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## Canopy and leaf level 2-methyl-3-buten-2-ol fluxes from a ponderosa pine plantation

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### Abstract

Canopy and leaf level 2-methyl-3-butene-2-ol (methylbutenol, MBO) emissions were measured from a ponderosa pine plantation in the Sierra Nevada mountains from July to October 1998. Canopy scale fluxes were measured using a gradient approach, leaf level fluxes used a flow-through chamber. Emissions were dependent on ambient light and temperature levels and showed a diurnal cycle very similar to isoprene in deciduous forests. Maximum fluxes occurred between 1000 and 1700 h with an average of  $2 \text{ mg C m}^{-2} \text{ h}^{-1}$  in July and August, which equaled approximately 0.3–0.5% of the simultaneously measured gross carbon uptake. MBO mixing ratios and fluxes over the pine plantation were also measured with a relaxed eddy accumulation (REA) system operated during part of our measurement campaign (Baker et al., 1999 *Journal of Geophysical Research*, in press). Mixing ratios measured by both systems were in good agreement but the gradient approach estimated MBO fluxes twice as high than the REA approach. Leaf level investigations revealed a seasonal cycle in basal emission rate (emissions at  $1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$  PAR and  $30^\circ\text{C}$ ) with a maximum in August, decreasing towards the end of the season. We developed an emission model to scale MBO fluxes from the leaf level to the ecosystem level based on the well-known isoprene algorithm. The model estimates are substantially lower than our gradient flux measurements, and match better with the REA flux measurements, and we conclude that the gradient approach overestimated MBO fluxes at this site. Comparing seasonal changes of measured with modeled fluxes showed a pattern of basal emission rates similar to those observed at the leaf level, and the basal emission rate was related to daytime air temperatures. While MBO contributes substantially to local photochemistry and its oxidation contributes significantly to the regional acetone budget, the latter probably does not represent a significant global source of atmospheric acetone. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Volatile organic compounds; MBO; Emission model; Seasonality; Acetone source

### 1. Introduction

Atmospheric volatile organic compounds (VOCs) are important in tropospheric air chemistry, especially as precursors of tropospheric ozone (McKeen et al., 1991; Fehsenfeld et al., 1992; Chameides et al., 1988). In the planetary boundary layer, they constitute a significant portion of OH reactivity, and it has been shown that

biogenically emitted hydrocarbons can dominate the oxidative capacity of the lower troposphere in forested regions such as the Sierra Nevada mountains (Lamanna and Goldstein, 1999). Most studies on VOC emissions from terrestrial vegetation have focused on isoprene and monoterpenes, although recent reports on oxygenated VOCs (OVOCs) suggest significant impact on regional and global photochemistry (Arey et al., 1991; Goldan et al., 1993; Ciccioli et al., 1993; König et al., 1995; Fall et al., 1999).

Several recent studies have focused on 2-methyl-3-buten-2-ol (methylbutenol or MBO) as an abundant

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atmospheric OVOC (Goldan et al., 1993; Harley et al., 1998; Lamanna and Goldstein, 1999; Baker et al., 1999). It accounted for approximately 20% of local OH reactivity during the day in the Sierra Nevada mountains (Lamanna and Goldstein, 1999). Oxidation of MBO by OH has a 50% yield of acetone (Ferronato et al., 1998), a long-lived atmospheric constituent whose further oxidation in the atmosphere significantly contributes to mid-tropospheric HO<sub>2</sub> production (Singh et al., 1994, 1995; Wennberg et al., 1998). The main MBO emitters seem to be pine species of western North America (Harley et al., 1998), and their instantaneous emission rate can be described by an emission algorithm similar to that for isoprene. Though only a limited number of plant species investigated emit MBO, its emission may play an important role in regional photochemistry and could contribute a significant source of acetone to the atmosphere (Harley et al., 1998; Ferronato et al., 1998; Goldstein and Schade, 2000).

In this paper, we describe canopy scale MBO emission measurements carried out above a ponderosa pine plantation in the Sierra Nevada mountains from July to October 1998. The flux similarity approach was used to calculate MBO fluxes from simultaneous measurements of latent heat flux, and vertical gradients of H<sub>2</sub>O and MBO. Leaf level measurements during the same period, and local biomass data were used to create an emission model for MBO, for comparison with canopy scale flux data. This, and our previous work (Lamanna and

Goldstein, 1999), show that regional VOC air chemistry in the Sierra Nevada mountains is dominated by biogenic hydrocarbon emissions, from ecosystems on the western slope and transported up the mountain range during daytime.

