

Characterization of secondary atmospheric photooxidation products: Evidence for biogenic and anthropogenic sources

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[1] Measurements of the biogenic hydrocarbons isoprene and 2-methyl-3-buten-2-ol (MBO), their first-, second-, and third-generation photooxidation products methacrolein (MACR), methyl vinyl ketone (MVK), acetone, 2-hydroxy-2-methylpropanal (2-HMPR), glycolaldehyde, hydroxyacetone, methylglyoxal, and glyoxal, and carbon monoxide (CO), were obtained above a ponderosa pine plantation, near the Blodgett Forest Research Station, California on 15–19 August and 11–15 September 2000. Diurnal cycles for all the compounds were similar, with maximum mixing ratios in the afternoon and minimum mixing ratios in the early morning. The diurnal cycles of the second-generation isoprene photooxidation products were similar to their precursors, while changes in 2-HMPR, a compound unique to MBO photooxidation, lagged behind corresponding changes in MBO. These observations are consistent with transport of isoprene and its photooxidation products from a strong source several hours upwind, and a predominantly local source of MBO with in situ photochemical production of 2-HMPR. Glycolaldehyde and hydroxyacetone mixing ratios exceeded the mixing ratios of their biogenic precursors on days with high CO, and were generally correlated more strongly with CO than with their biogenic precursors. The agreement between measured product ratios and ratios predicted by a box model improved when anthropogenic precursors were added to the model. Quantification of the source apportionment demonstrated that photooxidation of anthropogenic precursors contributed significantly to the mixing ratios of glycolaldehyde and hydroxyacetone measured in this rural environment. More research into the photochemistry and yields of multifunctional carbonyl compounds from hydrocarbon photooxidation is needed in order for models to accurately predict their role in tropospheric chemistry.

INDEX TERMS: 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; **KEYWORDS:** isoprene, 2-methyl-3-buten-2-ol, glycolaldehyde, glyoxal, methyl glyoxal, 2-hydroxy-2-methylpropanal

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1. Introduction

[2] Volatile organic emissions from biogenic and anthropogenic sources play an important role in the formation of tropospheric ozone and secondary organic aerosols [Andreae and Crutzen, 1997; Chameides et al., 1988;

Jenkin and Clemitshaw, 2000]. Photochemical oxidation of volatile organic compounds (VOCs) produces atmospheric carbonyl and multifunctional carbonyl intermediates that can photolyze, affecting atmospheric radical chemistry and the oxidizing capacity of the atmosphere. Although laboratory studies document the formation of carbonyls and multifunctional carbonyls from ·OH reaction with unsaturated VOCs [Seuwen and Warneck, 1996; Tuazon and Atkinson, 1989, 1990a, 1990b; Yu et al., 1995, 1997], little is known about their mixing ratios, lifetimes, and potential sinks in the atmosphere. For instance, considerable attention

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has been paid to the globally dominant biogenic VOC isoprene [Fuentes *et al.*, 2000; Guenther *et al.*, 1995], and its first-generation photooxidation products formaldehyde, methacrolein (MACR) and methyl vinyl ketone (MVK) [Biesenthal *et al.*, 1997, 1998; Montzka *et al.*, 1993, 1995; Stroud *et al.*, 2001; Yokouchi, 1994]. However, a paucity of data exists on the second- and third-generation photooxidation products and the ultimate fate of atmospheric MACR and MVK.

[3] Known second-generation isoprene photooxidation products include glycolaldehyde ($\text{HOH}_2\text{C-CHO}$), methylglyoxal ($\text{H}_3\text{C-CO-CHO}$), and hydroxyacetone ($\text{HOH}_2\text{C-CO-CH}_3$). Photooxidation of glycolaldehyde produces glyoxal (OHC-CHO), and photooxidation of hydroxyacetone yields methylglyoxal [Jenkin *et al.*, 1993; Niki *et al.*, 1987; Tuazon and Atkinson, 1989, 1990a]. These multifunctional carbonyl compounds are also formed from the photooxidation of anthropogenically emitted VOCs, such as alkylbenzenes, ethene, propene, and 1,3-butadiene, but the reaction yields for many of the products have not been determined experimentally [Atkinson, 1990; Liu *et al.*, 1999; Seuwen and Warneck, 1996; Tuazon *et al.*, 1998; Yu *et al.*, 1997].

[4] Ambient mixing ratios of glycolaldehyde, methylglyoxal, and glyoxal, studied at a rural site in the southeastern United States [Lee *et al.*, 1995, 1998], were thought to originate from isoprene rather than from anthropogenic precursors, because of low contribution (about 7%) of anthropogenic alkanes and alkenes to formaldehyde production [Lee *et al.*, 1998], and strong correlations of the multifunctional carbonyls with formaldehyde [Lee *et al.*, 1995]. No correlations between the first- and second-generation products were examined, and the method was unsuitable for measurement of hydroxyacetone [Lee *et al.*, 1995, 1998]. In a subsequent study, Klotz *et al.* [1999] measured hydroxyacetone near the Brookhaven National Laboratory, NY. Based on the hydroxyacetone/formaldehyde ratios (≤ 1.2), they concluded that the sole source of hydroxyacetone was isoprene, despite nearby vehicular traffic. Hydroxyacetone was also tentatively identified over the rain forest in Surinam, South America, by using proton transfer mass spectrometry. However, the authors acknowledge that the ion observed at m/z 75, which was attributed to the presence of hydroxyacetone, could be due to other atmospheric VOCs such as butanol, diethyl ether, and propionic acid [Williams *et al.*, 2001].

[5] Recently, several studies established high levels of 2-methyl-3-buten-2-ol (MBO), with mean afternoon mixing ratios ranging from 1 to 5 ppb in coniferous forests in western North America [Baker *et al.*, 1999; Goldan *et al.*, 1993; Schade and Goldstein, 2001; Schade *et al.*, 2000]. MBO is emitted from pine trees in western North America [Harley *et al.*, 1998]; its emission patterns from ponderosa pines are strikingly similar to those of isoprene, driven by both light and temperature changes; and it is highly reactive with the hydroxyl radical [Goldstein and Schade, 2000; Schade and Goldstein, 2001]. Although the relationship of MBO with its first-generation photooxidation product acetone was previously studied [Goldstein and Schade, 2000], the relationships between MBO emissions and the other first-generation photooxidation products glycolaldehyde, formaldehyde, and 2-hydroxy-2-methylpropanal (2-HMPR) were not explored. In this publication, we present a more

complete study of isoprene and MBO and their first-, second-, and third-generation photooxidation products at the Blodgett Forest Research Station, which is located on the western slope of the Sierra Nevada, California. Air chemistry at this site is dominated by the biogenically emitted VOCs isoprene and MBO and their photooxidation products [Lamanna and Goldstein, 1999]. Isoprene, MACR, and MVK chemistry and climatology in the Blodgett Forest were described by Dreyfus *et al.* [2002]. Herein, we further investigate the relationship between isoprene's second-generation products and their precursors, provide evidence of additional anthropogenic contributions to glycolaldehyde and hydroxyacetone mixing ratios, and estimate source apportionment for the photooxidation products. We also provide the first diurnal measurements of 2-HMPR in the environment, and examine the relationship between 2-HMPR and its precursor, MBO.

2. Experiment

2.1. Site Description

[6] Detailed descriptions of the site can be found in previous publications [Goldstein *et al.*, 2000; Lamanna and Goldstein, 1999; Schade *et al.*, 2000]. Briefly, the site is a ponderosa pine plantation, located on the western slope of the Sierra Nevada, near the Blodgett Forest Research Station ($38^\circ 53'$, $42.9''$ N, $120^\circ 37'$, $57.9''$ W, 1315 m elevation). The pine trees are even aged, were on average 4.5 m tall in the year 2000, and interspersed with various coniferous and deciduous trees. The climate is Mediterranean, with predominant rainfall between September and May, and almost no rain during the summer months. All measurements reported herein were performed from the onsite walk-up tower, erected in 1997. Regional meteorology was described by Goldstein *et al.* [2000], while the climatology of major trace gases was recently described by Bauer *et al.* [2000] (ozone), Schade *et al.* [2000] (MBO), Dillon *et al.* [2002] (anthropogenic hydrocarbons), and Dreyfus *et al.* [2002] (isoprene and its oxidation products). Routine meteorological data are reported from the top level of the tower, approximately 11 m above ground level. The VOC and CO sampling inlets were also located approximately 11 m above ground, while the inlet for multifunctional carbonyl sampling was approximately 8 m above ground.

2.2. Measurement of VOCs and Carbon Monoxide (CO)

[7] Isoprene, MBO, MACR, MVK, acetone, toluene, and β -pinene were measured with the automated relaxed eddy accumulation, gas chromatography dual flame ionization detection system described in detail by Schade and Goldstein [2001, and references therein]. The system was calibrated by the regular measurement of ppb-level standards (Scott-Marrin Inc., Riverside, CA). No significant differences existed between the mixing ratios of updrafts and downdrafts of the relaxed eddy accumulation system for the VOCs reported in this manuscript, and the accuracy of reported mixing ratios is ± 10 –20%, depending on compound.

[8] Carbon monoxide (CO) was measured in a manner similar to that described by Novelli *et al.* [1991]. CO and H_2 were separated from other trace gases on a Unibead 1S column (60/80 mesh; 1.8 m, 2 mm ID SS; Alltech Asso-

Table 1. Limits of Detection, Mean Recovery of Field Spikes, and Mean Collection Efficiencies Obtained for Multifunctional Carbonyls Collected at the Blodgett Forest in August and September 2000

| Analyte | Limit of Detection | | Field Spike Recovery, Mean \pm S.D. | Collection Efficiency, Mean \pm S.D. |
|-------------------------------------|--------------------|-------------|--|---|
| | Range, ppt | Median, ppt | | |
| Glycolaldehyde | 15–52 | 31 | 98 \pm 19% | 92 \pm 15% |
| Hydroxyacetone | 1.7–32 | 20 | 95 \pm 16% | 92 \pm 12% |
| 3-hydroxy-3-methyl-2-butanone | N/A | N/A | 112 \pm 30% | N/A |
| 2-hydroxy-2-methylpropanal (2-HMPR) | 17–99 | 40 | N/A | 91 \pm 21% |
| Glyoxal | 2.8–11 | 7.2 | 101 \pm 19% | 91 \pm 21% |
| Methylglyoxal | 2.5–11 | 5.2 | 103 \pm 16% | 84 \pm 11% |

ciates Inc., Deerfield, Illinois). The gases were separated from each other with a Molecular Sieve 5Å column (80/100 mesh; 1.8 m, 2 mm ID SS; Alltech Associates Inc., Deerfield, IL), and quantified using a mercury oxide reduction detector (RGD2, Trace Analytical, Menlo Park, CA). Ultrahigh purity (UHP) air (Airgas, Sacramento, CA), filtered through Molecular Sieve 5Å and Sofnocat Oxidation Catalyst (Molecular Products Ltd., Thaxted, UK), was used as the carrier gas. Ambient air was pulled from the tower at approximately 2 L min⁻¹ and a subsample was introduced out of a 2 L buffer volume into a 1-mL sample loop at 0.5 L min⁻¹. Injections were carried out automatically every three minutes. Herein, we report the median values obtained over a 30-minute period. The instrument was calibrated by analyzing two CO standards (Scott-Marrin Inc., Riverside, CA), whose concentrations bracketed the range of ambient mixing ratios (103–277 ppb CO in UHP air). The standards were introduced into the sample four times every eight hours. The accuracy of measured CO mixing ratios, as estimated from multiple regression curves, was ± 1 –2 ppb above 100 ppb CO.

