

Canopy fluxes of 2-methyl-3-buten-2-ol over a ponderosa pine forest by relaxed eddy accumulation: Field data and model comparison

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Abstract. Canopy level flux measurements of 2-methyl-3-buten-2-ol (MBO) were made over a 7 year old ponderosa pine plantation in the Sierra Nevada range of California using the relaxed eddy accumulation method. Fluxes peaked in late afternoon (1600 LT), at an average rate of $1.11 \text{ mg C m}^{-2} \text{ h}^{-1}$. This corresponds to the time of peak temperatures. MBO fluxes were strongly correlated with both temperature and photosynthetically active radiation (PAR). Model calculations of MBO flux from this site using a model developed for isoprene provide an accurate simulation of the diurnal emissions pattern but overestimate the measured flux by a factor of 2. Discrepancies between the measurements and the model predictions are likely due to the uncertainties in choosing model inputs. These results indicate a significant flux of reactive carbon in the western United States where MBO-emitting pines are the dominant forest vegetation.

1. Introduction

Biogenic emissions of volatile organic compounds (VOCs) play an important role in the photochemical production of ozone in both rural and urban scenarios [Trainer *et al.*, 1987, Chameides *et al.*, 1988]. Modeling exercises have shown that globally, isoprene and some monoterpenes are the most important biogenically produced hydrocarbons with respect to ozone production in the lower troposphere, because of their high rates of emission and high reactivity in the atmosphere relative to other hydrocarbons [Guenther *et al.*, 1995]. For this reason, most attention is given to these compounds in field campaigns designed to quantify biogenic VOC emissions. There is evidence that the most abundant VOC (other than methane) at some sites is not isoprene or monoterpenes but instead certain oxygenated volatile organic compounds (OVOCs). Goldan *et al.* [1995] found methanol and acetone to be the two most abundant VOCs above a loblolly pine forest in rural Alabama. Other studies, carried out at the leaf level, have shown that methanol [MacDonald and Fall, 1993a, Nemecek-Marshall *et al.*, 1995] and acetone [MacDonald and Fall, 1993b] are biogenically produced. These studies have generated a growing interest in the biogenic emission of OVOCs to the atmosphere. However, it is unclear what the importance of many of these compounds is in

the atmosphere, particularly with respect to tropospheric ozone production. The alcohol 2-methyl-3-buten-2-ol (MBO) is an OVOC that has been measured in concentrations greater than that of isoprene over a lodgepole pine forest in the mountains of Colorado [Goldan *et al.*, 1993] and over a ponderosa pine forest in the Sierra Nevada Mountains of California [Lamanna and Goldstein, 1999]. Harley *et al.* [1998] have shown that MBO is biogenically produced and that instantaneous emission rates can be fit to the same light and temperature algorithms as those for isoprene. Compared to methanol and acetone, MBO is relatively reactive and could lead to regional ozone production. It is possible that in the western United States, where pine forests dominate over deciduous forests, MBO is the primary biogenic hydrocarbon contributing to rural tropospheric ozone formation. MBO could also be a significant source of acetone in the troposphere by its reaction with OH radical; interest in tropospheric sources of acetone has increased with the recent finding that acetone photolysis may be a major source of HO_x radicals in the upper troposphere [Singh *et al.*, 1995].

To better understand the importance of MBO in the atmosphere, the flux of MBO from the biosphere needs to be quantified. In this paper, canopy level flux data obtained by relaxed eddy accumulation (REA) techniques over a ponderosa pine forest are reported. REA flux measurements are the most direct measure of canopy flux available (owing to the technical difficulties of eddy accumulation) when a fast sensor is not available for eddy covariance (as is the case for almost all hydrocarbons). The technique does not suffer some of the possible problems of leaf/needle level measurements. It is non-obtrusive to vegetation, and there are no sampling biases, i.e., choosing healthy looking needles over damaged ones. However, this technique requires greater analytical precision and a well-developed field site that includes a sampling tower.

The measured flux data are compared to the needle level enclosure measurements of Harley *et al.* [1998] (obtained at the same field site) by scaling the needle level flux data with a landscape emission model developed by Guenther *et al.* [1995] and modified by Guenther [1997]. This modeling exercise is particularly useful in evaluating the various factors which make up the model, since the field site is located on relatively flat

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ground and consists of one species of tree, which makes it a relatively simple case for this scaling-up procedure. There has also been a considerable amount of work done to characterize this particular site. A scaling-up procedure such as this is of further importance when one considers that global emission estimates of biogenic hydrocarbons are based on calculations using this model.

