

Investigating the Contribution of Isoprene Oxidation to Ozone Production

Gabrielle B. Dreyfus*, Gunnar W. Schade†, Allen H. Goldstein‡

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* College of Arts and Sciences, Harvard University; † Division of Ecosystem Sciences, Department of Environmental Science, Policy, and Management, University of California, Berkeley; ‡ Lawrence Berkeley National Laboratory

Abstract

Measurements of isoprene, its oxidation products methacrolein (MACR) and methyl vinyl ketone (MVK), and ozone were used to calculate the contribution of isoprene oxidation to ozone production downwind of Sacramento, CA. Oxidation of isoprene by OH in the atmosphere leads to the production of both MVK and ozone in distinct quantities. During the early afternoon, mixing ratios of MVK and ozone were highly correlated at our measurements site on the western slope of the Sierra Nevada mountains. We analyzed the slope of this correlation for individual days from July 12 through October 31, 1998, and compared it to the theoretical value of ozone per MVK produced in the oxidation of isoprene. The ratio of calculated to measured slope indicates the contribution of isoprene oxidation to the region's ozone production. Isoprene's contribution was found to increase exponentially with temperature, which is consistent with its temperature dependent emission from plants. Ozone production was dominated by isoprene oxidation on over 40% of the observed days and 66% of hot days ($T_{\max} > 26^{\circ}\text{C}$). This suggests that reducing anthropogenic hydrocarbon emissions in the Sacramento valley would not be a good strategy for reducing ozone levels in the Sierra Nevada mountains.

Measurement Site

• *Location*

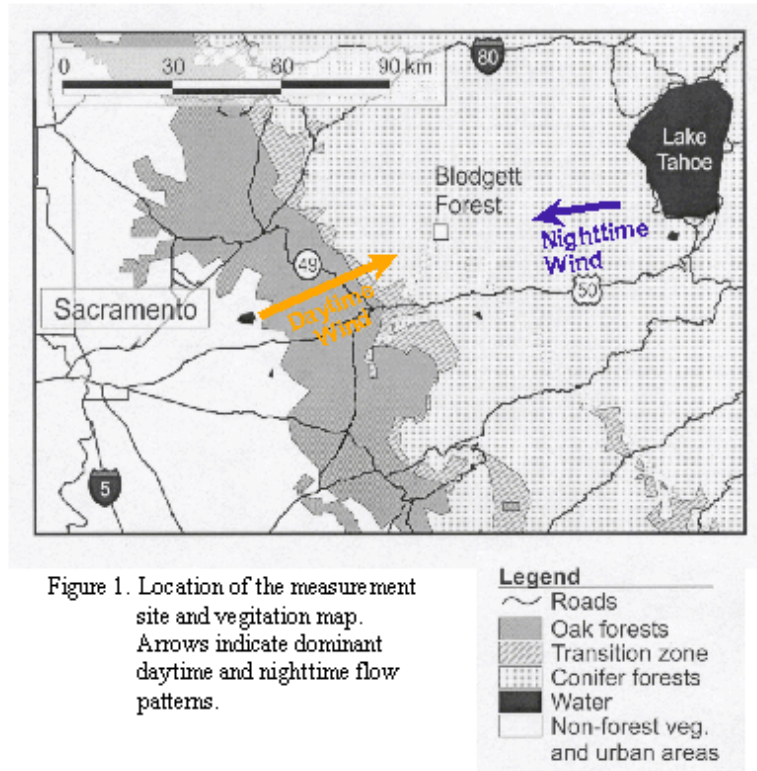
Blodgett Forest Research Station in the Sierra Nevada mountains, CA ($38^{\circ}53'42.9''\text{N}$, $120^{\circ}37'57.9''\text{W}$). Measurements are presented from July 12 through October 31, 1998.

• *Isoprene Source*

The principal source of isoprene in the region is a band of oaks ~30 km to the southwest of the site (Figure 1).