2.3. Measurement of Multifunctional Carbonyls

[9] Sampling and analysis procedures for measurement of multifunctional carbonyls were previously described in detail [Spaulding *et al.*, 2002a, 2002b]. Brief descriptions are included here for convenience.

2.3.1. Standard Solutions

[10] Reagents were purified and glassware silylanized as previously described [Spaulding *et al.*, 2002a]. A standard stock solution was used to prepare calibration standards in the laboratory and to enrich solutions that were employed as “field spike” samples (a field spike is a solution of PFBHA enhanced with known concentrations of the analytes). The solution contained 4.16 ng μL^{-1} glycolaldehyde, 3.90 ng μL^{-1} hydroxyacetone, 3.69 ng μL^{-1} 3-hydroxy-3-methyl-2-butanone, 1.01 ng μL^{-1} glyoxal, and 1.88 ng μL^{-1} methylglyoxal in methanol. The internal standard stock solution contained 1.82 ng μL^{-1} of 4-fluorobenzaldehyde (internal standard for dicarbonyls) and 4.18 ng μL^{-1} of 4-hydroxybenz-¹³C₆-aldehyde (internal standard for hydroxycarbonyls) in methanol.

2.3.2. Collection of Multifunctional Carbonyls

[11] Air was sampled at 06:00, hourly from 10:00 to 17:00, and at 21:00 pacific standard time (PST) from 15–19 August; every 2 hours from 13:00 PST on 11 September to 19:00 on 13 September; hourly from 14:00 to 21:00 PST on 14 September; and hourly from 08:00 to 18:00 PST on 15 September 2000. Samples were collected using 2 mist

chambers in series at a flow rate of 23–25 L min⁻¹ for 10 min. Operating principals of the mist chamber were described previously [Cofer *et al.*, 1985; Klemm and Talbot, 1991; Spaulding *et al.*, 2001a].

[12] The reservoir of the mist chamber was filled with 20 mL of 1 mM aqueous *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA). After collection of air samples, the aqueous PFBHA solution was withdrawn from the mist chamber using a glass syringe, and transferred to a 40-mL amber vial. Fifty microliters of internal standard stock solution was added, and the solution was stored at room temperature for 18–38 hours.

2.3.3. Blanks, Field Spikes, and Limits of Detection

[13] Blank and field spike samples were prepared in the morning, before collection of the first sample, and in the evening, after collection of the final sample, on 15–19 August and 14–15 September. From 11 to 13 September, blank and field spike samples were prepared at noon and midnight daily. A “blank” consisted of a sample in which UHP air was collected in the scrubber, and treated identically to the samples. Field spike samples were prepared by enriching 20 mL of 1 mM aqueous PFBHA with 50 μL of the standard stock solution. Fifty microliters of internal standard stock solution were added to each field blank and spike sample, and the solutions were stored in amber vials at room temperature for 18 to 38 hours. The concentration measured in the blank extract was subtracted from the concentration measured in sample extracts. The limit of detection (LOD) was calculated as $3\sigma_{\text{blank}}$, where σ_{blank} is the standard deviation of the response factor for the analyte among all blank samples collected. Limits of detection and recoveries from field spikes are presented in Table 1. The limits of detection differed daily, depending on the amount of analytes measured in the blanks, and ranged from 1.7 to 99 ppt. Mean field spike recoveries ranged from 95% to 112%.

2.3.4. PFBHA and BSTFA Derivatization

[14] Multifunctional carbonyls were derivatized in order to decrease their polarity and allow quantitative analysis by GC/MS at low ppt levels. All carbonyls were reacted with PFBHA to form the corresponding pentafluorobenzyl oximes. Compounds that also contained an –OH group were then reacted with *bis*-(trimethylsilyl)trifluoroacetamide (BSTFA) to form trimethylsilyl ethers. Derivatization of the carbonyls using a 1 mM aqueous PFBHA solution was allowed to proceed for 18 to 38 hours at ambient temperature. The PFBHA derivatives were then extracted two times with 4 mL of CH₂Cl₂. Five mL of H₂O containing 2 drops of concentrated H₂SO₄ was added to

each vial to remove excess PFBHA. Extracts from samples, field blanks, and field spikes were stored on dry ice until their return to the laboratory, where they were stored at 4°C until derivatization with BSTFA and analysis by splitless injection-gas chromatography and ion trap mass spectrometry. The PFBHA derivatives of dicarbonyls and hydroxycarbonyls are stable at 4°C in CH₂Cl₂ for ≥66 days [Spaulding and Charles, 2002]. Details of the method and instrumental procedures were described previously [Spaulding et al., 2002a, 2002b].

2.3.5. Identification and Quantification of Multifunctional Carbonyls

[15] PFBHA derivatives of glyoxal and methylglyoxal and PFBHA-BSTFA derivatives of glycolaldehyde and hydroxyacetone were identified by interpreting the mass spectra generated by methane chemical ionization, and by matching the relative retention time and mass spectra of the tentatively identified compound to the relative retention time and mass spectra of an authentic standard. At the time of sample analysis, an authentic standard was not available for 2-HMPR. Therefore, the PFBHA and PFBHA-BSTFA derivatives of 2-HMPR were identified by interpreting the EI, methane CI, and PFBOH CI ion trap mass spectra, and by matching the relative retention times and mass spectra to those of a peak obtained from the reaction of MBO with hydroxyl radical in an atmospheric chamber experiment. Identification was later confirmed by matching the relative retention time and mass spectra to that from a derivative of a synthesized authentic standard [Spaulding et al., 2002b].

[16] Calibration solutions were prepared by diluting the standard stock solution and internal standard stock solution in aqueous PFBHA. These solutions were treated identically to samples. The resulting extracts, comprised of the PFBHA and PFBHA-BSTFA derivatives of authentic standards, ranged in concentration from 12.6 pg μL⁻¹ to 6.2 ng μL⁻¹ of the analytes, 455 pg μL⁻¹ 4-fluorobenzaldehyde, and 1.05 ng μL⁻¹ 4-hydroxybenz-¹³C₆-aldehyde. Calibration solutions were analyzed before and after samples, and a “midpoint” standard solution was analyzed after every 5 samples to evaluate the stability of the calibration curve. A calibration curve was considered linear if the coefficient of determination (r^2) was ≥0.95, the relative standard deviation among the relative response factors was ≤25%, and the calculated value for the midpoint standard was within ±20% of the actual value. For quantification of 2-HMPR a regression equation was obtained by plotting the response versus concentration for the surrogate compound, 3-hydroxy-3-methyl-2-butanone. The response from 2-HMPR in a sample extract was substituted into the regression equation to obtain an estimated concentration. This method only provides an estimate of the 2-HMPR concentrations in sample solutions. However, in previous work we compared this method to FT-IR measurements in which 2-HMPR mixing ratios were estimated by assuming a yield 29% (equal to the yield of formaldehyde) from the reaction of MBO with OH radicals. According to this comparison, the error of the method ranges from 6 to 41%, depending on the assumed yield of 2-hydroxy-2-methylpropanal [Spaulding et al., 2002b].

[17] The concentrations of the analytes were measured in each mist chamber (2 in series). The collection efficiency

was calculated as $[1 - (C_2/C_1)]$, where C_1 and C_2 are the concentrations measured in the first and second mist chambers, respectively. The concentration reported is the concentration in the first mist chamber, corrected for the collection efficiency. Concentrations are reported for samples whose collection efficiencies were ≥50%. The frequency of samples with collection efficiencies <50% is ≤1% for all compounds except glyoxal. For glyoxal, ~10% of the samples had collection efficiencies <50%. In these cases the concentrations of glyoxal measured were often near the detection limit, where a small amount of contamination in the second scrubber resulted in very low collection efficiencies. Mean collection efficiencies obtained during this study are presented in Table 1, and ranged from 84 to 92%.

3. Results and Discussion

3.1. Mixing Ratios of Isoprene and MBO, Their Photooxidation Products, and CO

[18] The Blodgett Forest field site provides an ideal environment to measure isoprene and MBO photooxidation products. Isoprene, mainly emitted from oak trees upwind of the site, and MBO, emitted from ponderosa pine trees on-site, account for greater than 50% of the OH radical chemistry at this site [Dreyfus et al., 2002; Lamanna and Goldstein, 1999]. Laboratory data predict that the OH radical will be the dominant oxidant for isoprene and MBO during daytime, and that under sufficiently high NO mixing ratios (>30 ppt), the reactions shown in Figure 1 will dominate [Alvarado et al., 1999; Atkinson and Arey, 1998; Bacher et al., 2001; Carter and Atkinson, 1996; Fantechi et al., 1998b; Ferronato et al., 1998; Jenkin et al., 1993; Niki et al., 1987; Orlando et al., 1999; Rudich et al., 1995]. This condition generally exists since daytime NO_x mixing ratios, influenced by the Sacramento urban plume, typically range from 0.5 to 1 ppb at the Blodgett Forest [Dillon et al., 2002]. Carbon monoxide is included in the analysis that follows as it is an excellent tracer of anthropogenic emissions (mostly combustion sources), exhibiting a general diurnal cycle that is very similar to those of primary anthropogenic hydrocarbons such as acetylene measured at the site (data not shown).

