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Ozone sensitivity to isoprene chemistry and emissions and anthropogenic emissions in central California

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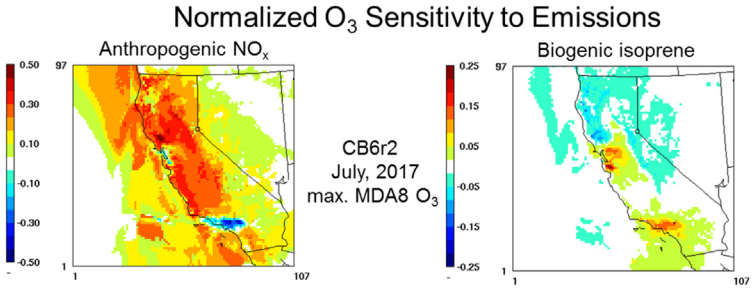
HIGHLIGHTS

- The isoprene chemistry in two recent condensed chemical mechanisms is compared.
- Additional OH production in the isoprene chemistry has little effect on ozone.
- Ozone has both positive and negative sensitivities to isoprene emissions.
- The extent to which organic nitrates from isoprene recycle to NO_x affects ozone.
- Effects of uncertainties in anthropogenic and isoprene emissions are evaluated.

GRAPHICAL ABSTRACT



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ABSTRACT

Ozone formation in California in year 2017 was simulated using three chemical mechanisms: the Statewide Air Pollution Research Center 2007 mechanism with updated toxics and isoprene chemistry (S07TIC); the Carbon Bond 6, revision 2 (CB6r2) mechanism; a modified CB6r2 mechanism with increased hydroxyl radical (OH) production from isoprene oxidation at low nitrogen oxide (NO_x) concentrations (CB6r2OH). The simulations with a photochemical grid model (PGM) showed little difference in ozone between CB6r2 and CB6r2OH. Further analysis with a box model found little sensitivity of ozone to OH production in the isoprene chemistry of all three mechanisms under conditions representative of California. The S07TIC generally predicts greater ozone than the CB6r2, and the difference in the predicted concentrations exceeds the uncertainty estimated from uncertainties in the emissions inventory. The sensitivity of ozone to anthropogenic volatile organic compound (VOC), NO_x and carbon monoxide (CO) emissions and to isoprene emissions was also calculated with the PGM. Accounting for uncertainties in the emissions inventory, the sensitivity to NO_x emissions is significantly different between S07TIC and CB6r2 in central and northern California; the sensitivity to isoprene emissions is significantly different in southern California. All mechanisms give a negative sensitivity of ozone to isoprene emissions in areas of northern California where NO_x emissions are small. The CB6r2 and S07TIC differ in the sensitivity of ozone to organic nitrate (ON) formation from isoprene oxidation, likely because all ONs recycle to NO_x in the S07TIC mechanism but only first-generation ONs do so in the CB6r2. For current California conditions, uncertainties in OH production from isoprene have little impact on ozone, but the extent to which isoprene ONs recycle NO_x does impact ozone concentration and ozone sensitivity to NO_x emissions.

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1. Introduction

Isoprene is a volatile organic compound (VOC) emitted in large amounts by vegetation (Guenther et al., 2006), and the emissions are thus essentially uncontrollable. It is also very reactive with ozone (O_3), the hydroxyl radical (OH), and the nitrate radical (NO_3) due to the presence of two carbon double bonds (Calvert et al., 2015). In rural areas, oxidation of isoprene generally dominates the formation of O_3, both because of its abundance and reactivity. However, isoprene chemistry also influences O_3 formation in urban atmospheres (Dunker et al., 2014). Isoprene chemistry will become even more important as states design emission-control strategies to meet the more stringent U.S. 8-h O_3 standard of 70 ppb and anthropogenic VOC emissions are reduced. Errors in estimating O_3 formation from isoprene will have a direct impact on the magnitude and type of anthropogenic emission controls that are projected to achieve attainment of the standard.

Isoprene chemistry has been the focus of numerous studies over the past 5 years, some of which are Crounse et al. (2011), Fuchs et al. (2013), Jacobs et al. (2013), Lelieveld et al. (2008), Paulot et al. (2009), Peeters et al. (2009), Peeters and Müller (2010), and Peeters et al. (2014). This information was used to create the isoprene chemistry in the Master Chemical Mechanism (MCM) version 3.3.1 (Jenkin et al., 2015). In particular, these studies improved how isoprene mechanisms represent OH production at low NO_x and organic nitrate (ON) production, which is a sink for NO_x. Other studies considered the fate of ONs, including heterogeneous chemistry, and the extent to which ONs can return NO_x (Ruiz and Yarwood, 2013; Fisher et al., 2016). The MCM is too detailed to use routinely in photochemical grid models (PGMs). A condensed mechanism that can be used in PGMs, the Carbon Bond version 6 mechanism, was updated to include the new information available in 2013, creating the Carbon Bond version 6, revision 2 (CB6r2) mechanism (Yarwood et al., 2012; Ruiz and Yarwood, 2013). Similarly, the Statewide Air Pollution Research Center (SAPRC) version 2007 mechanism (Carter, 2010; Hutzell et al., 2012), also a condensed mechanism, was revised to incorporate results from some of the recent studies on isoprene chemistry (Xie et al., 2013). This mechanism is called here the SAPRC 2007 Toxics, Isoprene Chemistry (S07TIC) mechanism.

