region of California (Figure ES-2), indicating that anthropogenic emissions must be significantly less than the projected 2017 emissions to achieve compliance with the standard. In

most of this region, O_3 formation is NO_x-limited. The exceptions occur in some urban areas where the sensitivity to ANO_x emissions is negative in at least part of the area, and O_3 formation is VOC-limited there.

The S07TIC isoprene chemistry is more detailed and has about 4 times more reactions than the CB6r2 chemistry, involving 65% more species and producing 70% more products. The added S07TIC detail does not give O_3 predictions or sensitivities to emissions that are very different from those of the simpler CB6r2 mechanism. Also, the box-model simulations showed that the S07TIC isoprene chemistry has more products that have little impact on O_3 formation than does the CB6r2 chemistry. The greater detail in the S07TIC isoprene chemistry and in the chemistry of other VOCs causes the computational time for 3-D concentrations to be 43% greater for the S07TIC mechanism than the CB6r2 mechanism and the time for sensitivities to be a factor of 3 greater. The added detail in the S07TIC chemistry may be important to the prediction of toxics or other secondary species but can limit the use of the mechanism for O_3 studies. Condensing a chemical mechanism through the use of product formation sensitivities and other techniques enhances the applicability of the mechanism for 3-D simulations.

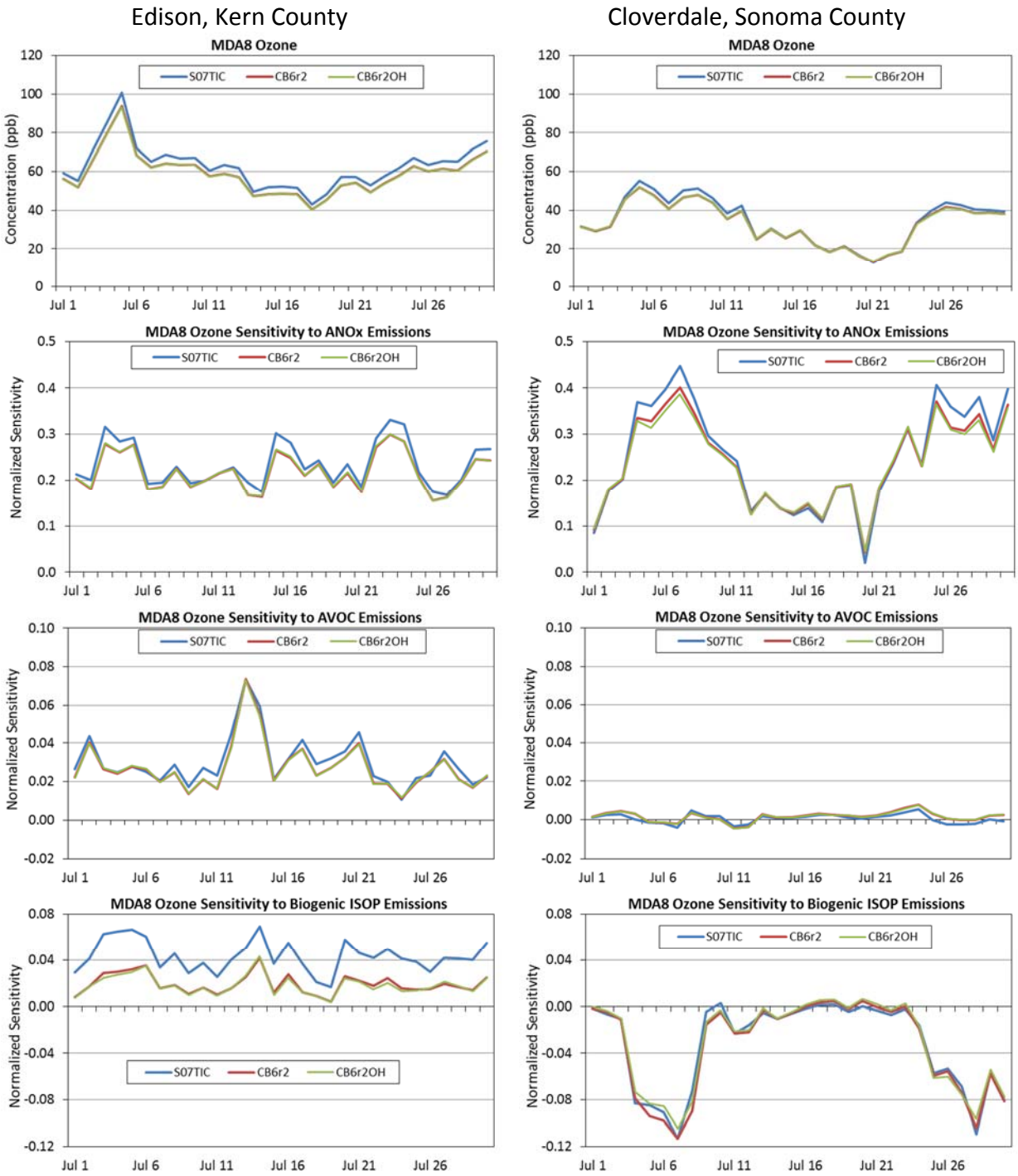

Figure ES-1. July MDA8 O_3 and normalized sensitivity of MDA8 O_3 to anthropogenic NO_x and VOC emissions in 2017 and biogenic isoprene emissions at the Edison and Cloverdale sites. The normalized sensitivity is the sensitivity divided by the O_3 concentration.