[19] Mean and median mixing ratios for each compound measured are presented in Table 2. The presence of 2-HMPR provides qualitative evidence that the laboratory-derived photooxidation mechanism for MBO occurs in the environment. The first-, second-, and third-generation isoprene photooxidation products glycolaldehyde, methylglyoxal, glyoxal, and hydroxyacetone were also detected. The mixing ratios of formaldehyde were not quantified due to contamination of blank solutions. The trends observed follow the trends expected from laboratory yields and photolysis and ·OH reaction rates. Specifically, MVK mixing ratios are greater than MACR mixing ratios, as expected, because the MVK yield exceeds the MACR yield from isoprene, and MACR reacts more rapidly than MVK with ·OH [Dreyfus et al., 2002]. The laboratory-derived yields of the second-generation products from isoprene photooxidation follow the order [glycolaldehyde] > [hydroxyacetone] ~ [methylglyoxal]. However, under ambient conditions hydroxyacetone mixing ratios are

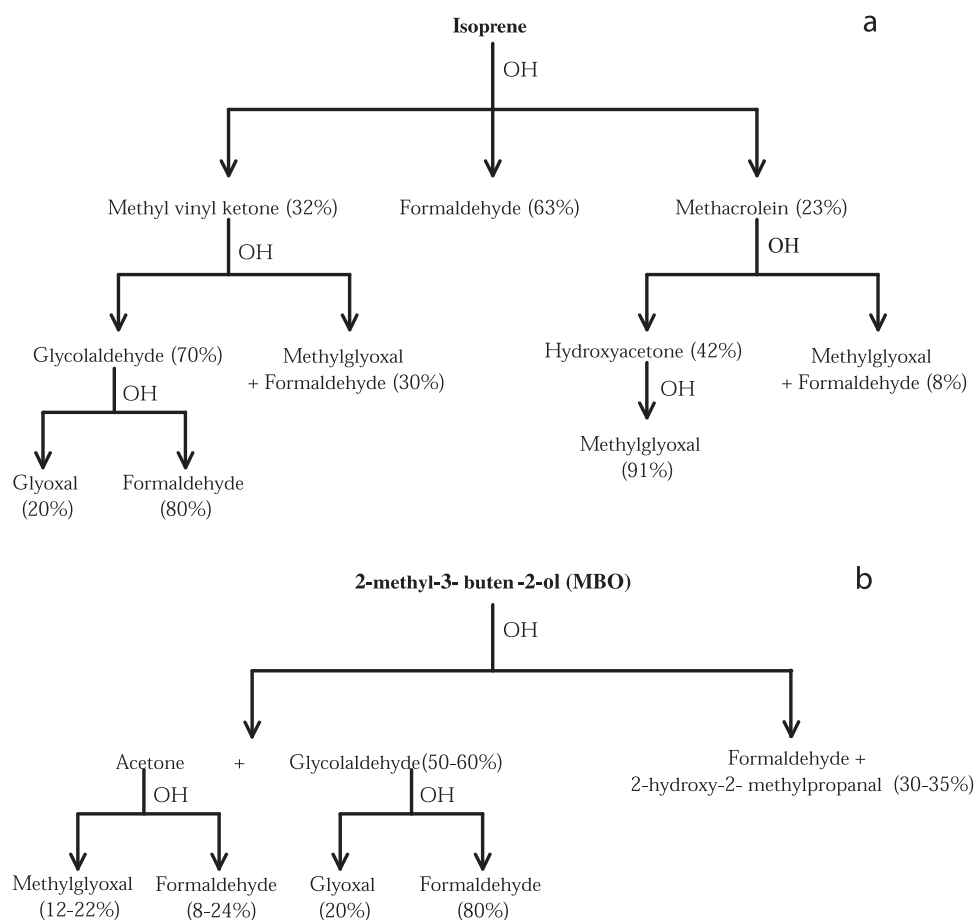


Figure 1. Hydroxyl radical reaction schemes for (a) isoprene, and (b) 2-methyl-3-buten-2-ol.

expected to exceed methylglyoxal mixing ratios because methylglyoxal has a shorter lifetime. Mixing ratios of the third-generation product, glyoxal, are expected to be the lowest. The expected trends from this simple analysis were indeed observed, providing cursory evidence that the laboratory-derived isoprene photooxidation mechanism occurs at this site. We present the expected daytime lifetimes of all compounds in Table 3, assuming that photolysis and $\cdot\text{OH}$ reaction are the only important loss

processes. The lifetimes were calculated using the following equation:

$$\tau = [(k_{\text{OH}} \times [\text{OH}]) + (k_{\text{photolysis}})]^{-1}$$

where, τ = lifetime, k_{OH} = rate constant for the reaction with OH, and $k_{\text{photolysis}}$ = the photolysis rate constant. We used an $\cdot\text{OH}$ value of $9 \times 10^6 \text{ molec cm}^{-3}$, as recently estimated by Dreyfus *et al.* [2002], and photolysis rates as estimated for

Table 2. Number of Samples Analyzed (Cases) and the Mean and Median Mixing Ratios Measured Above a Ponderosa Pine Plantation From 15–19 August and 11–15 September 2000

| Analyte | Cases | Mixing Ratio, ppb | | | |
|-----------------------------|-------|-------------------|-------------------|--------|-------------------------------------|
| | | Range | Mean \pm S.D. | Median | Comparison to Literature Mean |
| Isoprene | 220 | 0.01–2.4 | 0.40 \pm 0.34 | 0.43 | 0.25, ^a 1.7 ^b |
| Methyl vinyl ketone (MVK) | 220 | 0.01–1.7 | 0.51 \pm 0.29 | 0.54 | MVK + MACR = 1.3 ^b |
| Methacrolein (MACR) | 220 | 0.02–0.83 | 0.34 \pm 0.15 | 0.36 | MVK + MACR = 1.3 ^b |
| Glycolaldehyde | 98 | 0.092–1.7 | 0.69 \pm 0.37 | 0.63 | 0.70 ^a |
| Hydroxyacetone | 98 | 0.075–1.1 | 0.42 \pm 0.25 | 0.38 | 0.61 ^b |
| Glyoxal | 83 | 0.006–0.083 | 0.027 \pm 0.015 | 0.024 | 0.06 ^a |
| Methylglyoxal | 99 | 0.032–0.32 | 0.13 \pm 0.06 | 0.12 | 0.10 ^a |
| 2-methyl-3-buten-2-ol (MBO) | 219 | 0.01–7.9 | 1.1 \pm 1.1 | 0.73 | |
| Acetone | 205 | 0.22–4.6 | 2.2 \pm 0.7 | 2.2 | 2.9 ^b |
| 2-hydroxy-2-methylpropanal | 95 | 0.056–1.2 | 0.30 \pm 0.27 | 0.21 | |

^aLee *et al.* [1998].

^bWilliams *et al.* [2001].

Table 3. Expected Lifetimes of Isoprene, MBO, and Their Photooxidation Products at the Blodgett Forest

| Compound | k_{OH} , ^a $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ | $k_{\text{photolysis}}$, ^b $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ | Lifetime, hours |
|----------------------------------|--|--|-----------------|
| Isoprene | $1.0 \times 10^{-10\text{c}}$ | | 0.31 |
| MVK | $1.2\text{--}1.9 \times 10^{-11\text{c,d}}$ | $1.2 \times 10^{-6\text{d}}$ | 1.6–2.5 |
| MACR | $2.8\text{--}3.3 \times 10^{-11\text{c,d}}$ | $2.2 \times 10^{-6\text{d}}$ | 0.92–1.1 |
| Glycolaldehyde | $1.1 \times 10^{-11\text{e}}$ | $4.0 \times 10^{-6\text{e}}$ | 2.7 |
| Hydroxyacetone | $3.0 \times 10^{-12\text{f}}$ | $<1.5 \times 10^{-6\text{f}}$ | 9.8 |
| Methylglyoxal ^{b,f,g,h} | $1.7 \times 10^{-11\text{c}}$ | $0.68\text{--}2.0 \times 10^{-4\text{c,g,h,i}}$ | 0.94–1.5 |
| Glyoxal ^{b,i} | $1.2 \times 10^{-11\text{c}}$ | $5.6\text{--}8.7 \times 10^{-5\text{c,j}}$ | 1.5–1.7 |
| MBO ^{i,k,l} | $3.9\text{--}6.9 \times 10^{-11\text{k,l,m}}$ | | 0.45–0.79 |
| Acetone ^{m,n} | $2.2 \times 10^{-13\text{n}}$ | $9.0 \times 10^{-8\text{o}}$ | 141 |
| 2-HMPR ^o | $2.0 \times 10^{-11\text{p}}$ | not determined | 1.5 |

^a $[\text{OH}] = 9 \times 10^6 \text{ molec cm}^{-3}$.

^bPhotolysis rate constants were estimated at latitudes of 0–60°N, a blank cell indicates that photolysis is insignificant.

^cCarter and Atkinson [1996].

^dGierczak et al. [1997].

^eBacher et al. [2001].

^fOrlando et al. [1999].

^gStaffelbach et al. [1995].

^hKoch and Moortgat [1998].

ⁱChen et al. [2000].

^jKlotz et al. [2001].

^kFerronato et al. [1998].

^lFantechi et al. [1998a, 1998b].

^mRudich et al. [1995].

ⁿAtkinson [1990].

^oGierczak et al. [1998].

^pEstimated by the method of Kwok and Atkinson [1995].

solar zenith angles ranging from 0°–60°N latitude [Rudich et al., 1995; Gierczak et al., 1997; Bacher et al., 2001; Orlando et al., 1999; Plum et al., 1983; Klotz et al., 2001; Staffelbach et al., 1995; Koch and Moortgat, 1998; Chen et al., 2000]. A range of lifetimes is given in cases where different studies found different reaction rates.

[20] The mixing ratios of glycolaldehyde (0.092–1.7 ppb) and methylglyoxal (0.032–0.32 ppb) are similar to those measured by Lee et al. [1998] in flights over Tennessee. For comparison, we present the mixing ratios reported by Lee et al. [1998] in Table 2. The mean glyoxal mixing ratios measured in our study were lower (0.027 versus 0.06 ppb), and the mean isoprene mixing ratios were higher (0.40 versus 0.25) than those reported by Lee et al. [1998]. While it is difficult to directly compare their results to ours, it is possible that Lee et al. [1998] observed higher mixing ratios of glycolaldehyde, methylglyoxal, and glyoxal, relative to isoprene in Tennessee due to either higher isoprene emissions in the region, and thus greater accumulation of the photooxidation products, or a greater contribution from anthropogenic or other biogenic sources to the mixing ratios of the multifunctional carbonyls than the authors concluded. The mixing ratios of isoprene, MVK + MACR, and hydroxyacetone, measured by proton transfer reaction-mass spectrometry in the boundary layer over a tropical rain forest were higher (1.7 ppb, 1.3 ppb, and 0.61 ppb, respectively) than mixing ratios reported herein (mean values of 0.40, 0.51, 0.34, and 0.42 for isoprene, MVK, MACR, and hydroxyacetone, respectively), but the mean hydroxyacetone mixing ratios, relative to the mean (MVK + MACR) mixing ratios are similar in both studies (0.49 in this study versus 0.46) [Williams et al., 2001]. Unfortunately, other studies that report measurements of the second- and third-generation isoprene photooxidation products do not report isoprene concentrations, and therefore the results

cannot be compared to our results [Klotz et al., 1999; Lee et al., 1995; Spaulding et al., 1999].