## 2. Site description

Hydrocarbon measurements were made continuously above a ponderosa pine plantation at one-hour intervals. The measurements were part of a larger field experiment at the Blodgett Forest Research Station (38°53', 42.9° N, 120°37', 57.9° W, 1315 m elevation) (Lamanna and Goldstein, 1999; Goldstein et al., 2000). The field setup in 1998 is shown in Fig. 1. The tower fetch extends approximately 200 m to the southwest during daytime (upslope wind direction), and at night winds blow downslope from the east (Fig. 2). The pine trees were even aged (7–8 years old), were 3–5 m tall, and the plantation had an open canopy. Approximately 0.12 ponderosa pine trees are found per square meter of the fetch area, and their ground cover was estimated to be 30% in 1997 (Goldstein et al., 2000). Among the pine trees were a few individuals of douglas fir (*Pseudotsuga menziesii*), white fir (*Abies concolor*), black oak (*Quercus kelloggii*), and incense cedar (*Calocedrus decurrens*). The understory was dominated by manzanita (*Arctostaphylos* spp.) and white-thorn (*Ceanothus cordulatus*). The site is characterized by

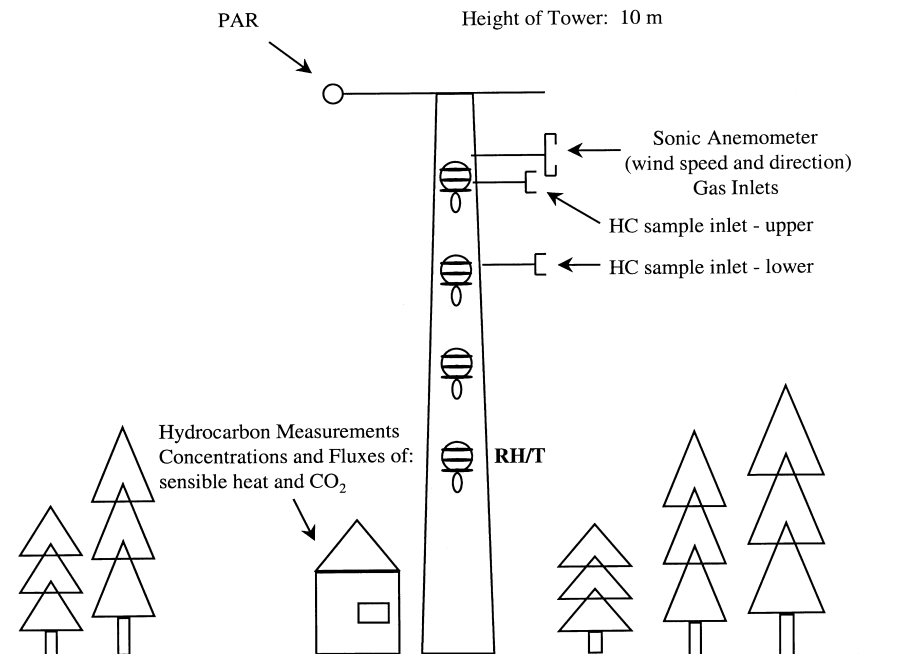


Fig. 1. Measurement setup.

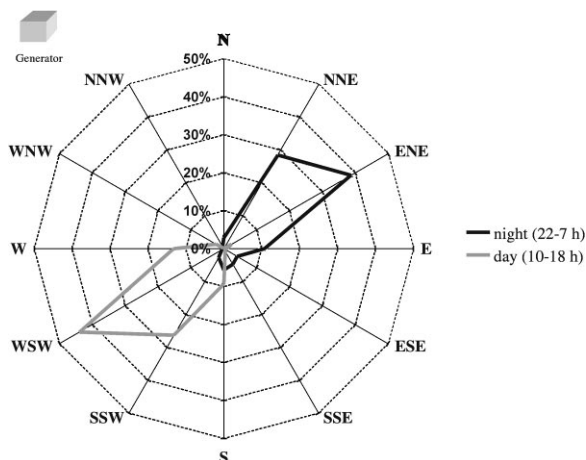


Fig. 2. Wind direction at the Blodgett Forest tower site for the days 190–250, 1998. Also indicated is the position of the generator.

a Mediterranean climate with predominant rainfall between September and May, and almost no rain during the summer months.