These measurements were part of a larger effort at the Blodgett Forest site to study biosphere-atmosphere exchange of radiatively and chemically active trace gases and their impacts on regional photochemistry. Other measurements that were made included wind speed and direction, net radiation, photosynthetically active radiation (PAR), relative humidity, air temperature, soil heat flux, soil temperature, soil moisture, needle temperature, concentrations and fluxes of CO₂, H₂O, and O₃, fluxes of sensible heat, and concentrations of a wide variety of hydrocarbons [Lamanna and Goldstein, 1999]. In addition, canopy-scale gradient flux measurements of MBO were made simultaneously with the REA flux measurements reported here. Results of these other measurements will be published elsewhere.

2. Experiment

2.1. Sampling Site

MBO flux measurements were made during the month of July 1998 on a ponderosa pine (*Pinus ponderosa*) plantation owned and operated by Sierra Pacific Industries and next to the Blodgett Forest Research Station near Georgetown, California. The Blodgett Forest Research Station is owned and operated by the University of California at Berkeley. The site (38°53'42.9"N, 120°37'57.9"W) was located ~ 90 km northeast of Sacramento at an elevation of ~ 1300 m in the foothills of the Sierra Nevada Mountains. The plantation was made up primarily of 7 year old ponderosa pine trees that were ~ 3.5-4 m tall. Two hundred meters upwind of the tower (to the southwest), the plantation was divided; the further section consisted of ponderosa pine trees that were 6 years older and ~ 2-3 m taller. There were also cedar and fir trees sporadically distributed throughout the site. Underbrush consisted mostly of manzanita, white thorn, and some scrub oak. Surrounding the plantation on all sides except the southwest was mature forest consisting of mostly ponderosa pine but also douglas fir, incense cedar, sugar pine, white fir, and some oak. To the southwest over 800 m away was a large clear-cut. Flux measurements were made on a 10 m walk-up tower; the tower stood in the northeastern end of the plantation. The sample inlets were located at 9 m, ~ 4 m above the canopy. Upslope winds came from the southwest during the sunlight hours. Power was supplied by a large diesel generator located 120 m to the northwest of the tower, just outside the plantation boundary. An aerial photo of the site is presented by A. H. Goldstein, et al. (Effects of seasonal drought stress on the carbon dioxide, water, and sensible heat fluxes above a ponderosa pine plantation in the Sierra Nevada (CA), submitted to *Agricultural and Forest Meteorology*, 1999).

2.2. Sample Collection

MBO fluxes above the forest canopy were estimated using the relaxed eddy accumulation technique. The theory behind REA is explained by Businger and Oncley [1990]. In short, two air samples are collected over a statistically meaningful time period (~ 30 min); one consisting of updrafts and one consisting of downdrafts. Although sampling alternates between up and down

reservoirs, it occurs at a constant flow rate. The frequency of sample collection for each reservoir is related to the speed at which the wind eddies change vertical direction. The flux F is then calculated using the following relationship:

$$F = \beta \sigma_w (C_u - C_d) \quad (1)$$

The value β is a unitless coefficient which in completely ideal conditions (e.g., over a smooth surface) has a value of 0.6 but which can also be determined empirically [see Gao, 1995]. The standard deviation of the vertical wind over the collection period is σ_w , and C_u and C_d are the average concentrations of the analyte of interest in the up and down reservoirs, respectively.

In this experiment an REA system similar to that described by Guenther et al. [1996] was deployed (see Figure 1 for a diagram). REA fluxes were averaged over 30 min periods with one sample pair collected each hour. A three-dimensional sonic anemometer (Applied Technologies Inc., Boulder, Colorado) measured vertical wind speed at 9 Hz at the end of a 2 m boom positioned 9 m up the sampling tower. The anemometer signal was sent to a portable computer which controlled four solenoid three-way Teflon isolation valves (Bio-Chem Valve Inc., Boonton, New Jersey) which made up the sampling part of the REA. A Teflon diaphragm pump (KNF Neuberger, Princeton, New Jersey, model NPH 30) drew the sample through a 1 m long, one-eighth inch OD inlet line at a flow rate of 500 cm³ min⁻¹ STP with the sampling end situated in the close vicinity of the sonic anemometer. Pump speed and therefore flow rate were controlled by varying the supply voltage to the pump. Over a half hour period, flow rate did not vary by more than 1 or 2%. The pump ran continuously, so air was always being passed through the system. After passing through the pump, the sample immediately encountered the vent valve where the sample was vented if the vertical winds (w_v) did not exceed the preselected threshold velocity. Having this threshold velocity increased the concentration difference between up and down air samples and improved the analytical determination of concentration differences between the up and down reservoir. This threshold velocity was set at $\pm 0.6\sigma_w$ on the basis of the argument of