3.2. Diurnal Trends

3.2.1. Abundances

[21] The mixing ratios of isoprene and its photooxidation products on 11–15 September 2000 are presented in Figure 2. Air temperature, CO mixing ratios, photosynthetically active radiation (PAR), and wind speed are presented in Figure 3. The diurnal cycles of the first-generation products MVK and MACR closely follow that of isoprene, with maximum mixing ratios measured in the afternoon, when the wind from the southwest brings in isoprene and its photooxidation products [Lamanna and Goldestein, 1999; Dreyfus et al., 2002]. The highest mixing ratios (2.4 ppb isoprene, 1.7 ppb MVK, 0.83 ppb MACR) were measured on the warmest day (257), while much lower afternoon maximum mixing ratios (0.43 and 0.40 ppb isoprene, 0.53 and 0.46 ppb MVK, 0.34 and 0.33 ppb MACR) were measured on the coolest days (258 and 259), which is consistent with temperature- and light-dependent emissions of isoprene [Harley et al., 1999].

[22] The diurnal cycles for the second-generation products hydroxyacetone, glycolaldehyde, and methylglyoxal generally follow the patterns of their precursors MACR and MVK. Although methylglyoxal is produced from ·OH reactions with MACR, MVK, hydroxyacetone, and acetone [Jenkin et al., 1993; Orlando et al., 1999; Tuazon and Atkinson, 1989, 1990a], the relatively long lifetimes of hydroxyacetone (11 hours) and acetone (151 hours) compared to MVK (1.8–2.9 hours) and MACR (1.0–1.2 hours) make hydroxyacetone and acetone much less important precursors. On days 255, 256, and 258, hydroxyacetone mixing ratios (0.77, 0.75, and 0.55 ppb) exceeded the mixing ratios of MACR (0.49, 0.49, and 0.34 ppb) and glycolaldehyde mixing ratios (1.12,

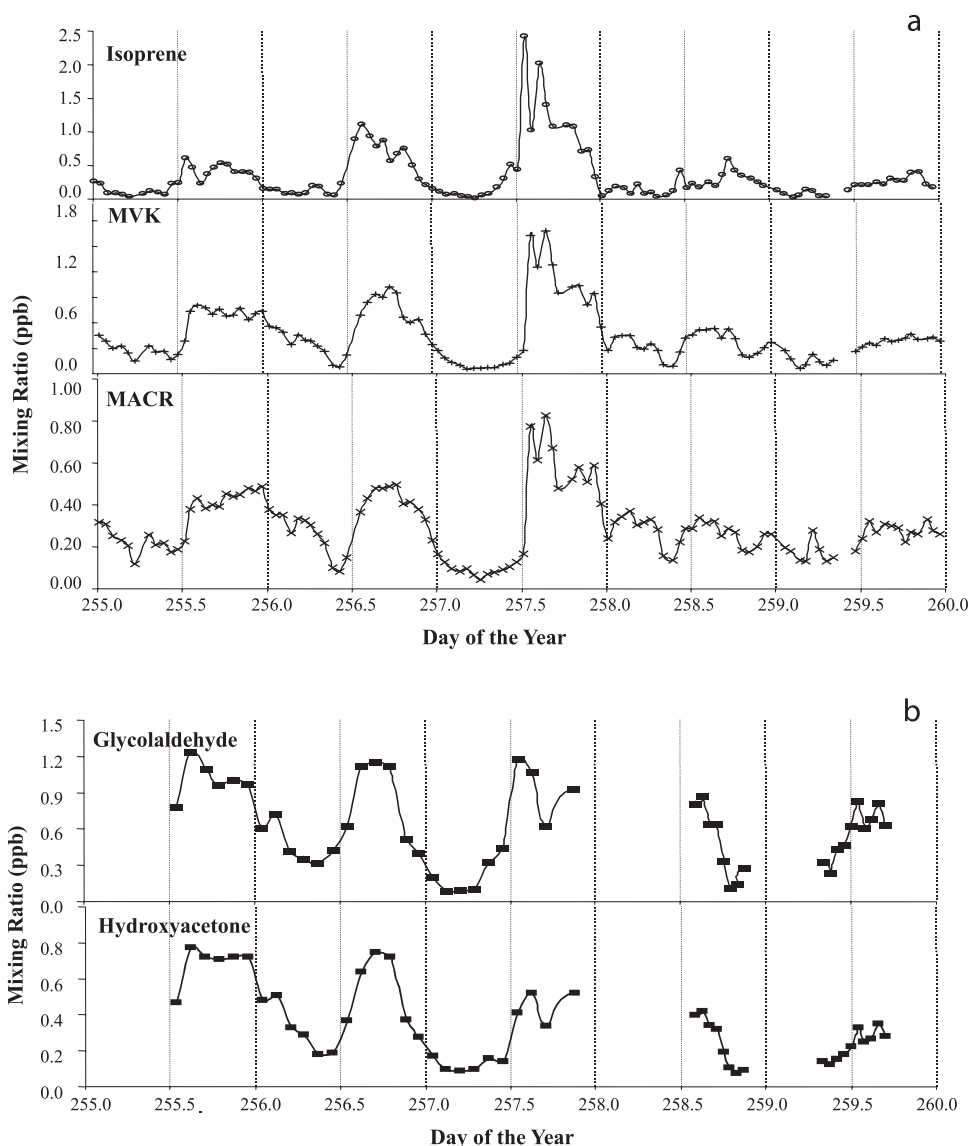


Figure 2. Isoprene and its oxidation product mixing ratios as measured from 11–15 September 2000 (PST = Pacific Standard Time).

1.11, and 0.87 ppb) exceeded the mixing ratios of MVK (0.80, 1.0, and 0.52 ppb), whereas on day 257 MACR (0.83 ppb) was higher than hydroxyacetone (0.75 ppb) and MVK (1.7 ppb) was higher than glycolaldehyde (1.1 ppb). These trends can be partially explained by air temperature, CO mixing ratios, and PAR (Figure 3). On day 257, high air temperatures (29°C) and sunny skies in the afternoon caused high emissions of isoprene, leading to high mixing ratios of MACR and MVK. On the same day, low CO mixing ratios (maximum = 128 ppb) indicated relatively low anthropogenic influence on the photochemistry. In contrast, on days 255, 256, and 258, lower air temperatures ($\leq 25^{\circ}\text{C}$), and partial cloud cover in the afternoon of day 256, lead to lower isoprene emissions and thus lower mixing ratios of MACR and MVK. On these days, relatively higher CO mixing ratios (≥ 158 ppb) suggest a larger anthropogenic influence on air composition at the site. Thus since hydroxyacetone and glycolaldehyde mixing ratios were higher on days with significant anthropogenic influence, their sources are pre-

sumably both anthropogenic and biogenic. Although the mixing ratios of methylglyoxal never exceeded those of its precursors, the overall trend for methylglyoxal was similar to the trends for glycolaldehyde and hydroxyacetone. Hence, methylglyoxal may also have been influenced by anthropogenic sources.

[23] Regarding the MBO photooxidation products, formaldehyde was not quantified in this study; acetone does not exhibit a strong diurnal cycle due to multiple sources that are both primary and secondary in origin, and include both anthropogenic and biogenic precursors [Goldstein and Schade, 2000]; and glycolaldehyde mixing ratios are also influenced by MVK and possibly by anthropogenic emissions, as described above. We expect, however, that 2-HMPR is produced predominantly from MBO reactions. MBO and 2-HMPR mixing ratios are presented in Figure 4a for 15–19 August 2000, and in Figure 4b for 11–15 September 2000. MBO mixing ratios generally began to increase at sunrise, and decreased at sunset, consistent with

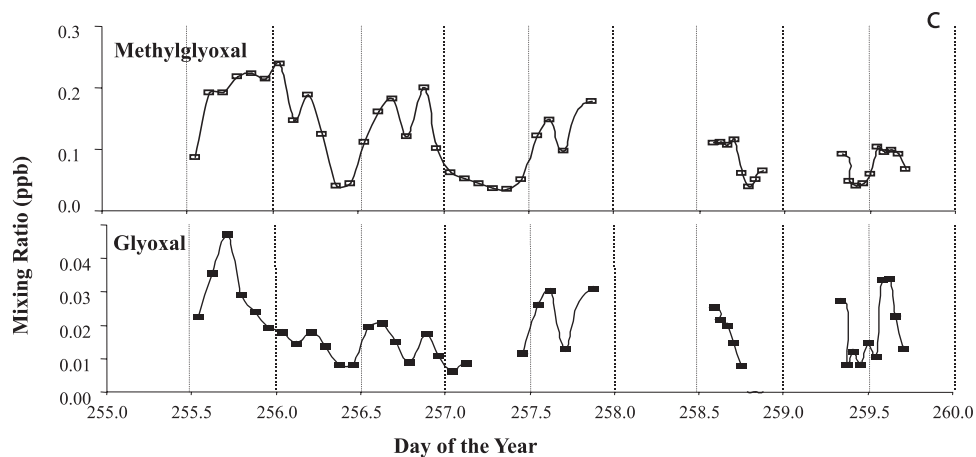


Figure 2. (continued)

a local light-dependent source [Harley *et al.*, 1998; Schade *et al.*, 2000]. Because MBO emissions are also temperature-dependent, MBO mixing ratios were higher on days that the maximum air temperatures exceeded 24°C (≥ 4.4 ppb on days 228, 229, 230, 255, 256, and 257). On cooler days, maximum MBO mixing ratios were lower (≤ 2.3 ppb). The 2-HMPR mixing ratios generally followed the same trend, with changes lagging several hours behind changes in MBO, and higher mixing ratios measured on the warmer days (≥ 0.74 ppb), compared to cooler days (≤ 0.25 ppb), excluding the night between days 255 and 256, which is discussed below. A typical phenomenon observed on the warm days, particularly days 228–230,

is a peak in the MBO mixing ratio early in the morning ($\sim 08:00$) (e.g., from 0.65 ppb to 6.3 ppb on day 229), and another in the evening ($\sim 18:00$) (e.g., from 1.8 ppb to 2.0 ppb on day 229), which corresponds to times when MBO emission from the pine trees was active but vertical mixing was limited [Schade *et al.*, 2000], causing MBO mixing ratios to increase at ground level. 2-HMPR mixing ratios showed a corresponding increase (e.g., from 0.12 ppb to 0.74 ppb on day 229) approximately 3–4 hours after the evening increase in MBO, possibly due to oxidation of MBO in the shallow evening boundary layer. A similar peak in 2-HMPR was not detected following the morning MBO peak, likely due to a daytime increase in vertical