• *Transport Pattern*

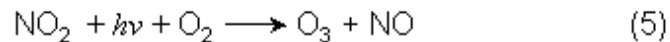
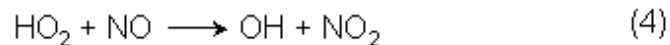
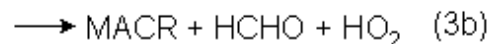
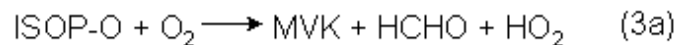
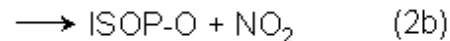
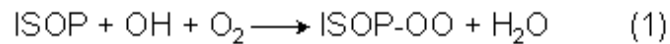
During the daytime, polluted air from the valley is carried up to the site. At night, the wind reverses direction and cleaner air descends from higher altitudes. Wind direction shifts occur around 0800 h and 2000 h PST.



Isoprene Chemistry

The reactions below and Figure 2 describe the oxidation pathway for isoprene. Ozone is produced when the NO_2 from (2b) and (4) photolyzes via reaction (5). In our calculations, we assume 10% of ISOP-OO reacts with NO to form alkyl nitrates via reaction (2a).

Product yields for reaction (3) are show in Figure 2.



For each isoprene oxidized:

1.8 O₃ produced directly

0.9 O₃ produced indirectly*

2.7 total O₃ produced

* Assuming an OH mixing ratio of 5×10^4 molecules cm^{-3} and a transport time of ~2 hours, we calculate an additional **0.9 ozone** molecules produced per isoprene oxidized due to oxidation of MVK, MACR and formaldehyde (50% oxidation to produce HO_2 , 20% photolysis to produce HO_2 , 30% of photolysis does not produce HO_2).

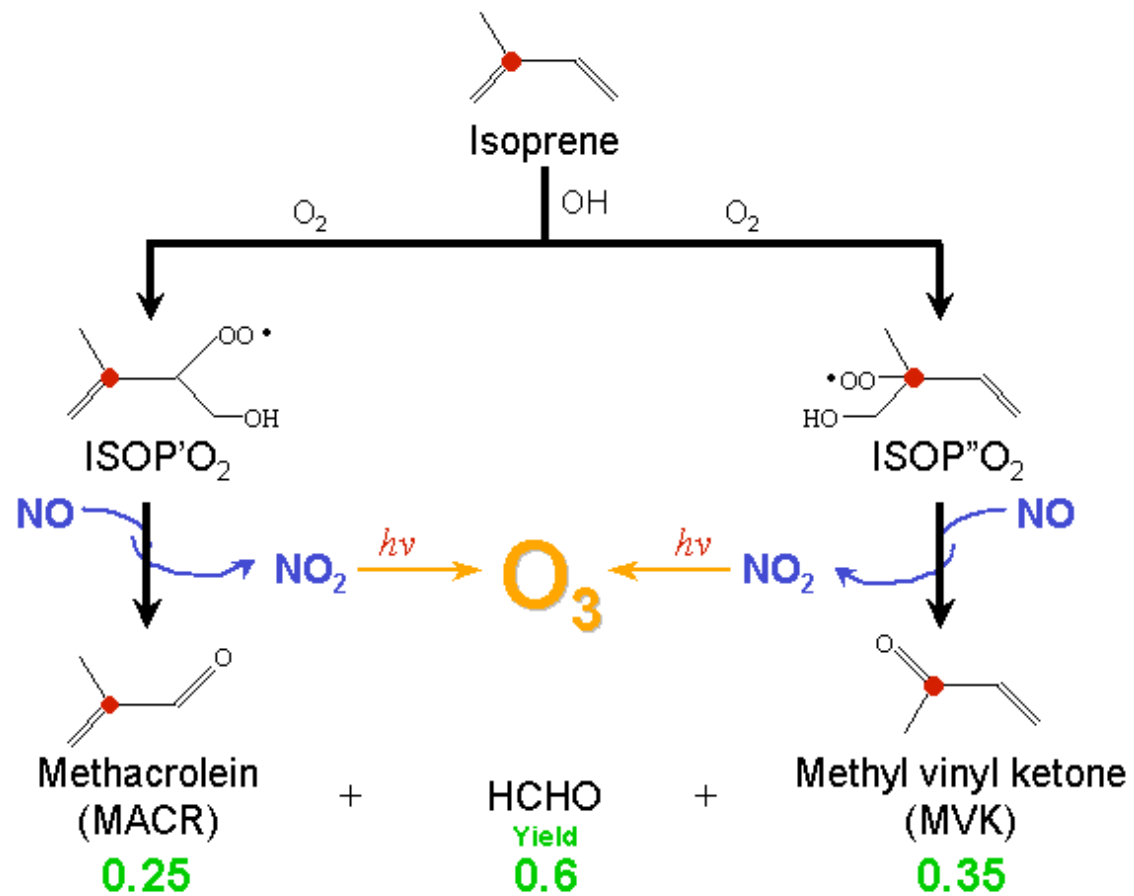


Figure 2. Diagram of the isoprene oxidation pathway showing the yields for the most important oxidation products.