Because the CB6r2 and S07TIC mechanisms are both used in PGMs for regulatory applications, an important question is whether they give similar O_3 predictions with the updated isoprene chemistry and similar sensitivities of O_3 to anthropogenic and isoprene emissions. Also, while these mechanisms include the generally accepted updates to the isoprene chemistry, there is a proposal that OH production from isoprene is greater than what is included in the mechanisms (Peeters et al., 2013). The sensitivity of O_3 to such increased OH production is thus of interest. Further, determining which products of isoprene oxidation are most important for O_3 formation provides an understanding of similarities and differences between the mechanisms and areas where future work might be focused. These topics are addressed in this study.

We apply the Community Multi-scale Air Quality (CMAQ) model (Byun and Schere, 2006) to simulate summer O_3 formation in central California using the S07TIC and CB6r2 mechanisms and a modified CB6r2 mechanism. We compare the O_3 predictions of the mechanisms and the sensitivities of O_3 to emissions of anthropogenic volatile organic compounds (AVOC), anthropogenic nitrogen oxides (ANO_x), anthropogenic CO (ACO), and isoprene. ($NO_x = NO + NO_2$.) Also, the sensitivity of O_3 to the products formed in the isoprene chemistry is explored using a box model implemented in the Comprehensive Air Quality Model with Extensions (CAMx; ENVIRON, 2015). The next section describes the modifications to the CB6r2 mechanism to increase OH formation, the calculation of sensitivities to product formation, and the inputs for the CMAQ and box models. The following section contains the model performance evaluation for the CB6r2, S07TIC, and modified CB6r2 mechanisms, O_3 predictions for 2017 from CMAQ for the 3 mechanisms along with the sensitivity of O_3 to emissions, and the sensitivity analysis with the box model. Lastly, we summarize our conclusions and give some recommendations.

2. Methods

2.1. Isoprene chemistry

The isoprene chemistry in the CB6r2 and S07TIC mechanisms is structurally sound, i.e., it contains the major pathways that operate at high and low NO_x, during day and night. We define the isoprene chemistry in CB6r2 and S07TIC to be those reactions for which at least one reactant can be traced back to isoprene and isoprene alone. With this definition, the CB6r2 isoprene chemistry consists of 22 reactions involving 38 species with 34 products formed. The S07TIC isoprene chemistry is more detailed and contains 86 reactions involving 63 species with 58 products formed. (The CB6r2 and S07TIC isoprene reactions and products are listed in the SI.) This isoprene chemistry, however, is greatly condensed compared to that in the MCM v3.3.1, which contains 1926 reactions involving 602 species.

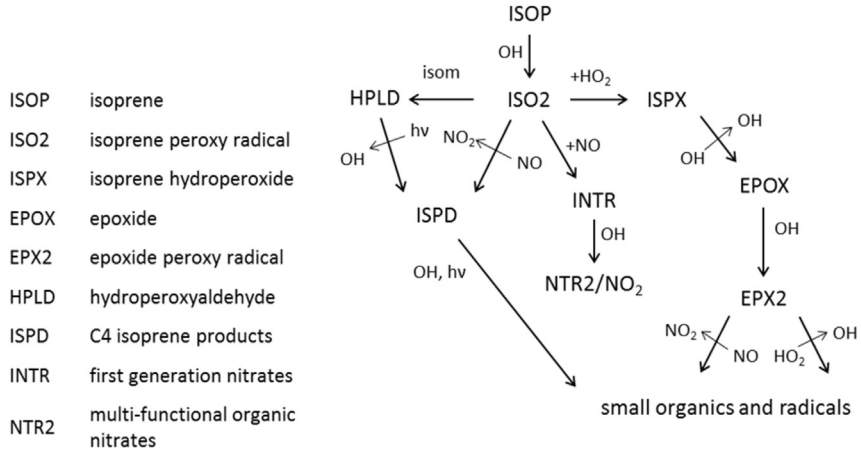

Fig. 1. Main features of the CB6r2 isoprene chemistry for the path beginning with OH addition to isoprene.