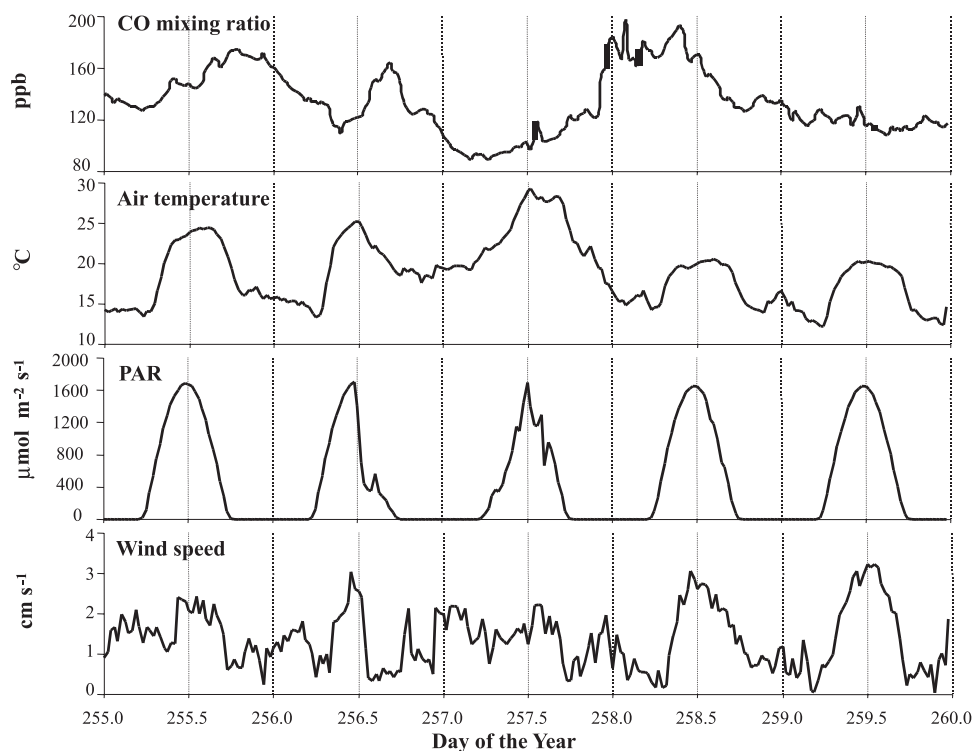


Figure 3. CO mixing ratios, photosynthetically active radiation (PAR), air temperatures, and wind speed as measured from 11–15 September 2000.

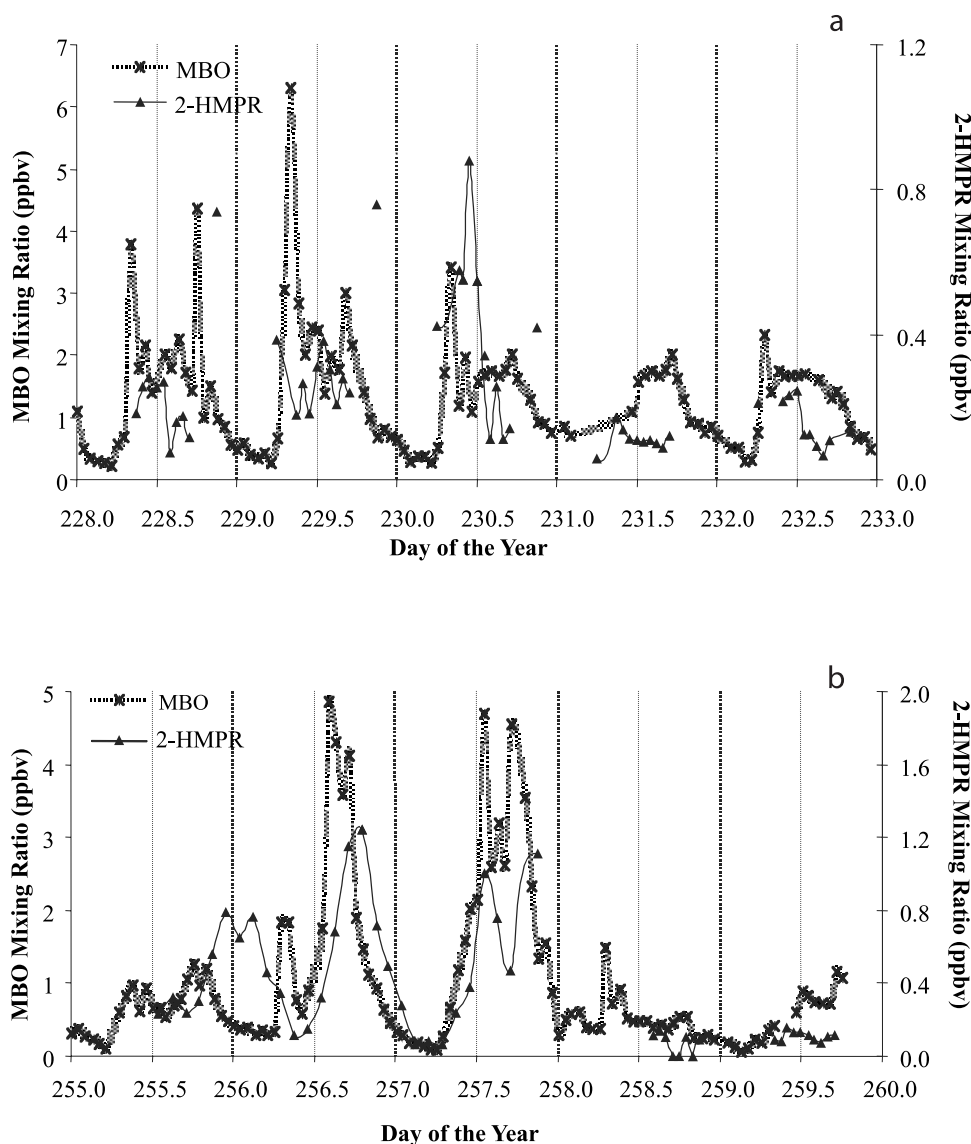


Figure 4. Mixing ratios of MBO and 2-HMPR measured from (a) 15–19 August and (b) 11–15 September 2000.

mixing, which diluted 2-HMPR before high levels could accumulate.

3.2.2. Product Ratios From Isoprene Photooxidation

[24] Models based on product and kinetic data predict that if isoprene were the predominant source, then the ratio of MVK to MACR would range from 1 at night to 2 during daytime [Montzka *et al.*, 1993]. Most measurements of MVK and MACR in air at rural sites where isoprene is presumed to be the dominant source agree with this prediction, and indicate a diurnal pattern that follows emissions of isoprene. The ratio is generally around 1.0 in early morning, when isoprene emissions are low, and at midday rises to around 2.0, reflecting an increase in isoprene emissions and OH radical oxidation of isoprene, MVK, and MACR. The ratio generally decreases at nighttime with decreased isoprene emissions and O₃ oxidation becoming the primary oxidation pathway [Montzka *et al.*, 1993, 1995; Stroud *et al.*, 2001]. The MVK/MACR ratio at the Blodgett Forest ranges from a low of 0.8 to 1.1 at night to a high of

1.7 to 1.9 during daytime, as discussed by Dreyfus *et al.* [2002]. The hourly averaged MVK/MACR ratios measured in this study are presented in Figure 5a. The mean ratio reached a maximum of 1.8 during the afternoon, and a minimum of 1.0 during nighttime/early morning, consistent with the previous studies.

[25] We also examined product ratios from MVK photooxidation (glycolaldehyde/methylglyoxal) and MACR photooxidation (hydroxyacetone/methylglyoxal) and for the third-generation photooxidation product glyoxal, to determine whether product ratios agreed with isoprene photochemical models. Hourly averaged hydroxyacetone/methylglyoxal, glycolaldehyde/methylglyoxal, and methylglyoxal/glyoxal are presented in Figures 5b, 5c, and 5d, respectively. A general comparison of theoretical and measured ratios between the second-generation isoprene reaction products is difficult because MBO photooxidation is an additional source of glycolaldehyde, methylglyoxal produced by both MVK and MACR photooxidation, and

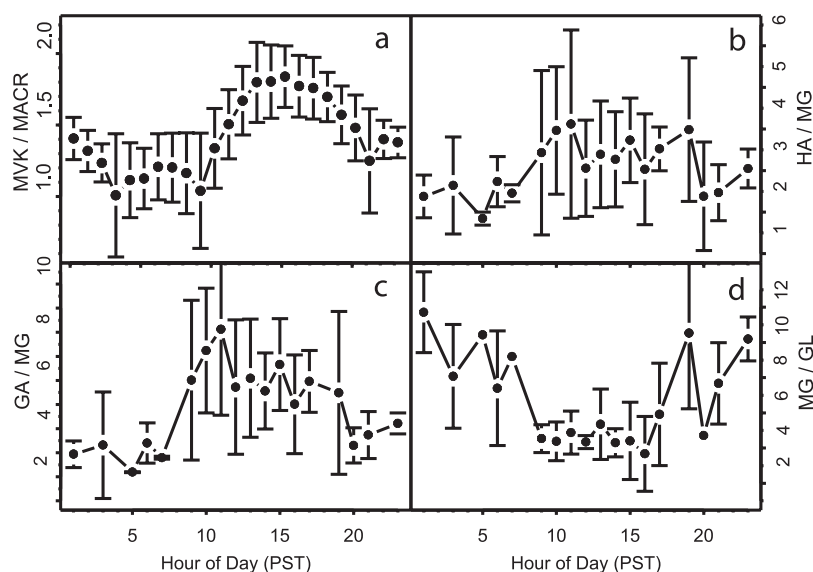


Figure 5. Diurnal cycles of the mean ratios of isoprene photooxidation products. (a) MVK/MACR. (b) Hydroxyacetone/methylglyoxal. (c) Glycolaldehyde/methylglyoxal. (d) Methylglyoxal/glyoxal. Error bars are 1 standard deviation.

all of the second- and third-generation isoprene photooxidation products can also be derived from photooxidation of anthropogenic sources. Nevertheless, we can obtain a steady state estimate of the theoretical ratios from yield and lifetime information provided in Figure 1 and Table 3, assuming that no other losses, such as deposition, occur. If isoprene were the sole source of MACR, MVK, hydroxyacetone, methylglyoxal, and glycolaldehyde, hydroxyacetone/methylglyoxal would be ~ 4.8 , and glycolaldehyde/methylglyoxal would be ~ 3 . Although it is unlikely that the second-, and third-generation isoprene reactions would reach steady state during the approximately 3 hours during transport from the source to the measurement site, mean measured values ranging from 2 during nighttime to 4 during daytime for hydroxyacetone/methylglyoxal, and ranging from 2 during nighttime to 8 during daytime for glycolaldehyde/methylglyoxal, included the steady state values. Both ratios increased during daytime, indicating faster loss of methylglyoxal to photolysis. The glycolaldehyde/methylglyoxal ratio exceeded the predicted steady state value during daytime, indicating additional sources of glycolaldehyde, which is expected since glycolaldehyde is also produced from MBO photooxidation. The methylglyoxal/glyoxal ratio reached ~ 10 during nighttime, and decreased to ~ 4 during daytime, while its theoretical steady state value is ~ 3 . The overall high ratio suggests either additional sources of methylglyoxal, lower yield of glyoxal from glycolaldehyde photooxidation than predicted, or that transport time from the isoprene source to the measurement site is insufficient for formation of third-generation isoprene photooxidation products. However, the decrease in the ratio during daytime is expected because of the more rapid photolysis of methylglyoxal [Plum *et al.*, 1983; Klotz *et al.*, 2001; Staffellbach *et al.*, 1995; Koch and Moortgart, 1998; Chen *et al.*, 2000]. The higher nighttime values could be a result of a significant source of methylglyoxal from ozone-isoprene chemistry. Overall, product ratios were consistent with isoprene photochemistry, but indicate addi-

tional sources of glycolaldehyde and methylglyoxal, and possibly hydroxyacetone.

