



## Biogenic 2-methyl-3-buten-2-ol increases regional ozone and HO<sub>x</sub> sources

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Received 25 May 2007; accepted 5 July 2007; published 8 August 2007.

[1] We present the first regional-scale chemistry simulation investigating the effects of biogenic 2-methyl-3-buten-2-ol (MBO) emissions on air quality. In a central California model domain, MBO emissions have a distinctly different regional pattern than isoprene but have similar daily maxima of about  $5 \text{ mg m}^{-2} \text{ hr}^{-1}$ . MBO oxidation causes an increase in ozone, formaldehyde, acetone and consequently hydrogen radical production (PHO<sub>x</sub>). The addition of MBO increases the daily maximum ozone as much as 3 ppb near source regions (2–5% in rural areas) and as much as 1 ppb in the Central Valley. Formaldehyde concentrations increase by as much as 1 ppb (40%) over the Sierra Nevada Mountains, increasing the production of HO<sub>x</sub> by 10–20% and accelerating local chemistry. This indicates that inclusion of MBO and other biogenic oxygenated emissions in regional simulations in the western and southeastern United States is essential for accurate representation of ozone and HO<sub>x</sub>. **Citation:** Steiner, A. L., S. Tonse, R. C. Cohen, A. H. Goldstein, and R. A. Harley (2007), Biogenic 2-methyl-3-buten-2-ol increases regional ozone and HO<sub>x</sub> sources, *Geophys. Res. Lett.*, 34, L15806, doi:10.1029/2007GL030802.

### 1. Introduction

[2] Volatile organic compounds (VOCs) from both biogenic and anthropogenic sources react in the atmosphere, promoting the formation of ground level ozone and organic aerosols. Current chemical transport models typically consider two dominant biogenic categories, isoprene and monoterpenes, due to their high reactivity and large quantity of emissions [Geron *et al.*, 1994; Guenther *et al.*, 1995; Guenther *et al.*, 2006]. Biogenic oxygenated species have traditionally played a minor role and, if included in models, are often lumped into a generic “other VOC” emission category (e.g., the GEIA inventory based on Guenther *et al.* [1995]). However, studies over the past decade have demonstrated high rates of primary biogenic emissions of

oxygenated compounds [Koenig *et al.*, 1995; Kirstine *et al.*, 1998; Warneke *et al.*, 1999, 2002; Schade and Goldstein, 2001]. These oxygenated compounds, including acetone, aldehydes, ketones and alcohols, can be emitted from vegetation under a wide variety of conditions [Kesselmeier and Staudt, 1999; Fall, 2003, and references therein].

[3] One oxygenated VOC, 2-methyl-3-buten-2-ol (MBO), is known to be emitted in significant quantities from vegetation. Goldan *et al.* [1993] first noted high ambient concentrations of MBO in the Colorado Rocky Mountains and deduced that these concentrations were biogenic in origin. Subsequent studies confirmed the presence and magnitude of MBO emissions, and emission factors have been determined for a variety of pine species [Harley *et al.*, 1998; Lamanna and Goldstein, 1999; Baker *et al.*, 1999; Schade *et al.*, 2000; Gray *et al.*, 2003]. MBO is one of the dominant biogenic VOC emitted from pine species in western North America [Schade and Goldstein, 2001], and some species in the southeastern US and in Scandinavia have also been observed to emit MBO [Harley *et al.*, 1998; Tarvainen *et al.*, 2005]. These leaf and canopy scale studies show that MBO can be emitted in quantities that rival isoprene, indicating their potential importance in geographic regions where MBO-emitting pine trees dominate ecosystems.