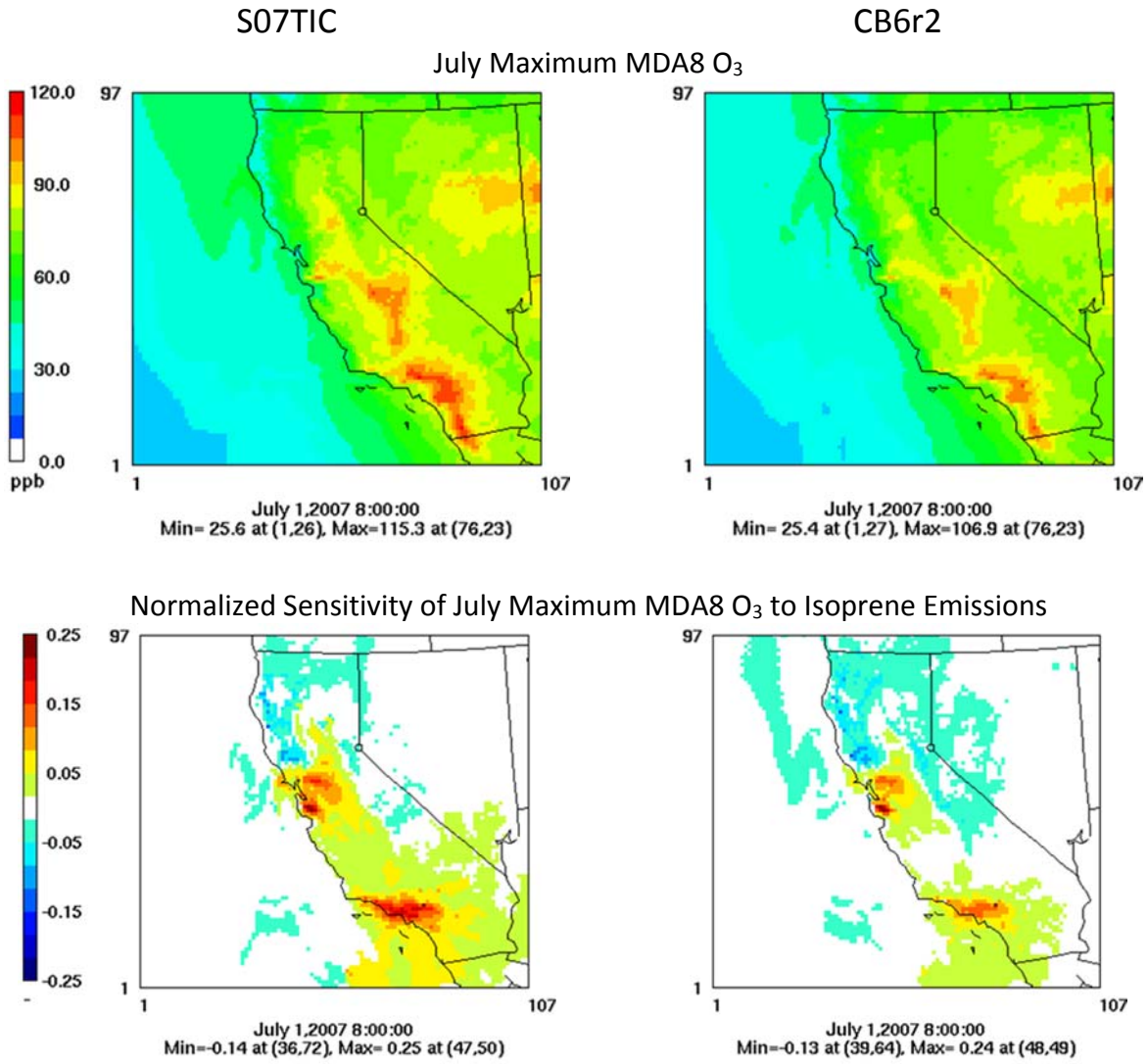

Figure ES-2. July maximum MDA8 O_3 concentrations from the S07TIC and CB6r2 mechanisms using emissions for 2017 and the normalized sensitivity of O_3 to the biogenic isoprene emissions.