### 3. Measurement systems

#### 3.1. Canopy scale

VOCs containing up to 10 carbon atoms were quantified using a dual channel GC-FID with two identical polyethylene-glycol columns (DB-WAX<sup>®</sup>, 60 m, 0.32 mm ID, 0.5  $\mu\text{m}$  film, later: RTX-WAX, widebore). Two aliquots (300 ml) taken from sampling lines approximately 2.5 and 4.5 m above the tree height ( $\sim 4$  m) were preconcentrated onto Silcosteel<sup>®</sup> micro-traps filled sequentially with glass beads, Carboxpack B, and Carboxieve SIII, embedded in a cold block ( $-25^{\circ}\text{C}$ ) and each equipped with an isolated resistance wire for rapid sample desorption. A ppm-standard of methylbutenol in UHP  $\text{N}_2$  (Scott-Marrin Inc., Riverside, CA) was diluted automatically into the sample stream at a controlled flow rate every 15 or 30 h. No significant differences could be noticed between standard additions done in front of the inlet filters or down the sampling line inside the temperature-controlled shed, housing the instrument. The relative standard deviation of the calculated response factors was 5%. Standard additions showed no systematic changes of the FID response during the whole measurement period. However, the accuracy of our MBO measurements was strongly influenced by the chromatography. All chromatograms were integrated manually to assure proper peak identification and peak area. MBO generally eluted as a broad peak from the WAX column due to both trapping and desorption of water and the slow

degradation of the WAX columns. Water was not removed from the sample as it was necessary to prevent MBO to isoprene conversion (Harley et al., 1998; Lamanna and Goldstein, 1999). Therefore, the error in calculating the MBO gradient between the two sampling levels is most probably bigger than indicated by the variation of the response factor. We estimate from measurements taken from the same height level every 5 h (NULL gradients), that gradients  $> 0.2$  ppb MBO could be distinguished at the 95% confidence level throughout most of the measurement campaign. Data acquisition and instrument control were achieved with HP Chemstation software automated sequences and a CR10 data logger (Campbell Scientific, Logan, Utah). The instrument has been fully described in Lamanna and Goldstein (1999) and Schade et al. (1999).

We used the flux similarity approach for determining MBO fluxes at the canopy scale (Goldstein et al., 1996, 1998).  $K$ , the eddy diffusivity, was computed by dividing measurements of sensible and latent heat flux (both by eddy covariance using a sonic anemometer) by vertical temperature and water gradients, measured with shielded and aspirated T/RH sensors (Vaisala Inc., Woburn, MA).  $K$  was then multiplied by the MBO gradient to calculate the MBO flux. Values for  $K$  were only used when temperature or water gradients were larger than two standard deviations of their agreement during an intercalibration of the sensors, and negative values of  $K$  were discarded. Measured MBO gradients were corrected for their NULL gradients taken every fifth measurement. The typical daytime accuracy of a single flux calculation based on the uncertainties of the individual measurements used to calculate it is estimated to be  $\pm 70\%$  (see Goldstein et al., 1996 for details). Calculated eddy diffusivities were, on average, slightly higher using temperature gradients and sensible heat flux instead of water gradients and latent heat flux, especially in the morning (slope = 0.9,  $r^2 = 0.6$ ,  $N = 534$ ). We used MBO fluxes calculated from water gradients and latent heat flux throughout this paper.

#### 3.2. Leaf scale

Leaf level MBO emissions from 8 trees inside the tower fetch were measured with a LiCor 6400 portable gas exchange system (LiCor Inc., Lincoln, NB) and a Voyager portable gas chromatograph equipped with a photoionization detector (PE Photovac Inc., Norwalk CT) according to methods described in detail in Lerda and Keller (1997). Two fascicles (6 needles) were clamped into the LiCor chamber and held at  $30^{\circ}\text{C}$  and  $1500 \mu\text{mol m}^{-2} \text{s}^{-1}$  PAR. The chamber was flushed at  $160 \text{ ml min}^{-1}$  with ambient air scrubbed of hydrocarbons by passage through an activated charcoal filter, and a 0.5 ml aliquot of the exiting air injected onto a methyl silicone column. The detection limit of this system was

5 ppb. Chamber air typically had mixing ratios between 10 and 100 ppb MBO. Total leaf area inside the chamber was calculated from caliper measurements made on each needle, and specific leaf area (based on all-sided LAI) was calculated after drying excised needles at 60°C for 72 h. Fluxes were scaled to the leaf dry weight. Details of the method and the results of an in depth study of MBO emission variability as affected by light, temperature, needle age and the seasonality of emissions will be reported elsewhere (Gray et al., in preparation).

## 4. Results

### 4.1. Canopy scale measurements

MBO mixing ratios in the atmosphere above the ponderosa pines, as depicted in Fig. 3a, were slightly higher than during approximately the same time period in 1997 (Lamanna and Goldstein, 1999), the increase most probably attributable to the increased biomass at the site. The MBO mixing ratios in both years were relatively constant during the hours of full sunlight, and were significantly higher in the early morning and evening when atmospheric vertical mixing was reduced, yet emissions continued. Mixing ratios were highest in July and August, then decreased through September and October, as shown in Fig. 3b.