[4] Once emitted to the atmosphere, MBO reacts with OH and NO<sub>3</sub> radicals and with O<sub>3</sub>. Locally, MBO can account for a significant portion of the OH reactivity. For example, up to 20% of the summer daytime total VOC reactivity at the Blodgett Forest Research Station in the Sierra Nevada Mountains is due to MBO oxidation [Lamanna and Goldstein, 1999]. Known products of MBO oxidation include acetone, aldehydes, HO<sub>x</sub> radicals, and organic nitrates. Reaction with OH has a ~60% yield of acetone [Alvarado *et al.*, 1999], a longer-lived species that can be transported globally within the troposphere where it contributes to HO<sub>x</sub> production and PAN formation [Singh *et al.*, 1995; Wennberg *et al.*, 1998]. Oxidation of MBO is estimated to contribute to 1–2% to the global acetone budget [Jacob *et al.*, 2002], and about 20% to the regional budget in the Sierra Nevada Mountains during the summer [Goldstein and Schade, 2000]. However, MBO emissions and the subsequent chemistry are generally not included in atmospheric chemical transport models, and to date there are no systematic studies that examine the impact of this oxygenated VOC on regional chemistry and ozone formation. Here, we investigate these emissions and the resulting chemistry over central California in a domain extending from the Pacific Ocean to Nevada and from approximately

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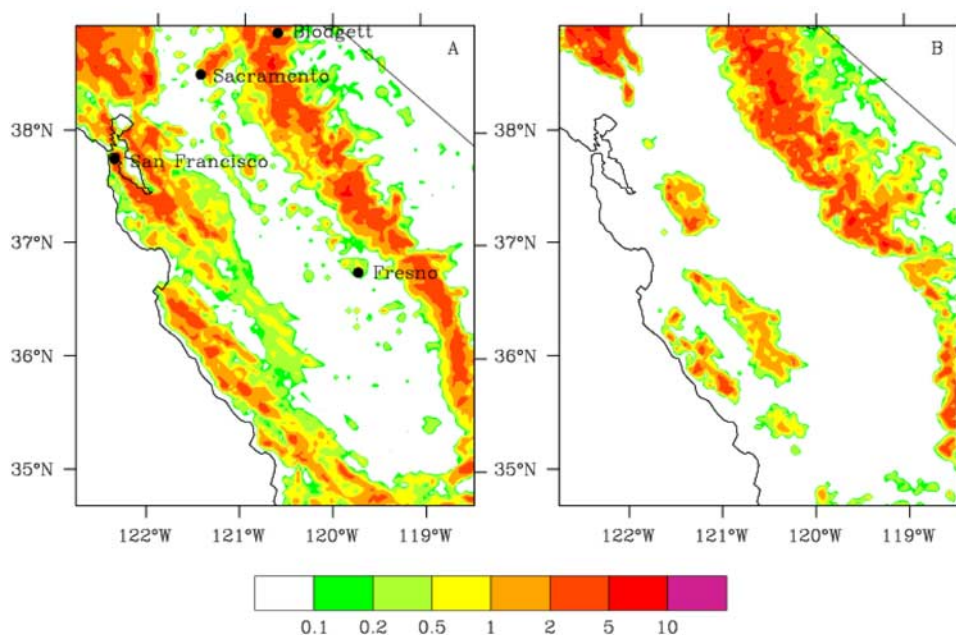
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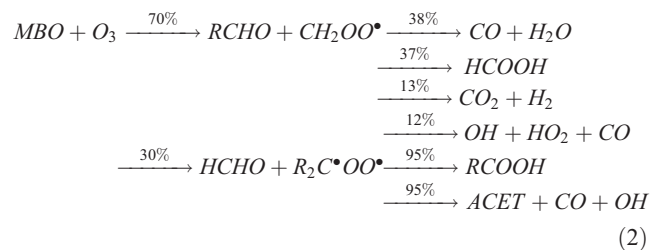
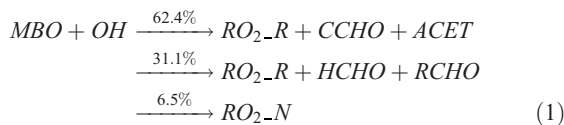


**Figure 1.** Average daily maximum emissions of (a) isoprene ( $\text{mg isoprene m}^{-2} \text{ hr}^{-1}$ ) and (b) MBO ( $\text{mg MBO m}^{-2} \text{ hr}^{-1}$ ).

34 to 39°N. This region includes a large area where MBO-emitting trees dominate the landscape.