3.2.3. Product Ratios From MBO Photooxidation

[26] The expected yield ratio for glycolaldehyde/2-HMPR under high- NO_x conditions is 2.1–3.2 [Alvarado *et al.*, 1999]. The $\cdot\text{OH}$ reaction rate constant for 2-hydroxy-2-methylpropanal has not been experimentally determined, but was estimated to be $2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by the method of Kwok and Atkinson [1995]. Using this reaction rate constant, and $1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for glycolaldehyde reaction with $\cdot\text{OH}$, with a yield ratio of 2.5, the steady state ratio of glycolaldehyde to 2-HMPR, in the absence of other sources, would be approximately 4.4. The measured glycolaldehyde/2-HMPR ratio showed a very strong diurnal cycle (Figure 6). In the morning, ratios of ~ 2 were observed, increasing to ~ 6 during late afternoon, and decreasing to ~ 1 at night. While the morning ratios are close to the yield ratio, higher than steady state daytime ratios are expected because glycolaldehyde is also a photooxidation product of isoprene. However, the sudden drop in the ratio during evening and low values at nighttime under northeasterly winds are inconsistent with the laboratory-derived yield ratio and indicate either faster loss of glycolaldehyde than 2-HMPR, or greater production of 2-HMPR than glycolaldehyde at night. Yet even a very significant glycolaldehyde deposition rate of 1 cm s^{-1} versus none for 2-HMPR cannot explain the low ratios observed at night. Nighttime mixing ratio increases of 2-HMPR could be due to transport from regions with higher 2-HMPR mixing ratios or due to reaction of MBO with O_3 , whose products are formaldehyde (29–46% yield), acetone (0–8% yield), and 2-HMPR (30–47% yield) [Alvarado *et al.*, 1999; Fantechi *et al.*, 1998b]. Of the two nights that measurements were taken, we did in fact observe an increase in 2-HMPR on day 256 between the hours of 01:00 and 03:00. We observed a similar, but smaller, increase in glycolaldehyde mixing ratios. Similar increases were not observed on the

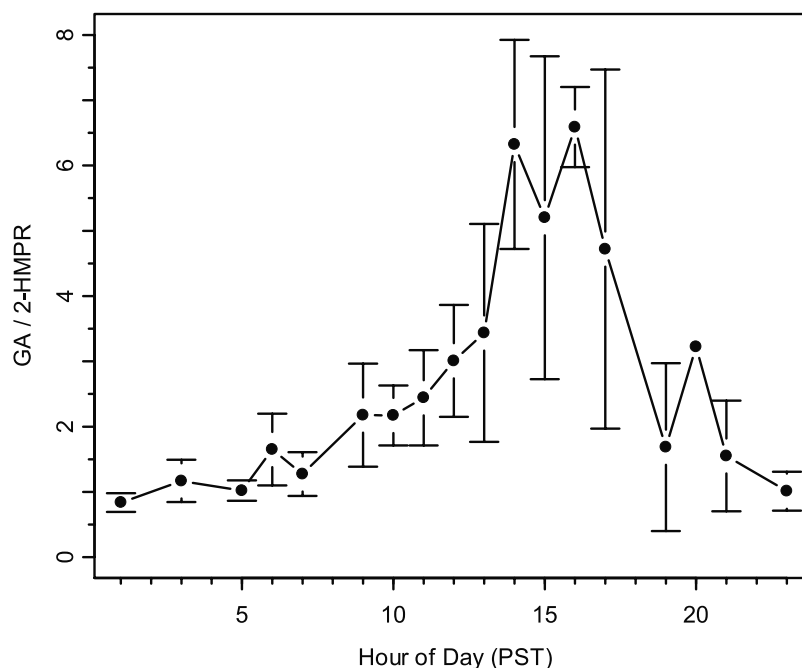


Figure 6. Diurnal cycles of the mean ratios of glycolaldehyde/2-HMPR. Error bars are 1 standard deviation.

night of 256/257. The increase in 2-HMPR concentrations could indicate the reaction of MBO + O₃ as a source of 2-HMPR. However, nighttime production of 2-HMPR through this reaction would not produce glycolaldehyde and, based on the reaction rate and yield data, less than 0.02 ppb hr⁻¹ 2-HMPR would have been produced during the night of days 255/256 [Alvarado *et al.*, 1999; Fantechi *et al.*, 1998a; Grosjean and Grosjean, 1994]. We thus consider transport a much more likely cause for our observations. During the calm and cool the night of days 255/256 (Figure 3) steady NE winds under a shallow boundary layer likely carried in significant amounts of 2-HMPR from daytime MBO photooxidation above the surrounding pine forest. A longer transport time from the surrounding forest to the NE of the measurement site, compared to the transport time from the forest to the SW of the site, would allow more time for MBO photooxidation to occur before 2-HMPR measurements are taken during NE winds, compared to SW winds. On the contrary, during the warm and turbulent night of days 256/257, an increase of 2-HMPR was probably not observed because 2-HMPR was diluted by cleaner air masses under a deeper boundary layer, as evident from low CO mixing ratios, before a significant evening/nighttime build-up could occur. This hypothesis, however, does not explain why the parallel increase in glycolaldehyde, which would also be produced from MBO photooxidation in the forests NE of the sampling site at concentrations 2–3 times higher than 2-HMPR, was not much higher.

[27] We analyzed the measured mixing ratio changes for glycolaldehyde after subtracting its “background” changes based on the regression equation from correlation with CO. Using the “background-subtracted” glycolaldehyde mixing

ratios, 2-HMPR and glycolaldehyde showed well-correlated two-hourly changes ($r^2 = 0.48$, $p < 0.1$) with a glycolaldehyde/2-HMPR slope of ~ 0.6 between 19:00 PST on day 255 and 05:00 PST on day 256. Again, this low ratio is not expected based on MBO photochemistry under high-NO_x conditions. As it is likely that the region east of our measurement site does not experience high-NO_x conditions, we suggest that, similar to isoprene photochemistry [Ruppert and Becker, 2000], the relative yields of glycolaldehyde and 2-HMPR from the MBO + ·OH reaction change as a result of the NO_x abundance. This could also explain the discrepancies between the MBO photooxidation product yields published by Ferronato *et al.* [1998], Alvarado *et al.* [1999], and Fantecchi *et al.* [1998b]. The latter group found substantially lower glycolaldehyde and acetone yields in a low-NO_x reaction system that allowed for significant RO₂ and HO₂ cross-reactions [Alvarado *et al.*, 1999]. According to our findings, these reactions may not significantly reduce the 2-HMPR yield. A potential explanation for our observations is a significant contribution (>20%) of initial ·OH attack to C₃ of MBO instead of C₄, as the former pathway would produce 2-HMPR but not acetone or glycolaldehyde [Fantechi *et al.*, 1998b]. This explanation is consistent with the reaction scheme presented by Alvarado *et al.* [1999], assuming that the decomposition of the alkyl peroxy radical produced after initial ·OH attack on C₄ is completely dominated by glycolaldehyde/acetone formation, as suggested by the author’s estimates of its decomposition and O₂ reaction rates. A reduced glycolaldehyde and acetone yield under low-NO_x conditions could then be accounted for by substantially faster RO₂ cross-reactions between the primary alkyl peroxy radicals that are formed after ·OH attack on C₃ (producing more formaldehyde and 2-HMPR) relative to the secondary alkyl

peroxy radicals that are formed after $\cdot\text{OH}$ attack on C_4 (producing less glycolaldehyde and acetone).

3.3. Identification of Common Factors

3.3.1. Factor Analysis

[28] In order to show more quantitative evidence for the hypothesis that the sources of glycolaldehyde, hydroxyacetone, and methylglyoxal at the Blodgett Forest are both biogenic and anthropogenic, we analyzed the data by factor analysis. Factor analysis is a statistical method that groups variables whose data show simultaneous and consistent variation, similar to analyzing numerous regression equations at one time. Similar methods have been found very powerful for determining the relationships of chemical species in the atmosphere in other studies [Buhr *et al.*, 1995; Lamanna and Goldstein, 1999; Lei *et al.*, 1996]. We performed factor analysis using the maximum likelihood method with varimax rotation. The maximum likelihood method allows the analyst to choose the number of common factors based on a hypothesis, and the varimax rotation produces more loadings close to 1 and 0, compared to direct methods, thus making the data easier to interpret [Child, 1990]. A factor loading close to 1 indicates strong correlation, whereas a factor loading close to 0 indicates weak or no correlation. We performed factor analysis on the entire data set as well as the daytime data only, which was defined as $\text{PAR} \geq 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$.

[29] We present results for factor analysis of MBO, isoprene, their photooxidation products, and CO on the entire data set in Table 4. The bottom two lines of the table display the “proportion of variation,” which is the amount of variation accounted for by grouping the particular compounds together in that factor, and the “cumulative variation,” which is the sum of the variation that is accounted for by all groups. Using either the entire data set or only daytime data, most of the variation (80% for entire data set; 84% for daytime data) was explained by the following 4 factors, which emerged after examining the results of the statistical analysis. The names assigned to these factors are: “biogenic emissions and photooxidation products” (factor 1); “anthropogenic photooxidation products” (factor 2), “mixed origin/short lifetime” (factor 3), and “unique biogenic photooxidation products” (factor 4). The analytes comprising factor 1 are methyl vinyl ketone, methacrolein, isoprene, MBO, CO and acetone. Glycolaldehyde, hydroxyacetone, CO and glyoxal were grouped in factor 2. Factor 3 was comprised of methylglyoxal, glyoxal, CO, and hydroxy acetone; and factor 4 of 2-HMPR and acetone, respectively.