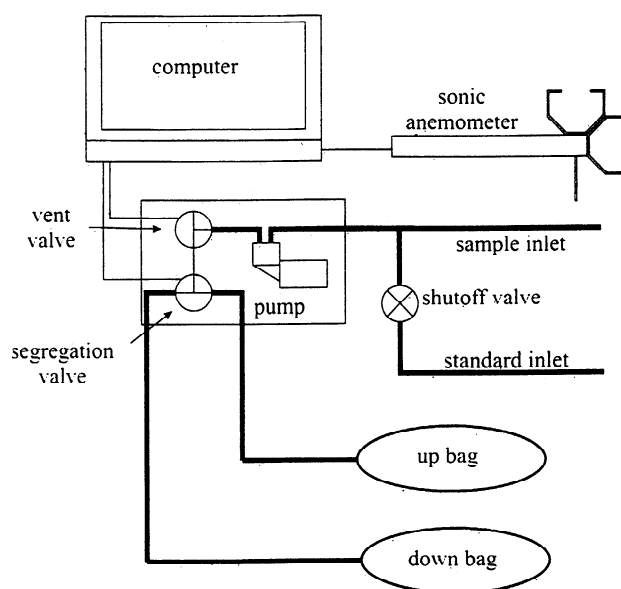


Figure 1. Schematic of the relaxed eddy accumulation (REA) sampling system.

Oncley *et al.* [1993]. The computer kept a running mean and standard deviation for vertical wind and calculated the threshold velocity based on this. When conditions were such that $|w_v| > 10.6\sigma_w$, the sample was sent to the segregator valve, which sent the air stream to the appropriate up or down reservoir. The pump, vent valve, and segregator valve were all housed in a small box suspended from the sampling boom to decrease the distance from where the air entered the inlet to where the sample segregation occurred (~ 1 m). Segregated air was sent through one-eighth inch Teflon tubing to the bottom of the tower, where it was collected in the appropriate up or down reservoir. The sample reservoirs consisted of Tedlar bags of ~ 10 L volume. Sampling bags were covered to prohibit any photochemistry during and after sampling. Storage tests for MBO in a Tedlar bag, including situations with high levels of ozone and high relative humidities, showed that for times less than a few hours, MBO was recovered completely. After chemical analysis and before returning bags to the REA system, bags were evacuated, filled with hydrocarbon free air, and evacuated again.

To determine the dimensionless constant β , sensible heat fluxes were calculated by eddy covariance using the virtual temperature measured by the sonic anemometer. The flux determined by eddy covariance was then substituted into equation (1) (using measured temperature data instead of concentrations), and the constant β was determined. Temperature "concentrations" used for this calculation took into account the vertical wind threshold, and therefore the empirically derived β becomes smaller as the sampling threshold becomes larger. The assumption was made that MBO fluxes and sensible heat fluxes covary similarly.

Incorrect REA sampling has the potential to cause large biases in flux measurements. A thorough discussion of the use of REA for estimating fluxes of biological trace gases and some of the potential problems is given by *Bowling et al.* [1998]. One error in sampling that could cause a large underestimation in flux involves not coordinating the response of the segregator valve with the air velocity flowing through the pump. Timing this correctly involves knowing the volume the sample must travel before reaching the segregator valve, the computer delay for

responding to a change in vertical wind velocity and switching the valve, and the pump speed. If the timing is such that there is a longer delay between an air sample entering the inlet tube and reaching the segregator valve than between the computer responding to the change in vertical wind velocity and switching the valve, then up eddies could be directed into the down reservoir and vice versa. The result will always be a decrease in the measured concentration difference between up and down reservoir, and therefore a decrease in the measured flux. Temperature data from this experiment were used to evaluate the magnitude of this problem. Figure 2 shows what effects the sampling offsets of up to 1 s can have on the measured flux. During the course of this campaign the pump flow was routinely checked, and an offset of 0.2 s was normal. The offset was never found to be greater than 0.4 s. This offset would have introduced an error of anywhere between 1 and 10% in the measured flux in the negative direction. The error is quite small because most of the sampled mass comes from eddies that last on the order of seconds rather than fractions of a second. Reported measurements have been corrected for this error.

2.3. Sample Analysis

The concentrations of MBO in the up and down reservoirs were determined by gas chromatography (GC). Figure 3 is a schematic of the analytical system. REA samples in Tedlar bags were drawn through an ozone scrubber (one-fourth inch OD glass tube, 4 cm long, packed with glass wool impregnated with potassium iodide) before being preconcentrated on glass beads packed in a one-eighth inch fused silica lined stainless steel tube cooled to liquid nitrogen temperature. Previous to the experiment, tests had been carried out to determine if ozone would be a problem in the determination of MBO. Standards were made up with ozone concentrations up to 100 ppbv and passed through the entire analytical system. No losses were seen for MBO, but the scrubber was left in place, since it was not detrimental to the analysis. Ozone in the standards may not have had a noticeable effect, owing to the small volume of sample drawn into the analytical system, and hence not enough ozone