## 2. Methods

[5] We use a three-dimensional air quality model (the Community Multi-scale Air Quality Model (CMAQ) [Byun and Ching, 1999] to simulate an ozone episode in the summer of 2000. Full model simulation details are presented by Steiner *et al.* [2006]. We modify the CMAQ SAPRC99 mechanism [Carter, 2000] to include biogenic MBO chemistry. During the daytime, reactions with OH ( $k(300\text{K}) = 6.26 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ) and O<sub>3</sub> ( $k(300\text{K}) = 9.30 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ) dominate with the following product yields [Alvarado *et al.*, 1999]:

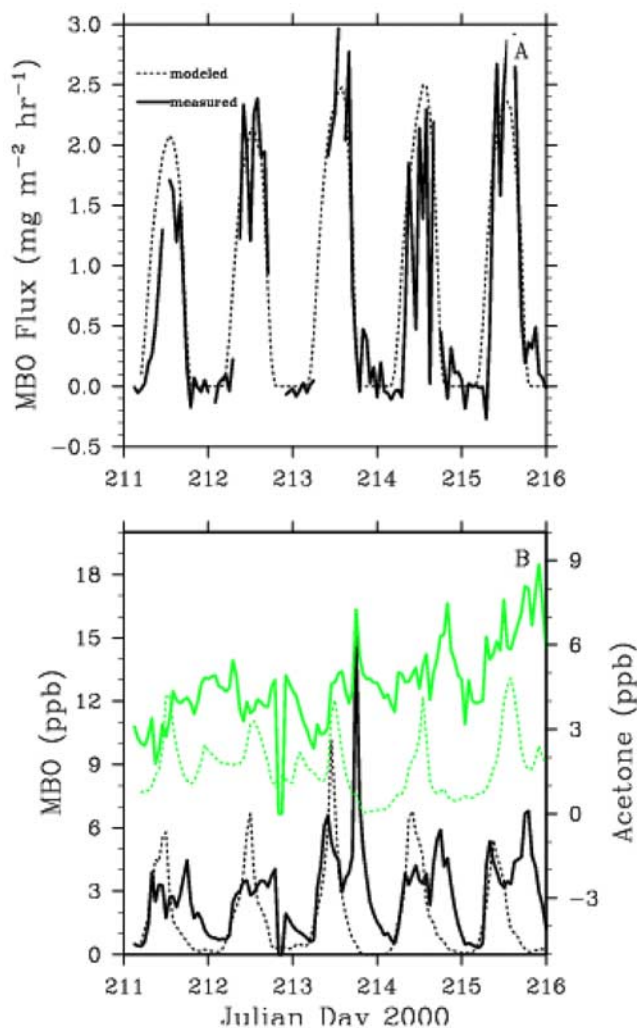


where RO<sub>2</sub>\_R represents RO<sub>2</sub> radicals that undergo a NO-to-NO<sub>2</sub> conversion and RO<sub>2</sub>\_N represent RO<sub>2</sub> radicals that react with NO to form organic nitrates. Additionally, both RO<sub>2</sub>\_R and RO<sub>2</sub>\_N react with HO<sub>2</sub> or other RO<sub>2</sub> radicals to

form peroxides under low-NO<sub>x</sub> conditions. HCHO, CCHO, and RCHO are formaldehyde, acetaldehyde and higher aldehydes, respectively, where the MBO oxidation product 2-hydroxy-2-methyl-propanal is represented in the model as RCHO. Explicit species include carbon monoxide (CO), acetone (ACET) and formic acid (HCOOH), and lumped species include higher order organic acids (RCOOH). CH<sub>2</sub>OO and R<sub>2</sub>COO represent Criegee biradical intermediates that quickly decompose to the stable products detailed above.