The mean MBO flux for the days 193–215 is shown in Fig. 4. Emissions began at sunrise, increased as light levels and air temperature increased, and ended around sunset. Considerable variability was observed during the daytime hours, and the average MBO flux between 10:00 and 17:00 hours was  $2.1 \text{ mg C m}^{-2} \text{ h}^{-1}$ . This is roughly two times higher than the fluxes calculated by Baker et al. (1999) at the same site for a time period within part of the data set presented here. An intercomparison of our calibration gas with the one used by Baker et al. (1999) from the same manufacturer showed excellent agreement, and both data sets showed a very similar diurnal mixing ratio variation (Fig. 3a; B. Baker, pers. comm.).

MBO fluxes from ponderosa pine are strongly dependent on light and temperature changes (Harley et al., 1998), and emissions have been modeled using the algorithms developed for isoprene by Guenther et al. (1993) (Baker et al., 1999). The dependencies of our own, aggregated canopy scale MBO flux measurements on light and air temperature are shown in Figs. 5a and b for the same period as in Figs. 3 and 4. Mean MBO fluxes rose sharply with incident PAR, with only slight increases for  $\text{PAR} > 1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ , somewhat smaller than the canopy leaf level results obtained in 1997 at the same site (Harley et al., 1998). Mean MBO fluxes also rose sharply with temperature. The nearly linear increase is consistent with results obtained at the leaf level in 1997 (Harley et al., 1998). No significant improvement in correlation

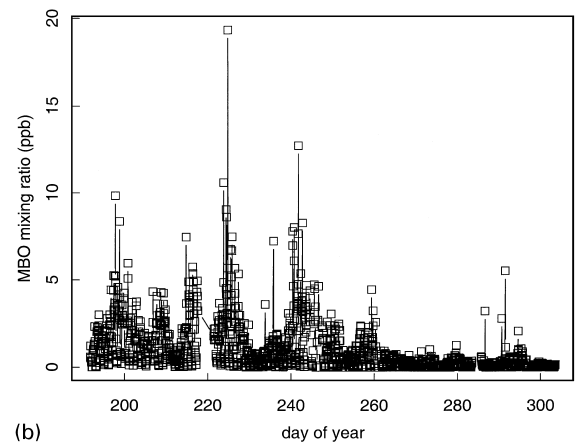
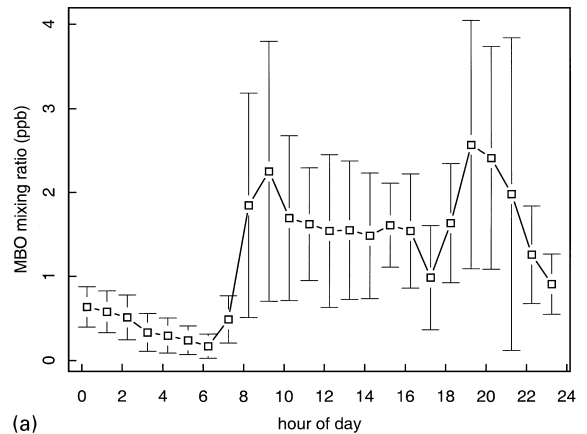


Fig. 3. (a) Mean MBO mixing ratios ( $\pm 1$  SD) for the days 193–215 (upper level); (b) MBO mixing ratios (lower level) throughout the 1998 measuring campaign.

was found when fluxes were plotted against average leaf temperature, measured at three needles on a single tree near the tower, instead of air temperature.

We compared measured MBO fluxes versus net ecosystem exchange of carbon (NEE) measured by the eddy covariance method at the top of the tower, as well as with gross primary productivity ( $\text{GPP} = \text{NEE} - \text{soil and bole respiration}$ ; numbers in parentheses). Carbon lost as MBO from the ecosystem varied between 0 and 2 (0 and 1)%, with maximum loss in July and August. On average 0.55 (0.3)% of carbon fluxes were lost as MBO during the daylight hours 10:00–17:00 from July to September, dropping to only 0.1 (0.05)% by the end of October.

### 4.2. Leaf level measurements and emission model

Leaf level MBO fluxes were investigated until mid-October 1998. MBO emissions were significant from current year needles as soon as they were long enough to