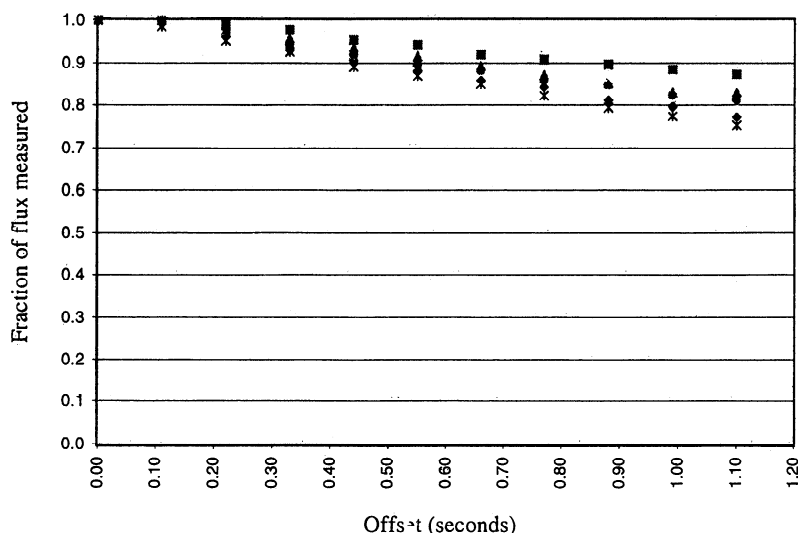


Figure 2. Potential underestimation of flux by having a sampling offset in the REA system. Data were acquired by simulating REA sampling using real-time fast temperature data. Each marker represents the simulation of a different half hour sampling period.

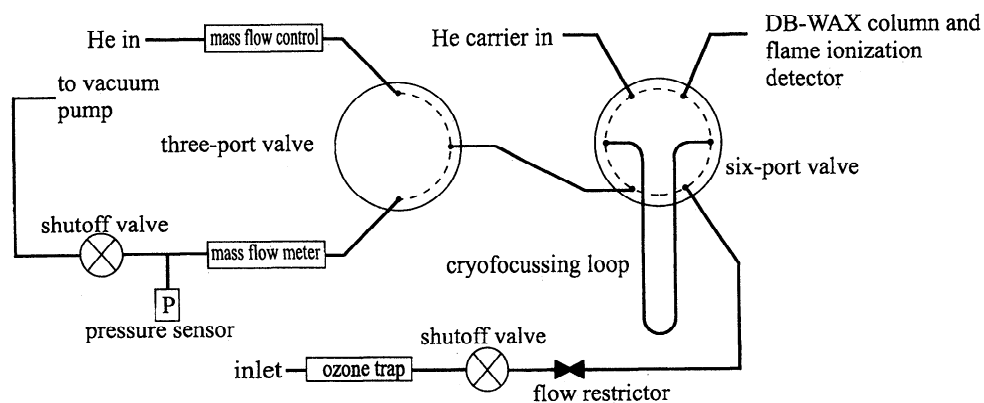


Figure 3. Schematic of the inlet for the gas chromatography system. Bags from the REA sampler are attached to the inlet of this system for analysis.

was preconcentrated with the sample to be a problem. Sample sizes were usually only 150 mL, taken at a rate of $\sim 30 \text{ mL min}^{-1}$ measured by a mass flow meter.

This small sample volume was chosen to avoid possible problems with water. No attempt was made to scrub the water from the air sample before the chemical analysis. This was because our experience has shown that when water is removed from the sample, polar compounds (such as MBO) are also at least partially removed. *Goldan et al.* [1995] encountered this in their initial measurements of MBO and calibrated their system to account for the loss. Instead of calibrating for MBO losses, the entire sample, including water, was collected on the glass bead cryogenic trap. The sample size was small enough and the trap large enough so that frozen water did not cause plugging of the trap. Although corrections must be made to the flux of many trace gases because of the differences in density between the up and down samples due to water vapor, it has been shown that for many VOCs this correction is negligible [*Pattey et al.*, 1992].

After sample collection, a six-port valve was switched so that the trap was in-line with the analytical column. The trap was rapidly heated to 150°C by resistance heating so that the concentrated sample would be swept off the trap by the He carrier gas and onto the column. The column was a DB-WAX, 30 m, 0.32 mm ID, $0.5 \mu\text{m}$ film thickness (J&W Scientific, Folsom, California) kept at 50°C in a Shimadzu Mini-GC2 (Kyoto, Japan) isothermal GC oven. Compounds eluted off the column were detected by flame ionization. Again, water concentrations were not high enough to have a detrimental effect on the chromatography. The detector signal was digitized and stored on a computer for later analysis.

In between samples the cryotrap was heated to 200°C and back-flushed with helium for at least 5 min at a rate of 50 mL min^{-1} . After three consecutive analyses the GC oven was heated to 200°C for ~ 5 min to bake out slow eluting compounds which might have shown up as interference in consecutive runs otherwise. All lines on the analytical system which contacted the sample were constructed of fused silica lined stainless steel heated to 100°C or were made from perfluoroalkoxy (PFA) Teflon.