[6] Biogenic MBO emissions, along with isoprene and monoterpenes, are modeled offline with a modified version of BEIGIS [Scott and Benjamin, 2003]. Emission fluxes are calculated as the product of a biogenic VOC emission factor, an estimate of the amount of foliar biomass, and the temporal effect of light and/or temperature [Guenther *et al.*, 1995]. A detailed land cover database [Davis *et al.*, 1998] provides the spatial distribution of plant species in California, which determines the appropriate biogenic VOC emission factors and foliar density. In the model domain, there are six different species of pine trees that emit MBO with emission factors ranging from 5 to 71  $\mu\text{g C g}^{-1} \text{ hr}^{-1}$ , and the dominant pine species (ponderosa pine) has an emission factor of 25  $\mu\text{g C g}^{-1} \text{ hr}^{-1}$  [Harley *et al.*, 1998]. All other species are assumed to be non-emitters. Isoprene and MBO emissions are modeled as a function of both light and temperature, while monoterpene emissions are temperature-dependent only. Instantaneous MBO light and temperature dependencies are based on the parameterizations developed by Harley *et al.* [1998], and longer-term impacts of other environmental variables here such as temperature and light history, water stress, or needle age are not included [Gray *et al.*, 2003; Gray *et al.*, 2005].

[7] Two simulations are performed for this study: one with biogenic fluxes of isoprene and monoterpenes only (MBO emissions are zero), and the second including all three biogenic species (MBO, isoprene and terpenes). Both



**Figure 2.** Comparison of measured (solid line) and modeled (dashed line) (a) MBO fluxes ( $\text{mg MBO m}^{-2} \text{hr}^{-1}$ ) and (b) MBO concentrations (ppb, black, left axis) and acetone concentrations (ppb, green, right axis) during the simulation time period (29 July–2 August 2000) at the Blodgett Forest Research Station site ( $38.9^{\circ}\text{N}$ ,  $120.6^{\circ}\text{W}$ ).

simulations include anthropogenic emissions of VOC, CO and NO<sub>x</sub> emissions, as detailed by Steiner *et al.* [2006]. Here we compare the change in near-surface trace gas concentrations and chemical production rates at the time of the daily ozone maximum in the model domain, which occurs at approximately 3PM local time.

### 3. Results and discussion

[8] In the central California model domain, isoprene and MBO emissions are similar in magnitude but have different spatial patterns (Figure 1). High isoprene emissions occur from oak trees forming a ring around the Central Valley, with a particularly dense population stretching along the foothills of the Sierra Nevada Mountains. MBO is emitted from pine trees which dominate the landscape at slightly