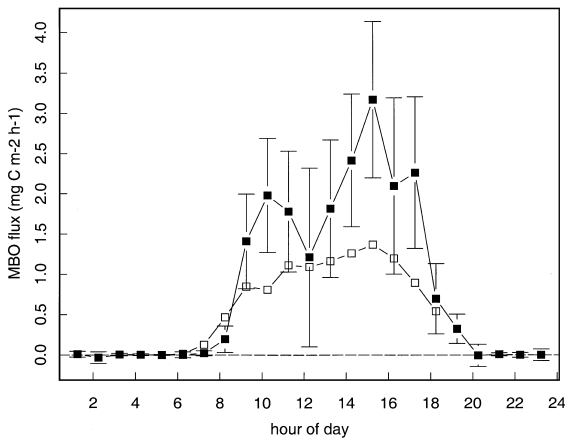
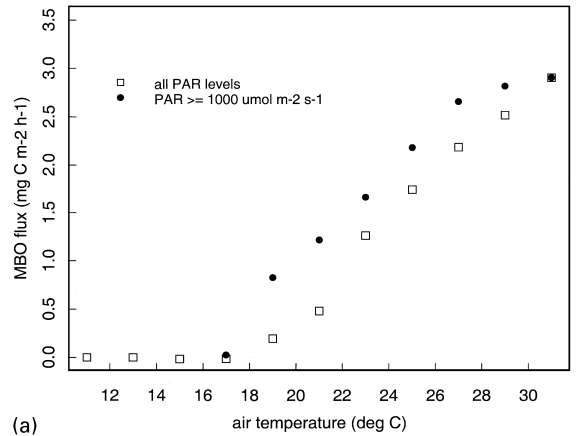


Fig. 4. Mean diurnal cycle of MBO fluxes for the same period as in Fig. 3a. Error bars are 90% confidence levels, indicating a high variability. Open symbols show the respective modeling results.

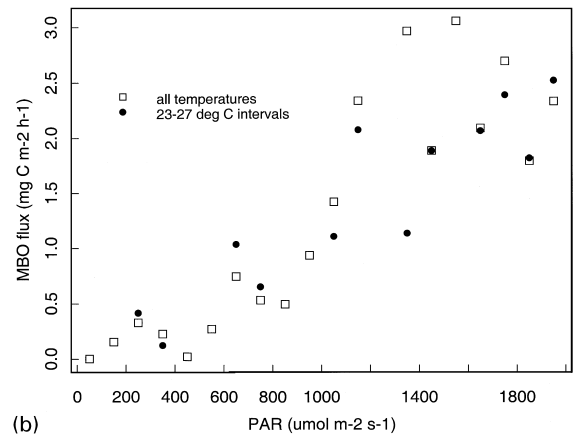
be clamped inside the leaf cuvette ( $\sim 3.5$  cm). Highest emissions were measured from current year and one-year old needles, and the maximum mean basal emission rate (emissions at  $30^\circ\text{C}$  and  $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$  PAR) was  $18 \mu\text{g C g}^{-1} \text{h}^{-1}$ , which was significantly lower than the  $25 \mu\text{g C g}^{-1} \text{h}^{-1}$  found by Harley et al. (1998). Basal emissions showed a seasonal cycle with a maximum in August when both ambient temperatures and ecosystem carbon uptake peaked. One-year-old needles showed slightly lower MBO emissions than current year needles, and two-year-old needles showed on average 50% lower MBO emissions on a mass basis. Data on the variation of the basal emission rate are summarized in Fig. 6 (Gray et al., in preparation).

For the emission model, we assumed relative emission rates to be 10 : 9 : 5 for current to one-year to two-year-old needles, stable throughout the season. At the start of the canopy level measurements on July 12, 1998, current year needles were still developing due to a preceding cold and wet spring. The initial LAI distribution was approximately 20% current year needles, 45% one-year and 35% two-year-old needles. However, the new needles developed quickly throughout July and August and kept growing more slowly thereafter until the fall. We modeled the new leaf biomass based on leaf elongation measurements by a linear function from measurement start to the first rain event at the beginning of September, achieving 85% of final leaf elongation. Thereafter, modeled leaf elongation slowed down, reaching 100% at the beginning of October. Two-year-old foliage had mostly fallen by the end of October, and was modeled with a linear function from the beginning of October down to zero by the end of the measurement season.

We estimated total LAI for each needle age class from June until September 1998 from allometric measure-



(a)



(b)

Fig. 5. Temperature dependence (a) and PAR dependence (b) (aggregated into  $2^\circ\text{C}$  or 100 PAR units) of the measured MBO fluxes for the same period as in Fig. 3a.

ments, and light measurements using an LAI-2000 plant canopy analyzer with specific corrections for ponderosa pine (Goldstein et al., 2000). LAI and derived biomass estimates are summarized in Table 1. Using an average specific leaf weight of  $100$  and  $120 \text{ g m}^{-2}$  for current-year and older needles (based on all-sided LAI), respectively, total ponderosa pine needle biomass increased from approximately  $534$  (start) to  $774$  (max) then decreased to  $582 \text{ g m}^{-2}$  (end) in the tower fetch area.