Isoprene and its Oxidation Products

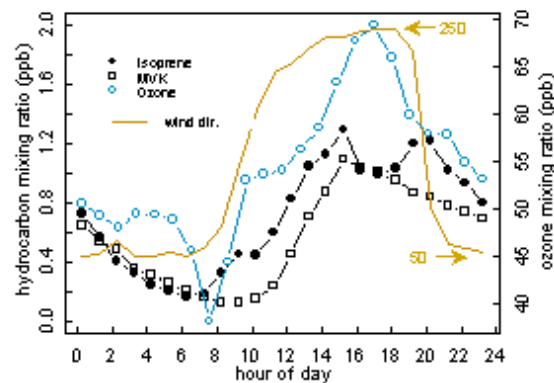


Figure 3. Typical diurnal pattern for isoprene, MVK, MACR, ozone, wind direction.

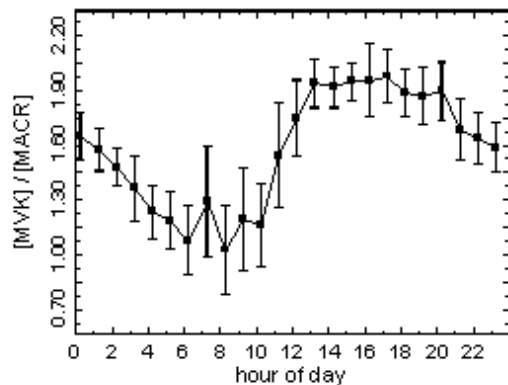


Figure 4. Diurnal cycle of measured MVK to MACR ratio.

Isoprene is principally emitted from a band of oak trees ~30 km to the southwest of the measurement site (Figure 1), and it takes approximately 3 hours after the wind shift (0800 h) for this air to reach the site (Figure 3). Isoprene, followed by ozone and MVK, increases as air masses travel up the mountain. The early morning depression in ozone occurs in a shallow surface layer due to local deposition when vertical mixing is slow.

The diurnal cycle of the ratio MVK/MACR (Figure 4) is driven by both chemical production and loss. OH dominated production and loss results in a ratio of about 2 during the day. Dilution and ozone dominated oxidation bring this ratio down to 1 by the early morning.

Method

The relative increases in ozone and MVK were analyzed for the period of simultaneous increase (Figure 3), usually beginning 3 hours after the wind shifted. These measured slopes were compared to the calculated ratio of ozone to MVK produced in the oxidation of isoprene.

If isoprene oxidation were the only source of ozone, we would observe an ozone to MVK ratio of:

$$d[\text{O}_3]/d[\text{MVK}] = 2.7/0.35 = 7.714.$$

Biesenthal et al. (*J. Atmos. Chem* 31(14), p. 2049f, 1997) calculated an ozone to MVK production ratio of 5.0. However, this calculation did not include ozone produced indirectly from the oxidation of isoprene's oxidation products (MVK, MACR, HCHO), which we believe to be significant due to the 2-3 hour transport time between the isoprene source and our measurement site.

The ratio of calculated to measured slope indicates the contribution of isoprene oxidation to the region's ozone production.

Results

Measured (total ozone) to MVK

Measured slopes of ozone/MVK ranged from 4.36 to 78.0 (Figure 5). Since slopes varied with the exact time window chosen, 95% confidence intervals were calculated by comparing the slopes using two different time window methods (Figure 7). The measured ozone to MVK slope approached the calculated ozone from isoprene level on days with greater isoprene emission and oxidation. Over 40% of measurement days had at least 50% of ozone production due to isoprene oxidation.