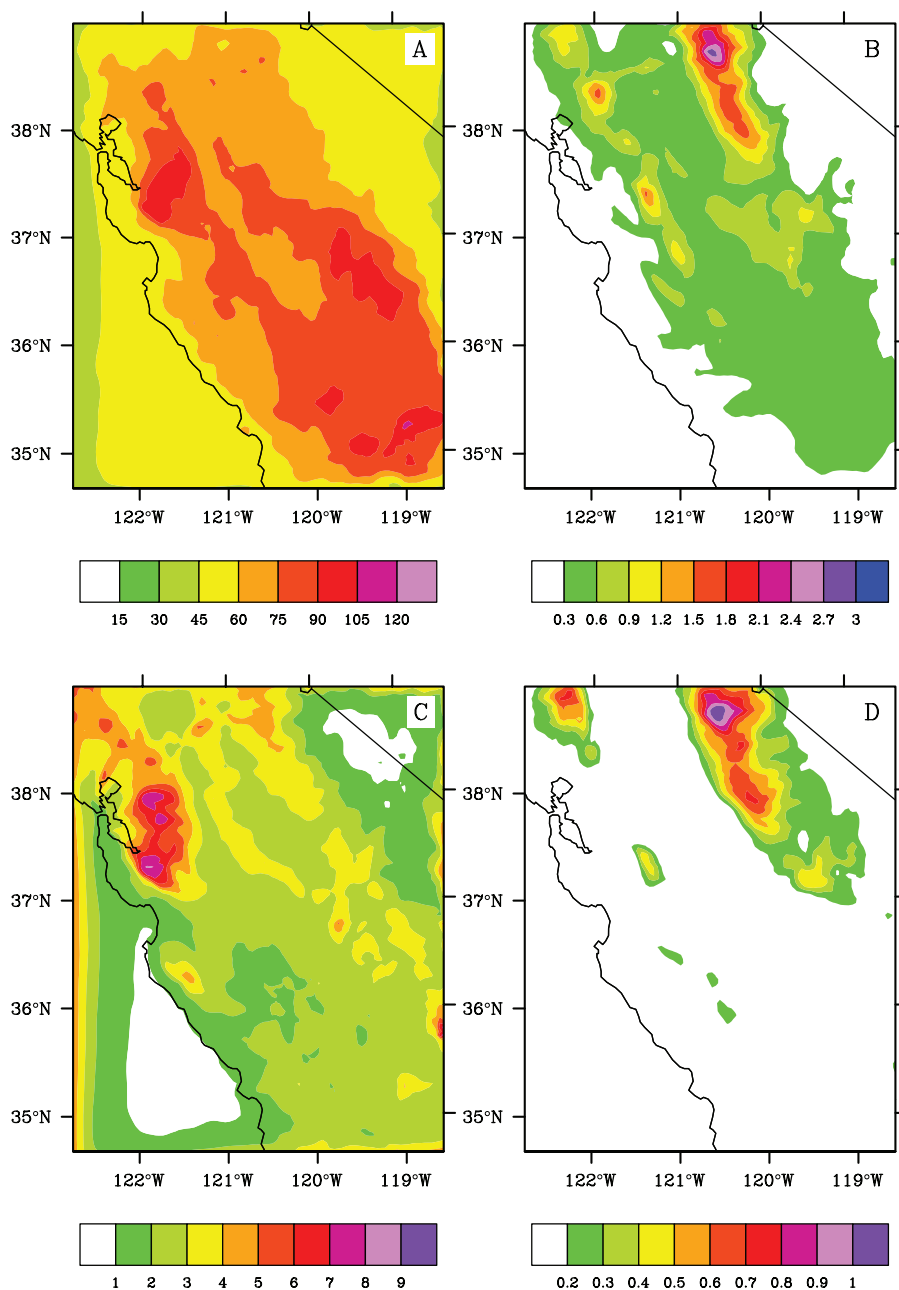
higher elevations. Average afternoon peak fluxes reach approximately  $5 \text{ mg m}^{-2} \text{hr}^{-1}$  for both isoprene and MBO.

[9] Modeled emission fluxes are validated by comparison with ecosystem scale flux measurements made during the summer of 2000 at the Blodgett Forest Research Station in the Sierra Nevada Mountains (location marked in Figure 1) [Schade *et al.*, 2000]. Measured MBO fluxes have a strong diurnal cycle due to the light and temperature dependency of emissions, and the peak measured MBO flux during the modeled period ranges from  $2\text{--}3 \text{ mg MBO m}^{-2} \text{hr}^{-1}$  (Figure 2a). Measured fluxes agree well with the model and are typically within 20% of the modeled fluxes. Measured and modeled MBO concentrations at Blodgett Forest are more variable, with the model typically predicting an earlier and higher daily maximum concentration (Figure 2b) and the measurements showing a second concentration peak at the end of the day. These differences between the model and the measurements likely result from improper representations of the oxidation or dilution rates near the surface, particularly during the late afternoon when stable conditions occur and the wind shifts direction from the daytime upslope flow to the nighttime downslope flow.