Model MBO emissions were calculated using the isoprene emission algorithm outlined by Guenther et al. (1995)

$$F = \varepsilon D \gamma \delta. \quad (1)$$

The total flux ( $F$ ) is calculated from the emission potential ( $\varepsilon$ ), the foliar density ( $D$ ), a light and temperature emission activity factor ( $\gamma$ ), and other emission activity

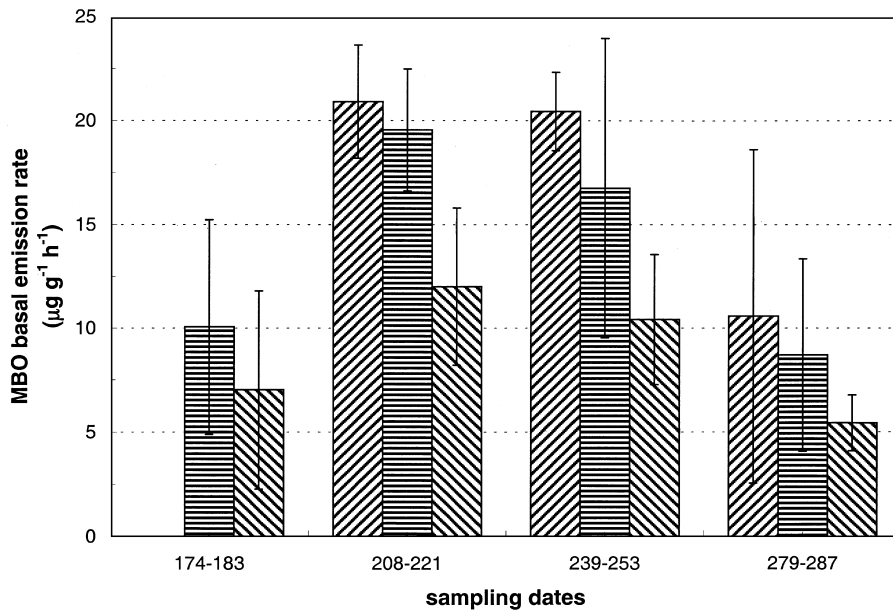


Fig. 6. Influences of season and leaf age on the basal emission rate (at 30°C and 1500  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) of several ponderosa pine trees (Gray et al., in preparation). Bars from left to right represent current-year, one-year, and two-year old needles, respectively. Error bars represent 1 SD.

Table 1  
MBO emission model input parameters

	$\varepsilon \times \delta$ ( $\mu\text{g C g}^{-1} \text{h}^{-1}$ )			$D$ ( $\text{g m}^{-2}$ )	LAI ( $\text{m}^2 \text{m}^{-2}$ ) <sup>a</sup>		
	Age 0	Age 1	Age 2		Age 0	Age 1	Age 2
Beginning (day 191)	18	16	9	534	0.9	2.1	1.6
Maximum	18	16	9	774	3.3	2.1	1.6
End (day 303)	18	16	9	582	3.3	2.1	0
relative error (%)	30	40	40	10	25	20	30

<sup>a</sup>LAI represents all-sided LAI. For projected LAI divide by 3.3 (Johnson, 1984).

factors ( $\delta$ ). We present the respective factors chosen in the model calculation at this field site in Table 1. Values for the factors in  $\gamma$  were taken from Harley et al. (1998). Air temperature at the lowest tower measurement height was used to approximate leaf temperature. Sunlit and shade leaf PAR for each age class were estimated by the light attenuation model described in Guenther et al. (1995) using measured above-canopy PAR values. Diffuse and direct PAR were estimated from measured total PAR and the solar elevation angle,  $B$ , by

$$\text{PAR}_{\text{dir}} = \text{PAR} \tau^{1/\sin(B)} \sin(B),$$

$$\text{PAR}_{\text{diff}} = \text{PAR} - \text{PAR}_{\text{dir}}. \quad (2)$$

For simplicity, the atmospheric transmissivity,  $\tau$ , was estimated to be 0.7, constant throughout the measurement period.

As the plantation had an open canopy with little if any inter-tree shading, light attenuation was modeled for an average ponderosa pine tree and then scaled by the ponderosa pine ground coverage. As a new age class of needles grows on the branch edges of the pine tree, light attenuation was modeled in three layers “outside-in” instead of “top to bottom”. Older needle age classes are “inside” the tree and receive only light attenuated by the younger age classes. Hence, light attenuation was modeled assuming that the tree has three vertical instead of horizontal layers, each consisting of one needle age class with its estimated LAI corrected for the average ponderosa pine ground coverage. Then, the plantation was treated as a homogeneous collection of individual trees. It should be noted that the particular light attenuation model used (Guenther et al., 1995) has not been optimized for conifers, in particular, it has not been