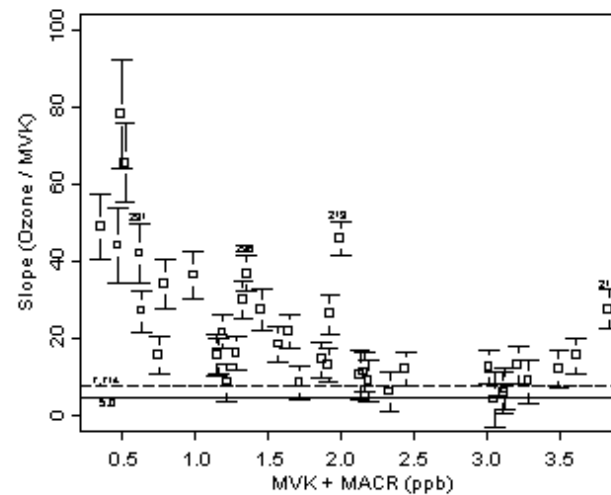


Figure 5. Measured ozone/MVK slope compared to theoretically calculated ozone per MVK from isoprene.

Isoprene's contribution

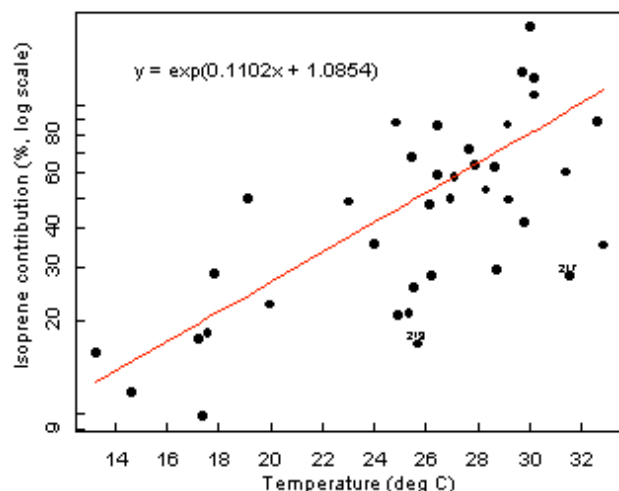


Figure 6. Isoprene's contribution to ozone production is shown to increase exponentially with temperature, which is as expected since isoprene emissions increase exponentially with increasing temperature, and ozone produced from isoprene is proportional to isoprene oxidized.

The contribution of isoprene oxidation to ozone production increased exponentially with temperature (Figure 6). We calculated that isoprene's contribution increased by a factor of three for every 10°C increase in temperature. Isoprene oxidation dominated ozone production on **two-thirds** of hot days ($T_{\max} > 26^{\circ}\text{C}$).

Temperature may be the dominant factor, but it is not the only factor determining isoprene's contribution to regional ozone production. Other potentially important factors include NO_x mixing ratios, anthropogenic hydrocarbon mixing ratios, light, humidity and transport.

Time window comparison

Hour of wind shift and duration of coincident increase varied, and two methods for choosing time windows for analysis were used. In one method, correlations were determined over a consistent time window (1000-1700 h). In the second, windows were selected separately for each day based on the timing of the wind shift and the coincident increase of MVK and ozone. The ozone/MVK slopes calculated using each method are compared in Figure 7. The day specific method did not greatly change the calculated slope for the majority of days, however the four days indicated were highly effected.

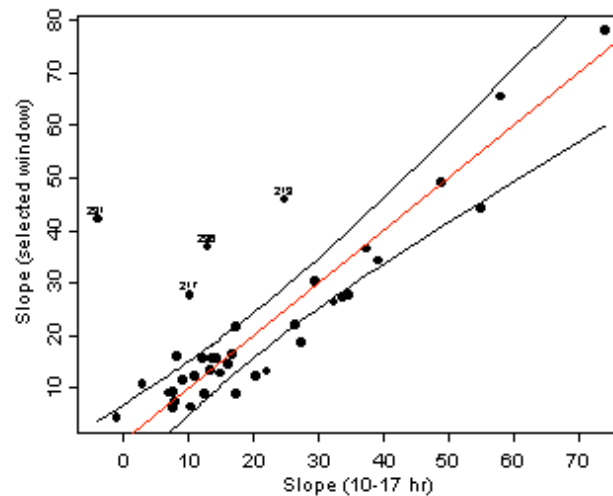


Figure 7. Comparison of slopes measured with consistent time window (x-axis) and selected time window (y-axis). Selected windows reflect the concurrent ozone and MVK increase more accurately and take into consideration time required for transport from the isoprene source. Upper and lower curves indicate the 95% confidence level, and the 1:1 line is shown in red.

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