[30] We state that compounds exhibit a strong loading if the loading strengths were ≥ 0.6 , and that the compounds exhibit weak loading if the loading strengths were ≤ 0.4 . Isoprene, MBO, MACR, and MVK loaded strongly in factor 1, with weak loadings of acetone and glycolaldehyde. The high loadings of MACR and MVK indicate that they are solely derived from photooxidation of isoprene. The anthropogenic tracer CO, glycolaldehyde, and hydroxyacetone loaded strongly, while glyoxal loaded weakly, in factor 2. These results indicate anthropogenic influences on glycolaldehyde and hydroxyacetone, and a weaker anthropogenic influence on glyoxal. Glyoxal and methylglyoxal loaded strongly in factor 3, with weaker loadings of their

Table 4. Results From Factor Analysis Using Entire Data Set

| Compound | Loadings (Values < 0.30 Omitted) | | | |
|-------------------------|----------------------------------|----------|----------|----------|
| | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
| Isoprene | 0.896 | | | |
| MBO | 0.682 | | | |
| MACR | 0.794 | | 0.365 | |
| MVK | 0.898 | | 0.308 | |
| Acetone | 0.459 | | | 0.634 |
| Glycolaldehyde | 0.389 | 0.824 | | |
| Hydroxyacetone | | 0.815 | 0.405 | |
| Methylglyoxal | | | 0.904 | |
| 2-HMPR | | | | 0.763 |
| Glyoxal | 0.282 | 0.427 | 0.710 | |
| CO | | 0.478 | 0.425 | 0.348 |
| Sum square loadings | 3.24 | 2.04 | 1.98 | 1.52 |
| Proportion of variation | 0.30 | 0.18 | 0.18 | 0.14 |
| Cumulative variation | 0.30 | 0.48 | 0.66 | 0.80 |

precursors (MVK and MACR), hydroxyacetone, and CO. Methylglyoxal and glyoxal likely loaded together because of similar loss processes. Both have short lifetimes due to rapid photolysis and reaction with $\cdot\text{OH}$ (Table 3). Weaker loadings of hydroxyacetone, MVK, and MACR likely occurred because all are precursors to glyoxal and methylglyoxal. The weak CO loading indicates additional influence from anthropogenic sources.

[31] When the entire data set was used, acetone and 2-HMPR loaded strongly in factor 4, indicating their common source, MBO. In the daytime data, 2-HMPR loaded strongly with MBO and isoprene, with weak loadings of acetone and glycolaldehyde. These results indicate that while the glycolaldehyde variability is more influenced by anthropogenic precursors and isoprene emissions, 2-HMPR is strongly influenced by its precursor during daytime. During the remaining times, 2-HMPR appeared to act more like acetone, indicating a common transport scheme for the two compounds from areas with intense MBO photooxidation.

3.3.2. Correlation of Products to Their Precursors

[32] In order to strengthen the conclusions reached by factor analysis, we analyzed correlations between the photooxidation products and their precursors. For $N = 48$, a 0.2% probability exists that a coefficient of determination (r^2) value of 0.2 or greater will occur for two unrelated variables. The full data set contains 99 points, and the daytime data set contains 48 points. The full data set was used to investigate correlations, unless otherwise indicated.

[33] Linear correlations of MVK and MACR with isoprene yielded r^2 values of 0.75 and 0.58, respectively. Correlations of these compounds with CO were ≤ 0.10 , indicating that they arose from isoprene photooxidation and were not significantly influenced by anthropogenic sources. CO correlation with glycolaldehyde, hydroxyacetone, methylglyoxal, and glyoxal yielded r^2 values of 0.38, 0.46, 0.39, and 0.17, respectively, indicating that, with the exception of glyoxal, each of these compounds was influenced by anthropogenic sources.

[34] We present multiple correlation plots for each second- and third-generation isoprene photooxidation product versus its expected precursor(s) and CO in Figure 7. For each product compound in Figure 7, we calculated the relative precursor and background contributions by using

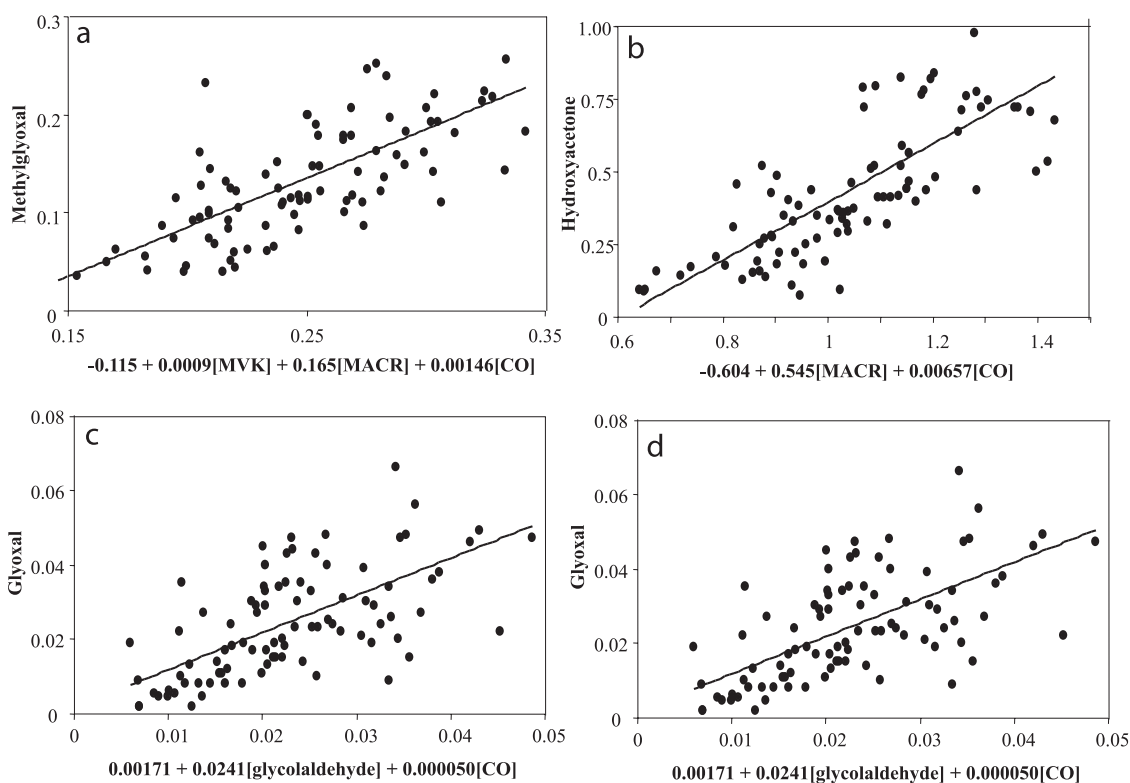


Figure 7. Correlations of (a) methylglyoxal, (b) hydroxyacetone, (c) glycolaldehyde, and (d) glyoxal, with their precursors, using the full data set.

the resulting regression equations, and assuming a regional background of 100, 0.1, 0.1, 0.15, and 0.2 ppb of CO, MACR, MVK, MBO, and glycolaldehyde, respectively, similar to *Schade and Goldstein* [2001]. Based on these regressions, we estimated that 44% of the glyoxal comes from glycolaldehyde photooxidation, 6% from other anthropogenic sources (CO), and 49% from other background. Of the 44% from glycolaldehyde, we calculated 13% from background, 18% anthropogenic, and 13% biogenic, by multiplying by the glycolaldehyde apportionment. The resulting source apportionment is presented in Table 5. According to the regression equations, and considering that $\geq 90\%$ of the background for all compounds other than glyoxal is associated with CO, anthropogenic sources are the dominant factor determining hydroxyacetone and glycolaldehyde mixing ratios. However, biogenic sources were still significant. In comparison, methylglyoxal and glyoxal appeared to be somewhat less influenced by anthropogenic sources but still significantly influenced by biogenic sources. These conclusions are consistent with the factor analysis results. The regression equations, however, bring out the greater influence of anthropogenic sources on the longer-lived compounds hydroxyacetone and glycolaldehyde. In all cases, a significant portion of the variability was unaccounted for, in particular for glyoxal. While one reason for this is the measurement uncertainty, more ambient measurements are necessary to draw further conclusions on the source apportionment of these compounds.

3.4. Sources of Anthropogenic Influence

[35] Because factor analysis and correlation data indicated anthropogenic influences for all of the multifunctional

carbonyls, we examined the potential anthropogenic sources. $\cdot\text{OH}$ reactions with alkylbenzenes and alkenes, and some ozone reactions are documented sources of glycolaldehyde, hydroxyacetone, glyoxal, and methylglyoxal [*Grosjean and Grosjean*, 1994; *Liu et al.*, 1999; *Seuwen and Warneck*, 1996; *Tuazon et al.*, 1998; *Yu et al.*, 1997]. $\cdot\text{OH}$ reactions that produce the multifunctional carbonyls measured in this study are listed in Table 6, along with the reaction rate constants, atmospheric lifetimes at $[\text{OH}] = 0.8 - 1.1 \times 10^7 \text{ molec cm}^{-3}$ [*Dillon et al.*, 2002; *Dreyfus et al.*, 2002], and yields of the multifunctional carbonyls. We assumed that $\cdot\text{OH}$ reactions dominate during the day, and thus did not include ozone reactions.

[36] We hypothesized that photochemical production of multifunctional carbonyls from aromatic and olefinic compounds emitted in Sacramento, the nearest urban center ($\sim 75 \text{ km}$ upwind), significantly contributed to the mixing ratios of the carbonyls measured at the Blodgett Forest. In order to test this hypothesis, we obtained nonmethane organic carbon (NMOC) data from the California Air

Table 5. Relative Contribution of Background, Biogenic, and Anthropogenic Sources of Multifunctional Carbonyls Measured at the Blodgett Forest, and the Coefficient of Determination From Multiple Regression Equation

| Compound | Relative Contribution to Measured Concentrations | | | r^2 |
|----------------|--|----------|---------------|-------|
| | Background | Biogenic | Anthropogenic | |
| Hydroxyacetone | 25% | 28% | 47% | 0.54 |
| Glycolaldehyde | 30% | 30% | 40% | 0.58 |
| Methylglyoxal | 37% | 28% | 34% | 0.51 |
| Glyoxal | 63% | 13% | 24% | 0.38 |

Table 6. Anthropogenic Precursors to Multifunctional Carbonyls, Precursor Reaction Rates, Lifetimes, and Product Yields

| Reaction | k_{OH} , $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ | Lifetime, hours ^b | Product Yields ^a | | | |
|---------------------------------------|---|------------------------------|-----------------------------|----------------|-----------|---------------|
| | | | Glycolaldehyde | Hydroxyacetone | Glyoxal | Methylglyoxal |
| Toluene + OH ^{c,d} | 6.0×10^{-12} | 4.2–5.8 | minor | minor | 0.08–0.15 | 0.08–0.25 |
| Xylenes + OH ^{c,d} | $1-2 \times 10^{-11}$ | 1.3–3.5 | minor | minor | 0.03–0.13 | 0.11–0.42 |
| Trimethylbenzenes + OH ^{c,d} | $3-6 \times 10^{-11}$ | 0.4–1.2 | minor | minor | 0.05–0.08 | 0.15–0.64 |
| Ethene + OH ^{d,e} | 8.5×10^{-12} | 3.0–4.1 | ND | – | – | – |
| Propene + OH ^{d,f} | 2.6×10^{-11} | 1.0–1.3 | – | ND | – | ND |
| 1,3-butadiene + OH ^{d,g} | 6.7×10^{-11} | 0.4–0.5 | ND | ND | ND | ND |

^aND = compound detected, but yield not determined.

^bOnly OH reaction considered at $[\text{OH}] = 0.8-1.1 \times 10^7 \text{ molec cm}^{-3}$.

^cYu *et al.* [1997].

^dAtkinson [1990].