[10] When MBO emissions are added to the model, they react with oxidants to form aldehydes, acetone, HO<sub>x</sub> radicals, organic nitrates, and other products (equations 1 and 2). OH reactions dominate MBO loss at a rate of  $1\text{--}2 \text{ ppb hr}^{-1}$  near source regions, followed by reactions with ozone at  $0.1\text{--}0.2 \text{ ppb hr}^{-1}$ . NO<sub>x</sub> concentrations tend to decrease from west to east in the model domain, with a maximum of  $\sim 20 \text{ ppb}$  near urban areas decreasing to less than  $1 \text{ ppb}$  in the Sierra Nevada Mountains. As a result of this gradient, NO<sub>x</sub> is slightly higher in the isoprene emissions belt ( $0.3\text{--}1 \text{ ppb}$  in the afternoon) than in the MBO-emitting pine region ( $<0.3 \text{ ppb NO}_x$ ). MBO emissions increase ozone concentrations by about 3 ppb at 3PM in the MBO source region, corresponding to a  $\sim 3\%$  increase during the peak ozone time period (Figures 3a and 3b). As a result of transport of MBO oxidation products, MBO emissions impact ozone on a broader spatial scale, increasing O<sub>3</sub> by as much as 1 ppb throughout the Central Valley. This effect on the Central Valley is likely due to two factors: (1) the nocturnal drainage of air from the Sierra Nevada to the Central Valley, and (2) the mountain-valley counter flow aloft with subsequent downward mixing. The time scale of these processes is too long for the direct transport of MBO, but these processes can transport O<sub>3</sub> and other longer-lived oxidation products that contribute to HO<sub>x</sub> sources and sinks in the Central Valley. This increase in ozone is the same magnitude as that resulting from increasing temperature and relative humidity due to climate change [Steiner *et al.*, 2006].

[11] Near MBO source regions, HCHO concentrations increase 20–40% over a baseline concentration of 4–5 ppb (Figures 3c and 3d). Other aldehyde concentrations (CCHO and RCHO) increase by a similar magnitude (20–40%), causing the total aldehyde concentration to increase by about 4 ppb (80%). Locally, HCHO photolysis is a major source of HO<sub>x</sub> radicals, rivaling the source from O(<sup>1</sup>D) reaction with water. In the Sierra Nevada Mountains, modeled PHO<sub>x</sub> increases about 20% over a base production rate of about 4–5 ppb/hour, predominantly due to HCHO photolysis. Increases in HO<sub>x</sub>, acetaldehyde and other alde-





**Figure 3.** (a) Ozone concentrations in the zero MBO simulation (ppb) and (b) change in ozone concentration when MBO is added to the mechanism (ppb). (c) HCHO concentrations in the zero MBO simulation (ppb), and (d) change in HCHO concentrations when MBO is added to the mechanism (ppb).

hydes raise the production of peroxyacetyl (and higher analogs) radicals and PAN concentrations downwind of the MBO emissions by about 10%.

[12] In simulations without MBO, modeled acetone concentrations in the rural mountain areas are quite low (typically <1 ppb). Acetone is produced with a 62% yield from the MBO+OH reaction, and simulations including MBO increase daily maximum acetone concentrations by up to 4 ppb, although modeled acetone is consistently lower than the measurements (Figure 2b). Because the measured and modeled MBO fluxes compare well, the prediction of higher MBO and lower acetone concentrations than observed indicates that the model OH is too low. Using

VOC measurements along an upwind transect from Sacramento to Blodgett Forest, [OH] is estimated to be  $9 \pm 4 \times 10^6$  molecules  $\text{cm}^{-3}$  [e.g., Dreyfus *et al.*, 2002], compared to model estimates of  $[OH] = 2.5 \times 10^6$  molecules  $\text{cm}^{-3}$  at Blodgett Forest. Therefore, this suggests that MBO oxidation is more rapid in the atmosphere than in the model, consistent with other locations where biogenic VOC emissions are high [e.g., Tan *et al.*, 2001]. Other secondary acetone sources, such as those from the oxidation of terpenoid compounds, are likely too low in the model as well. Additionally, observations from Blodgett Forest show a direct biogenic emission of acetone with a peak summertime flux of  $\sim 0.2 \text{ mg C m}^{-2} \text{ hr}^{-1}$  [Schade and Goldstein,

2001] that accounts for about  $0.02 \text{ s}^{-1}$  of the VOC reactivity at 3PM. Other biogenic fluxes of methanol (peak summertime flux  $1\text{--}1.5 \text{ mg C m}^{-2} \text{ hr}^{-1}$ ), ethanol ( $\sim 0.3 \text{ mg C m}^{-2} \text{ hr}^{-1}$ ), and acetaldehyde ( $\sim 0.15 \text{ mg C m}^{-2} \text{ hr}^{-1}$ ) have also been observed, corresponding to about  $0.2 \text{ s}^{-1}$ ,  $0.1 \text{ s}^{-1}$ , and  $0.6 \text{ s}^{-1}$  respectively, to the VOC reactivity at Blodgett Forest. None of these direct biogenic oxygenated VOC emissions has been included in the model and these emissions will likely impact regional chemistry.