2.4. Calibration

The analytical system was calibrated daily. Standard gases consisted of a commercially prepared compressed gas mixture which contained a number of VOCs in the parts per million range including MBO (Scott-Marin, San Bernidino, California).

Dilution of this standard was carried out using a dynamic dilution system which consisted of several mass flow controllers (Tylan Corp., San Diego, California; Unit Instruments Inc., Yorba Linda, California) used to precisely mix the standard gas with hydrocarbon free air and produce a gas stream with MBO concentrations of the order of one part per billion. The standard gas itself was calibrated against a butane/benzene primary standard. For this calibration a GC linked to an atomic emission detector (Hewlett Packard 5921A set to 496 nm for carbon) was used. The atomic emission detector is ideal for calibrations because of its one to one response per chosen atomic species. Although a flame ionization detector (FID) responds linearly to the number of carbon atoms in most cases, this is not true for oxygenated species, where some carbon atoms in the molecule are already partially oxidized [*Jorgensen et al.*, 1990]. In the field the diluted standard gas was sampled into the same bags as those used for flux analysis and then analyzed on the GC system. For the course of the experiment the percent standard deviation between all standard runs was less than 4% for MBO. In several cases, the standard gas was sent through the entire REA and collected into bags this way. These samples also fell within the 4% relative standard deviation.

2.5. REA Samples

Atmospheric REA samples were often analyzed more than once. This was possible since the bags contained several liters of sample, but only 150 mL was needed for analysis. Concentrations were determined by peak area with respect to the system calibration, and peak identification was determined by retention time, also relative to the calibration (see Figure 4). The average concentration of multiple analyses was used to determine the final flux. To determine the variance in all the repeated analyses of real air samples, the averages were normalized, and the normalization factor was applied to the area of each individual run. The relative standard deviation for all of the multiple analyses of the real air was just under 10%. This is a bit higher than that for the calibration data because of the fact that many of the real air concentrations were very much closer to the instrument's detection limit (~ 10 parts per trillion by volume (pptv)), particularly during the nighttime. During the daylight hours the sum of the standard deviations of the up and down samples never exceeded the concentration difference between the samples in any case. This was not necessarily true during the night, when the concentration difference was close to zero.

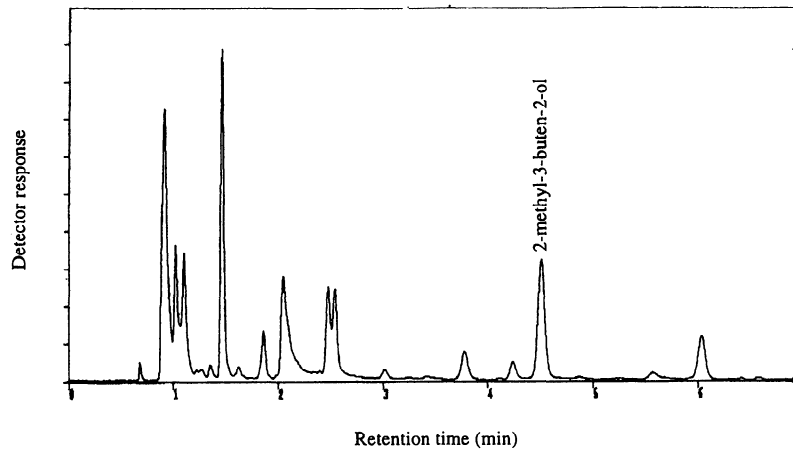


Figure 4. Sample chromatograph of a real air sample showing the peak shape and retention time for 2-methyl-3-buten-2-ol (MBO).

3. MBO Measurements

One hundred twenty-five canopy flux measurements were made between the dates of July 11 and 28, 1998. During daylight hours there were 6 to 11 measurements representing each hour, and during the nighttime there were 1 to 3. Sample collection time was 30 min. In addition to canopy level flux measurements, other measurements were useful in evaluating the flux of MBO including wind speed at three heights, temperature, and PAR. Hourly averaged fluxes of MBO are shown in Figure 5a; vertical bars represent 1σ of all the flux measurements made that hour over the course of the experiment or the variation in the flux from day to day.