^eOrlando *et al.* [1999].

^fTuazon *et al.* [1998].

^gLiu *et al.* [1999].

Resources Board in Sacramento, CA (05:00 PST) and in Folsom, CA (08:00 PST), for 3 August 1998 [Husar *et al.*, 2000]. The transport time from Sacramento to the Blodgett Forest is approximately 6–9 hours. Folsom lies between Sacramento and the Blodgett Forest, approximately 2–3 hours transport time from Sacramento [Dillon *et al.*, 2002]. We calculated the relative contribution of each compound to formation of each multifunctional carbonyl in Sacramento, Folsom, and Blodgett Forest, based on the measured ambient air mixing ratios at each site (measurements of ethene and propene at the Blodgett Forest are from 1997; Lamanna and Goldstein [1999]) and the $\cdot\text{OH}$ reaction rates and yields of multifunctional carbonyls from chamber studies. When yields were not available, we used 0.9 if the compound was known to be a “minor” product, and we used 0.5 if yield data were not available. Assuming that the data from Sacramento and Folsom are representative for summer conditions, the calculations predicted that formation of the multifunctional carbonyls will be dominated by the anthropogenic precursors in Sacramento. At Folsom, the anthropogenic precursors will still dominate methylglyoxal and glyoxal production and will contribute significantly to glycolaldehyde and hydroxyacetone, but isoprene will be more important for the latter two. At the Blodgett Forest, biogenic precursors will dominate production of all the multifunctional carbonyls. However, because the multifunctional carbonyls will be produced during transport from Sacramento to Blodgett Forest, and locally produced amounts will be transported away, the mixing ratios of the long-lived species hydroxyacetone and glycolaldehyde will mostly show the influence of the anthropogenic precursors at Blodgett Forest. Additionally, since anthropogenic precursors at Folsom were found to still dominate production of the shorter-lived species methylglyoxal and glyoxal, the measured mixing ratios of these compounds at Blodgett Forest will likely be dominated by anthropogenic precursors as well. However, the short-lived anthropogenic precursors will not likely correlate with the multifunctional carbonyls measured at Blodgett Forest, because these precursors will be largely depleted by the time the air mass reaches the measurement site. In fact, we did not find a significant correlation between the carbonyls and toluene measured at Blodgett Forest.

3.5. Comparison of Results to a Simple Kinetic Model

[37] We next examined product ratios predicted by a kinetic box model (AcuChem), which assumes a homoge-

neous, isothermal atmosphere. We compared the product ratios predicted by the model to product ratios measured in the early afternoon, to determine whether a model that included anthropogenic reactions would better predict product ratios than a model with only isoprene and MBO reactions. Two models were simulated. For both we used constant photolysis rates, ozone ($1.3 \times 10^{12} \text{ molec cm}^{-3}$) concentrations, and 0.2 cm s^{-1} deposition velocities for all compounds. In Model 1 we input a constant mixing ratio of 3 ppb isoprene and $1 \times 10^7 \text{ molec cm}^{-3} \cdot\text{OH}$ [Dillon *et al.*, 2002] for 1 hour of reaction, followed by 1 ppb isoprene and $9 \times 10^6 \text{ molec cm}^{-3} \cdot\text{OH}$ [Dreyfus *et al.*, 2002] for 1 hour, and then added a constant mixing ratio of 2 ppb MBO, 1 ppb isoprene, and $9 \times 10^6 \text{ molec cm}^{-3} \cdot\text{OH}$ for an additional 36 min. This model simulates a local source of MBO, and an isoprene source approximately 2–3 hours upwind [Lamanna and Goldstein, 1999; Dreyfus *et al.*, 2002]. Results of predicted product ratios versus ratios measured during mid-afternoon are presented in Table 7. The model predictions for MVK/MACR, hydroxyacetone/glycolaldehyde, hydroxyacetone/methylglyoxal, glycolaldehyde/methylglyoxal, and methylglyoxal/glyoxal were close to the measured values. However, the model underpredicted glycolaldehyde/2-HMPR values. Not surprisingly, the model overpredicted the value of 2-HMPR/acetone, because other acetone sources were not included in the model [Goldstein and Schade, 2000].

[38] For the second model, we incorporated reactions of anthropogenic compounds, including toluene, xylenes, trimethylbenzenes, ethene, propene, and 1,3-butadiene, using mixing ratios of each compound measured in Folsom, CA, on 3 August 1998 as a one-time input, and yield assumptions used in the previous section. We used a constant mixing ratio of 5 ppb isoprene (the average of 9.5 ppb measured at Folsom and 1 ppb measured at the Blodgett Forest) and $1 \times 10^7 \text{ molec cm}^{-3} \cdot\text{OH}$ for 2 hours of reaction, followed by 3 ppb isoprene and $1 \times 10^7 \text{ molec cm}^{-3} \cdot\text{OH}$ for 1 hour, 1 ppb isoprene and $9 \times 10^6 \text{ molec cm}^{-3} \cdot\text{OH}$ for another hour, and finally 1 ppb isoprene, 2 ppb MBO, and $9 \times 10^6 \text{ molec cm}^{-3} \cdot\text{OH}$ for 36 min. The results from this model agree well with experimental results for hydroxyacetone/glycolaldehyde, hydroxyacetone/methylglyoxal, and glycolaldehyde/2-HMPR (Table 7). Using anthropogenic compounds measured upwind of the measurement site helped to explain somewhat amplified concentrations of hydroxyacetone relative to glycolaldehyde and methylglyoxal (although these were slightly overpredicted), and highly amplified concentrations of glycolalde-

Table 7. Comparison of Measured Product Ratios to Product Ratios Predicted by a Simple Kinetic Model

| Products | Product Ratio | | |
|----------------|----------------------|----------------------|---|
| | Model 1 ^a | Model 2 ^b | Measurements at 14:00 LST, Mean ± S.D. |
| MVK | 1.8 | 3.1 | 1.8 ± 0.3 |
| MACR | | | |
| Hydroxyacetone | 0.52 | 0.89 | 0.59 ± 0.12 |
| Glycolaldehyde | | | |
| Hydroxyacetone | 2.5 | 4.0 | 3.3 ± 1.2 |
| Methylglyoxal | | | |
| Methylglyoxal | 4.2 | 2.0 | 4.3 ± 0.8 |
| Glyoxal | | | |
| Glycolaldehyde | 4.8 | 4.5 | 5.6 ± 1.8 |
| Methylglyoxal | | | |
| Glycolaldehyde | 3.9 | 7.0 | 6.3 ± 1.6 |
| 2-HMPR | | | |
| 2-HMPR | 0.59 | 0.59 | 0.07 ± 0.04 |
| Acetone | | | |

^aModel 1: 3 ppb isoprene and 1×10^7 molec cm^{-3} ·OH for 1 hour; followed by 1 ppb isoprene and 9×10^6 molec cm^{-3} ·OH for 1 hour; then 1 ppb isoprene, 2 ppb MBO, and 9×10^6 molec cm^{-3} ·OH for 36 min.

^bModel 2: anthropogenic compounds as measured at Folsom, CA, used as one-time input; 5 ppb isoprene and 1×10^7 molec cm^{-3} ·OH for 2 hours; followed by 3 ppb isoprene and 1×10^7 molec cm^{-3} ·OH for 1 hour; 1 ppb isoprene and 9×10^6 molec cm^{-3} ·OH for 1 hour; then 1 ppbv isoprene, 2 ppb MBO, and 9×10^6 molec cm^{-3} ·OH for 36 min.

hyde relative to 2-HMPR. However, this model overpredicted MVK/MACR, possibly due to unrealistic reaction conditions, such as too high and too early injection of isoprene or the assumption of high- NO_x conditions [Dreyfus *et al.*, 2002]. The second model also underpredicted methylglyoxal/glyoxal, whereas the methylglyoxal/glyoxal ratio predicted by Model 1 (isoprene and MBO chemistry only) was closer to the measured value. This result, along with the low mixing ratios of glyoxal measured at Blodgett Forest, argues that these compounds, particularly glyoxal, were not influenced as much by anthropogenic reactions, in agreement with results from factor analysis and regression analysis. More accurate data on the yields of glyoxal and methylglyoxal from anthropogenic photooxidation reactions might change the methylglyoxal/glyoxal ratio predicted from the second model to a value closer to that actually measured.

[39] Overall, the results from these simple models confirm the substantial anthropogenic influence on glycolaldehyde and hydroxyacetone mixing ratios measured at Blodgett Forest, and suggest that methylglyoxal and glyoxal were removed from the atmosphere rapidly enough that the anthropogenic influence on their mixing ratios was less important.

4. Conclusions

[40] We measured CO, MBO and its photooxidation products 2-HMPR, glycolaldehyde, and acetone, and isoprene and its first-, second-, and third-generation photooxidation products MACR, MVK, glycolaldehyde, hydroxyacetone, methylglyoxal, and glyoxal, above a ponderosa pine plantation, hourly during daytime for 2 weeks in the summer of 2000. Nighttime measurements were also collected during 2 nights. 2-HMPR correlated with its precursor during daytime, but was correlated more strongly with acetone at night, indicating either nighttime emissions or more likely, transport from areas with higher 2-HMPR mixing ratios that are produced, along with acetone, from MBO photooxidation in the surrounding pine forest. Simultaneous 2-HMPR and glycolaldehyde variations under a

stable boundary layer during the night of days 255/256 indicated a common source, but the glycolaldehyde/2-HMPR ratios were not in accord with published yield ratios from MBO under high- NO_x conditions, suggesting a different mechanism that produces 2-HMPR but less glycolaldehyde. Since glycolaldehyde and acetone are coproduced, a lower acetone yield from MBO photooxidation under low- NO_x conditions may have to be taken into account in tropospheric chemistry models. However, to support this finding, more ambient measurements of 2-HMPR and chamber studies with differing NO_x -conditions are needed.

[41] Glycolaldehyde and hydroxyacetone mixing ratios were strongly influenced by anthropogenic sources, as determined by factor analysis, regression analysis, and comparison to a kinetic model. Their relatively long lifetimes (particularly that of hydroxyacetone) indicate that they might be important for regional or even global photochemistry. As both compounds have ubiquitous anthropogenic and biogenic sources, more research into their tropospheric abundance and possible influences on radical chemistry are warranted.

[42] In comparison, lower correlation of methylglyoxal and glyoxal with CO, and agreement of the measured methylglyoxal/glyoxal ratio with the ratio predicted from a model that considered only isoprene photochemistry, suggest a smaller anthropogenic influence on these compounds. The disagreement in the methylglyoxal/glyoxal ratio when anthropogenic compounds from a nearby urban center were included in the model emphasizes the need for accurate reaction rates, product yields, and data on other loss processes for these compounds. In the future, it would also be useful to measure the multifunctional carbonyl compounds in Sacramento, the nearest urban area, and at several sites during transport to Blodgett Forest, in order to better characterize production, transport, dilution, and loss processes.

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