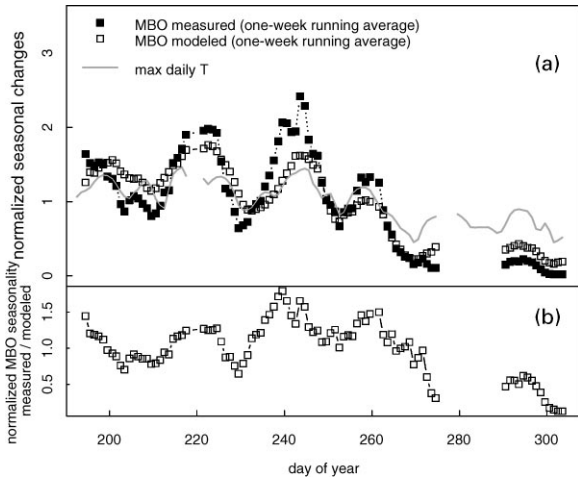


Fig. 7. (a) Normalized seasonal changes of measured and modeled MBO fluxes, and maximum air temperature; (b) Normalized ratio of measured and modeled fluxes, as indicator of seasonality.

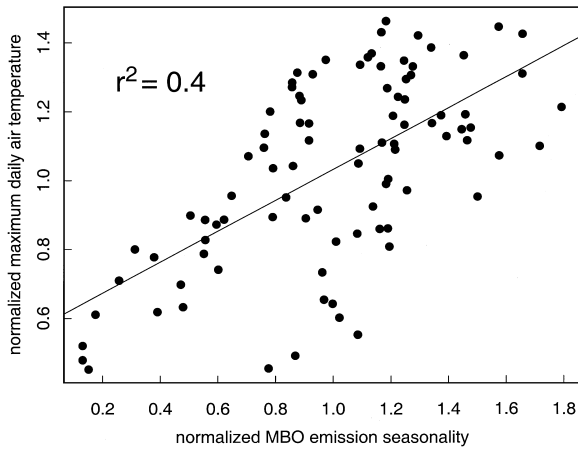


Fig. 8. Correlation between normalized ratio of measured and modeled MBO fluxes with daily maximum temperature.

adjusted for the “clumping” of needles as in ponderosa pine. It might therefore underestimate the light levels “inside” the tree.

Results of the model versus measurement comparison are shown in Fig. 4 for the July period. The model underestimates MBO emissions during July, August and September, but showed better agreement during October. For the July comparison shown in Fig. 4, the model agrees well with data collected with an REA system by Baker et al. (1999) during a period bracketed by our measurements (note that the model emissions of Baker and coworkers were higher, were based on lower biomass estimates, and did not take the openness of the canopy into account).

To investigate the seasonality of MBO fluxes for the plantation, we compared the normalized seasonal changes of the measured and modeled fluxes to the recent ambient temperature history (Petron et al., 1999; Sharkey et al., 1999). We calculated a running 2-day average maximum air temperature, and normalized to the seasonal mean value. Fig. 7a shows that the measured MBO fluxes deviated more from the mean compared to the modeled fluxes. The ratio of normalized measured and modeled fluxes (Fig. 7b) was calculated as an indicator of seasonality (Goldstein et al., 1998). This seasonality was correlated with ambient air temperatures (Fig. 8) and can be compared to the leaf level results shown in Fig. 6. While the overall trend is very similar, the fine structure can only be addressed after a more detailed analysis of the leaf level data (Gray et al., in preparation).

## 5. Discussion

### 5.1. Flux estimates

Measured MBO fluxes showed high variability. However, the basic features of the MBO emissions at this field site could be assessed by averaging over relevant time scales and aggregating the data. Canopy scale MBO fluxes rose sharply with increasing temperature and PAR levels as observed at the leaf level (Harley et al., 1998; Gray et al., in preparation). The isoprene emission algorithm developed by Guenther et al. (1993) can be used to describe the instantaneous MBO emission rate, which suggests that MBO may have very similar production mechanism and function in ponderosa pine as does isoprene in other species. In addition, the leaf level measurements indicated a seasonal variation of the basal emission rate similar to isoprene (Monson et al., 1994; Goldstein et al., 1998). We observed seasonality in the canopy scale flux data and showed its correlation with changes in air temperature (Figs. 7 and 8).

The leaf level measurements showed that carbon lost as MBO relative to assimilated carbon varied strongly with temperature and basal emission rate. The average for a number of individual trees was found to be approximately 0.5% at 30°C and 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR early in the season. This was higher than the canopy scale results for MBO loss compared to GPP (0.3%). The discrepancy is most probably due to generally lower ambient temperatures and a contribution of the understory to the GPP.