Maximum fluxes of MBO occurred in midafternoon with an average value of $1.11 \text{ mg C m}^{-2} \text{ h}^{-1}$. At nighttime, fluxes declined to zero. The maximum flux observed during the experiment was $2.14 \text{ mg C m}^{-2} \text{ h}^{-1}$ at 1600 LT. MBO emissions are positively correlated with light and temperature (Figure 5b). During the midday, winds generally came from the WSW at $2.0\text{--}2.5 \text{ m s}^{-1}$. These were upslope winds coming out of the valley from the direction of Sacramento. MBO emissions began in the morning ~ 1 hour after PAR levels began to rise at 0700 LT. Fluxes then dropped to zero at 2100LT, when PAR decreased to zero. Maximum fluxes occurred at 1600LT, the same time that maximum temperatures were observed. The small flux measured at 0300LT was from one measurement taken after a short rain

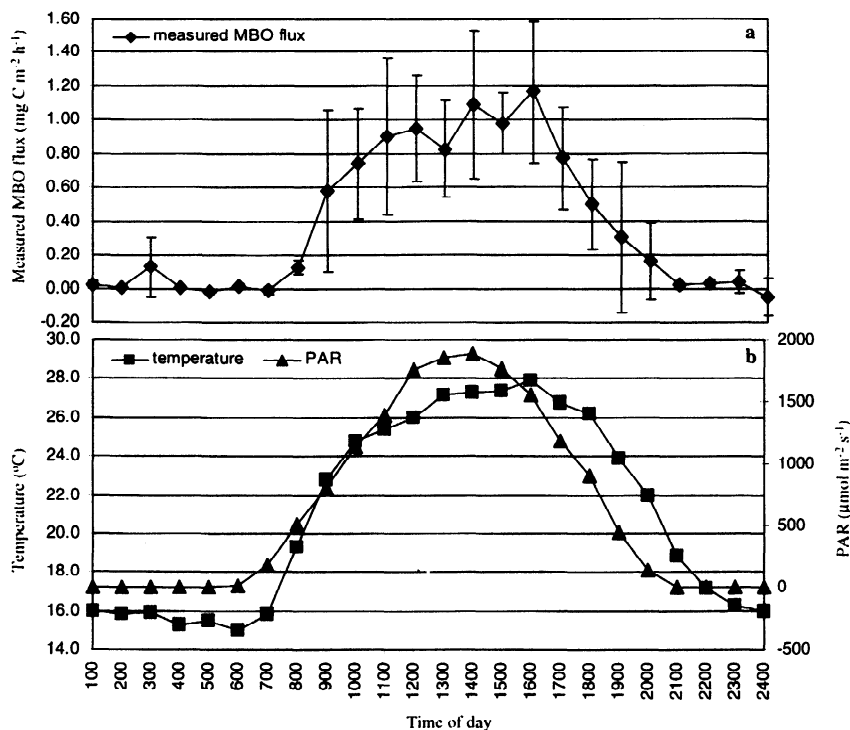


Figure 5. (a) Average measured MBO fluxes for the period July 11 to July 28, 1998 (not continuous). Vertical bars represent 1σ of all the measurements for that hour. (b) Average measured temperature and photosynthetically active radiation (PAR) for the same time periods as those for the MBO flux measurements.

shower. On the basis of the difficulties in evaluating nighttime fluxes, only a mention of this measurement, but no speculation on why it occurred, will be made.

Nighttime fluxes are reported here for the sake of showing the diurnal cycle of MBO emission and should be viewed critically. Problems with nighttime flux measurements include an inconsistent footprint due to variable winds within the measurement period, edge effects between the young plantation and the mature forest which surrounds it, and small friction velocities which will cause the measured flux to be an underestimate of the real flux. Since MBO is a light-dependent biogenic emission and the flux should be zero at night, these complications should have little effect on the flux measurements of this compound.

4. MBO Emission Model Evaluation

The biogenic emission model developed by *Guenther et al.* [1995] is the product of several terms, each of which affects the flux of VOCs to the atmosphere:

$$F = \varepsilon D \gamma \delta. \quad (2)$$

The terms include emission potential ε , foliar density D , light and temperature emission activity factor γ , and other emission activity factors δ . Table 1 lists the values chosen for each factor in the model calculation at this field site, and following is a discussion of how the factors were determined.

Emission potential describes the mass of carbon emitted by a plant needle per unit dry mass. This factor represents the maximum amount of carbon that could be emitted under standard conditions, which are 30°C and 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ of PAR. Other factors such as leaf age and growth conditions are not considered. Emission potentials for ponderosa pine were measured by *Harley et al.* [1998] at this site. One year old needles had the highest emission potential at 25.2 $\mu\text{g C g}^{-1} \text{h}^{-1}$. *Harley et al.* made their measurements at light levels slightly above 1000 PAR and normalized the data, so this may be a small overestimate since the best fit to the data using the isoprene light response algorithm has a slope which is not quite as steep as the data indicate it should be. These needle level emission measurements were made over a period of a few days and during a specific time of the year. It is likely that emission potentials change significantly during the growing season on the basis of any number of physiological factors. For instance, it is known that in at least some species,

isoprene emission potentials start off slowly in the spring and increase as the summer progresses [*Monson et al.*, 1994; *Schnitzler et al.*, 1997; *Goldstein et al.*, 1998]. It has not been determined if this is also true for MBO or if there are any other variables which might affect the emission potential of MBO-emitting trees. *Harley et al.* made their measurements in late June in the year previous to this experiment which was conducted in July, but it is difficult to compare across years, owing to seasonal variations in climate.