[13] The impact of biogenic MBO emissions on regional air quality could be significant in areas that do not meet federal ozone and particulate matter standards. In central California, the San Joaquin Valley Air Basin has exceeded the federal 8-hour ozone standard approximately 300 times over the past three years (California Air Resources Board, <http://www.arb.ca.gov/adam>). It is thought that local and regional anthropogenic emissions are responsible, and both NO<sub>x</sub> and VOC control strategies are proposed or implemented in the Sacramento and San Joaquin Valley air basins (Sacramento Metropolitan Air Quality Management District, Sacramento regional 8-hour ozone attainment plan, draft proposed control measures, available at <http://www.airquality.org/notices/CAPUpdate/SIPControlMeasureWorkshopOctNov2006.pdf>, 2006; San Joaquin Valley Air Pollution Control District, Extreme ozone attainment demonstration plan, available at [http://www.valleyair.org/Air\\_Quality\\_Plans/AQ\\_plans\\_Ozone\\_Final.htm](http://www.valleyair.org/Air_Quality_Plans/AQ_plans_Ozone_Final.htm), 2004). Our results indicate that primary biogenic VOC emissions can affect the region at large by forming secondary products that can be transported regionally, increasing VOC reactivity and ozone production in areas removed from direct biogenic sources. These additional biogenic sources can confound ozone control strategies by reducing the effectiveness of anthropogenic VOC control. Moreover, these primary and secondary oxygenated species can impact organic particulate matter, affecting regional chemistry and climate. Particulate matter in the Central Valley also exceeds the applicable air quality standards, and the understanding of the organic components and the role of oxygenated VOC may be important in this region as well.

#### 4. Conclusions

[14] We show that the impact of MBO oxidation on ozone, HCHO, and other HO<sub>x</sub> sources in California is significant. Due to the sparser and more rural MBO emission distribution, the magnitude of ozone changes from MBO chemistry is small but has a broad regional impact. MBO emissions increase HCHO concentrations by 20–40% in the source region. Because HCHO yields from MBO and isoprene oxidation are about the same, inversions of satellite HCHO observations to determine isoprene fluxes [e.g., Palmer *et al.*, 2006] may misinterpret MBO emissions as isoprene emission fluxes near MBO source regions. MBO oxidation by ozone and photolysis of HCHO and acetone lead to an increase in PHO<sub>x</sub> by 10–20%, increasing radical concentrations and NO<sub>x</sub> and HO<sub>x</sub> cycling. PHO<sub>x</sub> increases alter the predicted behavior of ozone production and the success of NO<sub>x</sub> and anthropogenic VOC reductions for ozone attainment. This indicates that MBO fluxes, as well as the biogenic fluxes of other oxygenated species such as aldehydes and alcohols, are important for accurate

prediction of ozone and identification of VOC precursors. As we show here, inserting realistic biogenic VOC emissions into chemical transport models improves the representation of VOC and their oxidation products in the atmosphere. However, this increase in biogenic VOC indicates that the fraction of anthropogenic VOC is a smaller portion of the total VOC reactivity. This suggests that achieving a given percentage reduction in total VOC reactivity could require larger reductions in anthropogenic VOC than those predicted by models without a complete representation of biogenic emissions. Biogenic oxygenated VOC also contribute to total organic carbon loading in the atmosphere, and the inclusion of these primary emissions and their secondary chemistry may lead to a better understanding of the atmospheric carbon budget.

[15] **Acknowledgments.** We thank Gunnar Schade for the use of VOC measurements at the Blodgett Forest Research Station. This research has been funded by the U.S. Environmental Protection Agency through grant RD-83096401-0 to the University of California, Berkeley. Although the research described in this article has been funded wholly or in part by the U.S. Environmental Protection Agency grant, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the view of the Agency and no official endorsement should be inferred.

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