The comparison between the model and individual measurements showed a large scatter ( $r^2 = 0.6$ ) influenced by the relatively poor MBO chromatography throughout most of the measurement campaign. In addition, the model underestimated measured emissions by a factor of two on average during the early part of the summer, but agreed well with REA flux measurements at

the same site. The difference between our results and the results of Baker et al. (1999) with the REA technique is striking. Although our measured mixing ratios at the top of the tower concurred, the REA estimates are much lower with little indication of systematic errors in either estimate. However, due to the open canopy of the plantation our own calculations most probably overestimate actual fluxes because a significant amount of the plantation's sensible heat and latent flux derives from the soil and understory instead of the pine canopy, causing our diffusivity estimates to be too high. The overestimate is smaller using latent heat flux and water gradients because little water is evaporated from the soil as compared to plant transpiration, whereas the soil contributes significantly to the sensible heat flux at this site. It is difficult to estimate the contribution of the shrubs to the total transpiration rate, but it could have been as high as 50%.

In addition to this major cause of the measurement discrepancies, the REA measurements would have underestimated actual fluxes if they poorly separated up- and downdrafts, or underestimated the b-factor (based on the sensible heat flux measurements) (Bowling et al., 1998). Furthermore, it is possible that the REA and gradient flux methods averaged over slightly different fetch areas: Tree density is slightly higher nearer to the tower, which would be picked up preferentially by the lower gradient inlet, and a higher light attenuation in the older plantation upwind where the canopy is closed could cause lower emissions, which would preferentially be picked up by the REA system.

To summarize, this measurement comparison suggests that the gradient approach is biased for the MBO flux estimates at this site, due to a possibly large difference between the average source emission heights of sensible heat, latent heat and MBO. This idea is supported by a good agreement between measurements and model estimates for high zenith angles (Fig. 4), when most of the sensible and latent heat fluxes presumably come from the ponderosa pine overstory. As the contribution of soil and understory to the sensible heat flux, and the understory to the latent heat flux of the plantation may also have changed seasonally, we cannot exclude that at least a part of the differences in MBO emission patterns between measurements and model shown in Fig. 7b might have occurred due to these changes.

### 5.2. Air chemistry

As ponderosa pine is a dominant tree of western North America, and large areas of the Sierra Nevada mountains are planted with ponderosa pine stands, it has been pointed out by Harley et al. (1998) that the boundary layer MBO mixing ratio produced from these high emission rates could "dominate" regional ozone production. In fact, Lamanna and Goldstein (1999) calculated that approximately 20% of the local OH loss rate was due to

MBO, whereas, due to the local wind patterns, isoprene and its major oxidation products blown up to the Blodgett Forest site from a band of oak trees in the Sierra Nevada foothills to the west accounted for approximately 40% of the local OH loss rate. Hence, the regional contribution of MBO air chemistry to ozone production in the Sierra Nevada depends on the origin of the air mass, but will generally be very significant.

Acetone formation from atmospheric MBO oxidation has drawn a lot of attention due to its influence on the free troposphere HO<sub>x</sub> budget (Singh et al., 1995). Depending on the amount and distribution of MBO emitters, it could be a non-negligible source of acetone to the atmosphere. Harley et al. (1998), based on the distribution of MBO emitting trees, calculated a possible source strength of only 1.3 Tg acetone per year out of a budget of 40–60 Tg. Based on the lower basal emission rate found in this study, and its seasonal variation, this is probably on the high end of possible acetone production. Though MBO is a significant regional source of acetone (Goldstein and Schade, 2000) it may not be a significant source of atmospheric acetone worldwide, unless MBO is emitted from more species than those listed in Harley et al. (1998).

## 6. Conclusions

We have presented whole ecosystem MBO flux measurements, carried out above a ponderosa pine plantation. Daytime mean fluxes during the hot summer period were 2 mg C m<sup>-2</sup> h<sup>-1</sup>, and were probably overestimated by the flux gradient approach used at this site. MBO fluxes represented less than one percent of canopy gross carbon uptake, and were dependent on both light and temperature levels exhibiting sharp increases with both variables, in accordance with leaf level measurement results from the same site in 1997 and 1998. The seasonality of canopy scale emissions was investigated by comparing normalized modeled emissions, based on a leaf level emission model using the isoprene algorithm, to normalized measured emissions. Differences showed a significant correlation to maximum air temperature. However, more research is needed to clearly relate changes in the basal emission rate to seasonal drivers.

MBO emissions are large enough to sustain ambient air mixing ratios up to 10 ppb, and to have an important influence on regional photochemistry and the regional acetone budget. However, our measurements suggest only a minor source of atmospheric acetone from MBO oxidation globally unless more MBO emitting trees are discovered.

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