Foliar density is the average biomass per square meter within the footprint of the flux measurement. To determine the footprint of the flux measurements, a footprint model based on the work of *Horst and Weil* [1994] was employed. The model assumes a flat surface and constant terrain. The surface roughness and displacement height were determined using wind data collected at three different heights. The release height was set at 3 m, near the top of the canopy. The Monin-Obukhov length was calculated from the momentum flux and sensible heat flux determined from the sonic anemometer measurements. Footprint model results show that between 85 and 95% of the footprint area is within the younger stand of ponderosa pine, particularly during the sunlight hours.

For this model calculation a constant footprint was assumed. The footprint was in the direction of the prevailing winds, which during the daytime after upslope flow had developed, did not vary substantially. A 300 m by 10 m transect was run out from the tower in the direction of the prevailing winds to determine biomass density at this site. A description of how transect data are acquired and translated into a biomass density is presented by *B. Baugh et al.* (Measurement of oak tree density with Landsat TM data for estimating biogenic isoprene emissions in Tennessee, USA, submitted to *Remote Sensing of Environment*, 1998). Although this should provide an average biomass for this plantation forest, there are differences in the biomass in slightly different directions, which would not be accounted for in the flux model (but which affect the measured flux).

Transect data showed that average biomass density for the 7 year old trees was 140 g m^{-2} . On the basis of the previous year's transect data and growth estimates, the older trees were 580 g m^{-2} . The final weighted biomass density figure used for the model calculation was 185 g m^{-2} . This is assuming that 90% of the biomass was younger trees and 10% was older as determined from the footprint model. For comparison, a mature coniferous forest has an average biomass density of $\sim 700 \text{ g m}^{-2}$ [*Geron et al.*, 1994].

Light and temperature have the largest instantaneous effect on MBO emissions. *Harley et al.* [1998] fit measured needle level emissions to existing light- and temperature-dependent isoprene emission algorithms which were developed by *Guenther et al.* [1993]. For the calculation here, 30 min averages of measured temperature and PAR from the tower are used as the model inputs. The model also accounts for light levels within the canopy including contributions from direct and diffuse light [*Guenther et al.*, 1995]. However, the model is not optimized for a needle-leaved canopy.

Some other factors which might affect MBO emissions include: leaf age, nutrient and water supply, ozone damage, herbivory, etc. Since almost no information is available on how these factors may alter MBO or other VOC emissions, they all are grouped into just one factor. In the case of MBO emission from ponderosa pines, there is some information with regard to leaf age. *Harley et al.* [1998] measured emissions from current year immature needles and 1 year old and 2 year old needles. It

Table 1. Inputs for the Model by *Guenther et al.* [1995] Used to Model MBO Fluxes at This Field Site

Factor	Value	Source	Uncertainty, %
$\varepsilon, \mu\text{g C g}^{-1} \text{h}^{-1}$	25.2	<i>Harley et al.</i> [1998]	+/- 40
$D, \text{g m}^{-2}$	185	on-site transect data and footprint model	+/- 30
γ	variable	on-site measurement of T and PAR	+/- 15
δ	0.64	<i>Harley et al.</i> [1998]	+/- 15

MBO, 2-methyl-3-buten-2-ol; T, temperature; PAR, photosynthetically active radiation.

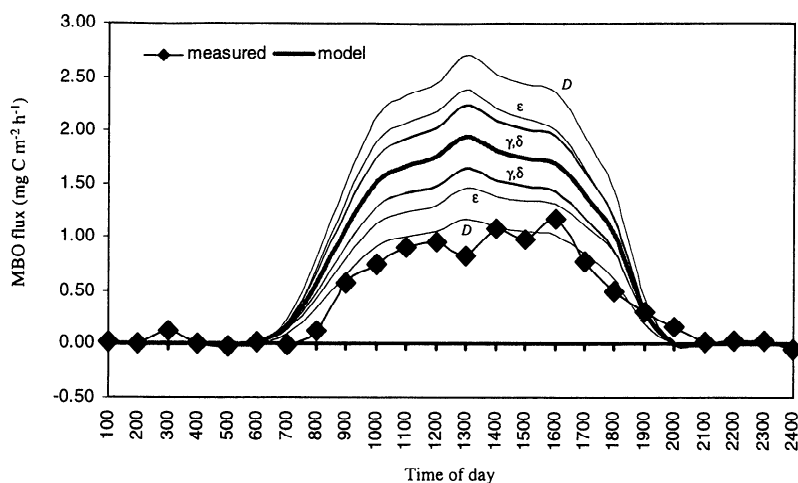


Figure 6. Modeled MBO fluxes compared to the measured MBO fluxes. Each measurement point was modeled using light and temperature data for that specific hour. The dark line represents the hourly averages of the model estimates. The lighter lines are model runs with the uncertainties listed in Table 1 factored in. Each variable is addressed individually; all others are kept at the original value.

was found that current year needles barely emitted any MBO at all ($<5 \mu\text{g C g}^{-1} \text{h}^{-1}$), 1 year old needles emitted the most ($25.2 \mu\text{g C g}^{-1} \text{h}^{-1}$), and 2 year old needles emitted a substantially smaller amount than that emitted by 1 year old needles ($\sim 15 \mu\text{g C g}^{-1} \text{h}^{-1}$); needles older than 2 years are assumed to not emit. A tree will hold several years' needles; however, there are not a substantial number of needles older than 2 years. For the calculation here it is assumed that 40% of the biomass is 1 year old needles, 40% is 2 year old needles, 5% is older than 2 years, and 5% is first year immature needles. These estimates are based on on-site observation of the trees themselves. Weighting these percentages with the appropriate emission rates gives this factor a value of 0.64.

Figure 6 compares average modeled MBO fluxes for this site with the average measured fluxes. The general shape of the modeled diurnal pattern agrees well with the measurements; however, the model overestimates the measured fluxes by a factor of 2. This is in contrast to a comparison of REA measurements of isoprene over an oak forest with modeled data that underestimated the measurements by $\sim 30\%$; however, this

underestimation was due in part to an underestimate of emission capacity for the oak species which made up that forest [Guenther *et al.*, 1996].

Since there are multiple factors contributing to each term in the model, including factors which may not be known, it is impossible to accurately determine errors associated with each. The greatest uncertainty likely exists in the determination of biomass density, because of the number of factors that can affect it. The emission potential also has a large uncertainty due to its possible seasonal variability. Table 1 lists reasonable uncertainty estimates for each of the four model variables. The values were chosen on the basis of some of the difficulties in measuring the variables and on the basis of possible seasonal variability, such as with the emission potential. The effects of these uncertainties are shown in Figure 6. Combinations of errors in the different factors could cause the model estimates to be even higher or they may cancel each other out. This is not an error analysis and should be looked upon only as an indication of how variable model results can be, based on differences in reasonable estimates of the inputs.

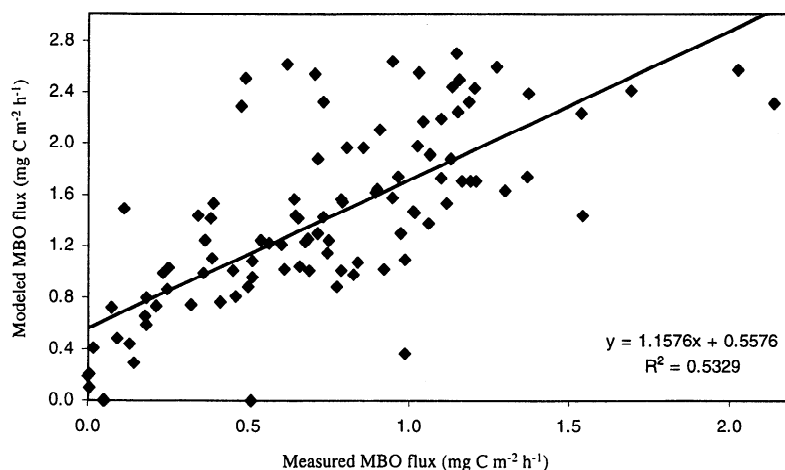


Figure 7. Correlation between modeled and measured MBO fluxes.

Figure 7 describes the correlation between the model and field measurements for all of the data acquired between 0700 and 2100 LT over the course of the experiment. This plot gives a good picture of how well the model represents the measured data on a per measurement basis. The correlation indicates that light and temperature can, for the most part, explain the short-term variations in MBO flux. The correlation is not tighter, because of a lack of knowledge of other variables which may affect the flux on short timescales, slight changes in biomass density due to small changes in wind direction and wind speed, or a combination of these factors.

5. Conclusion

Harley *et al.* [1998] estimated annual emissions of MBO from western U.S. pine forests to be 2.2 Tg MBO. In light of this and the work presented here, it is apparent that MBO emitted from ponderosa pine and other high MBO emitting pine species could make up a large fraction of the reactive hydrocarbon in the atmosphere over parts of rural western United States, and more needs to be learned of its emission patterns. This is especially important at sites such as the one described in this study, where prevailing winds bring polluted air from an urban area and the potential for ozone formation is high. Future studies should include work at the needle level, to help better understand physiological controls on emissions. There is also a need for better methods of determining biomass densities within the flux footprint and determining the footprint itself. These activities would help improve model estimates. Using regional and canopy level flux measurements to test model estimates of emissions of MBO by western pines will also be important. In particular, canopy flux measurements need to be made over mature pine forests which have biomass densities of the order of 700 g m⁻² and which should produce MBO fluxes comparable to those of isoprene in the southeast United States.

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