UC Irvine
UC Irvine Previously Published Works

Title

Emission of 2-methyl-3-buten-2-ol by pines: A potentially large natural source of reactive carbon to the atmosphere

Permalink

https://escholarship.org/uc/item/1g05q0xr

Journal

Journal of Geophysical Research, 103(D19)

ISSN

0148-0227

Authors

Harley, P
Fridd-Stroud, V
Greenberg, J
et al.

Publication Date

1998-10-20

DOI

10.1029/98jd00820

Peer reviewed

Emission of 2-methyl-3-buten-2-ol by pines: A potentially large natural source of reactive carbon to the atmosphere

Peter Harley, Verity Fridd-Stroud, James Greenberg, Alex Guenther, and Pérola Vasconcellos

Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado

Abstract. High rates of emission of 2-methyl-3-buten-2-ol (MBO) were measured from needles of several pine species. Emissions of MBO in the light were 1 to 2 orders of magnitude higher than emissions of monoterpenes and, in contrast to monoterpene emissions from pines, were absent in the dark. MBO emissions were strongly dependent on incident light, behaving similarly to net photosynthesis. Emission rates of MBO increased exponentially with temperature up to approximately 35°C. Above approximately 42°C, emission rates declined rapidly. Emissions could be modeled using existing algorithms for isoprene emission. We propose that emissions of MBO from lodgepole and ponderosa pine are the primary source of high concentrations of this compound, averaging 1-3 ppbv, found in ambient air samples collected in Colorado at an isolated mountain site approximately 3050 m above sea level. Subsequent field studies in a ponderosa pine plantation in California confirmed high MBO emissions, which averaged 25 μg C g^{-1} h^{-1} for 1-year-old needles, corrected to 30°C and photon flux of 1000 μmol m^{-2} s^{-1}. A total of 34 pine species growing at Eddy Arboretum in Placerville, California, were investigated, of which 11 exhibited high emissions of MBO (>5 μg C g^{-1} h^{-1}), and 6 emitted small but detectable amounts. All the emitting species are of North American origin, and most are restricted to western North America. These results indicate that MBO emissions from pines may constitute a significant source of reactive carbon and a significant source of acetone, to the atmosphere, particularly in the western United States.

1. Introduction

On a global basis, the biosphere contributes more volatile hydrocarbons to the atmosphere than does human activity [*Singh and Zimmerman*, 1992; *Guenther et al.*, 1995], and the majority of these biogenic emissions arise from forests. Many of the volatile organic compounds (VOC) emitted by vegetation are reactive constituents in tropospheric chemistry, affecting regional air quality and contributing to the photochemical production of ozone in both urban and rural landscapes [*Trainer et al.*, 1987; *Chameides et al.*, 1988]. For trees with high rates of VOC emission, between 0.5 and 2% of the carbon fixed by leaves in photosynthesis may be volatilized immediately, and under certain conditions, volatile losses may exceed 20% of fixed carbon over short periods of time [*Monson and Fall*, 1989; *Sharkey and Loreto*, 1993]. Over 1000 VOC are now known to be emitted by vegetation [*Graedel*, 1979; *Knudsen et al.*, 1993], but until recently attention has focused largely on isoprene (2-methyl-1,3-butadiene), generally the dominant hydrocarbon emitted by vegetation [*Guenther et al.*, 1995], and the monoterpenes. Recently, increased attention has been directed toward emission of oxygenated hydrocarbons by vegetation [*König et al.*, 1995], including methanol [*MacDonald and Fall*, 1993b;

Nemecek-Marshall et al., 1995], acetone [*MacDonald and Fall*, 1993a], aldehydes [*Kesselmeier et al.*, 1997], organic acids [*Talbot et al.*, 1990; *Kesselmeier et al.*, 1997], and a number of hexenal derivatives [*Arey et al.*, 1991].

Goldan et al. [1993] characterized the trace gas composition of ambient air at a remote mountain site (3050 m elevation) in Colorado in June 1991 and found that a C_5 alcohol, identified as 2-methyl-3-buten-2-ol (hereinafter referred to as methylbutenol or MBO), was the dominant trace compound, with concentrations 4 to 7 times those of isoprene. Based on the fact that diurnal changes in ambient MBO concentrations were very similar to those of isoprene, with known biogenic sources, and on the fact that MBO concentrations did not correlate well with those of benzene, an indicator of anthropogenic sources, they concluded that there was likely to be a large, unidentified local biogenic source of MBO. Results reported here trace the source of MBO to direct emission from needles of lodgepole and ponderosa pine and identify a number of other species of pine as potentially significant sources of MBO to the atmosphere. The effects on MBO emission rates of varying light and temperature are examined, and implications for tropospheric chemistry are discussed.

2. Methods

In the initial, laboratory phase of the study, measurements were made on potted trees of *Pinus ponderosa* Laws. (ponderosa pine) and *P. contorta* Dougl. var. *latifolia* Engelm. (lodgepole pine) obtained from Forest Farm Nursery,

Williams, Oregon. Plants were grown in commercial potting soil and maintained in the Frost Phytotron plant growth facility at the National Center for Atmospheric Research (NCAR) in Boulder, Colorado. Further laboratory measurements on ponderosa pine were made on branches cut from trees growing in a natural landscape adjacent to NCAR's Mesa Laboratory.

Measurements of net photosynthesis and stomatal conductance were made using a commercially available open-path gas exchange system (MPH-1000, Campbell Scientific, Logan, Utah) which consists of a temperature-controlled, fan-stirred leaf chamber, tethered to a measurement and control system. Air of specified water vapor and CO_2 concentration was generated using mass flow controllers (Model 825, Edwards High Vacuum International, Wilmington, Massachusetts) and passed to the cuvette. The flow rate of gas entering the cuvette was measured using a mass flow meter (Model 831, Edwards). The difference in water vapor before and after the cuvette was measured using two dew point mirrors (General Eastern, Watertown, Massachusetts) and the difference in CO_2 concentration determined by infrared gas analysis (Model 225 Mk3, Analytical Development Corp., Hoddleston, England). Artificial light was provided using a 1000-W high intensity discharge lamp (Philips MS1000/BU), and neutral density filters of blackened window screen were inserted in the light path to vary the irradiance. When a new set of pine needles was placed in the cuvette, a minimum of 30 min was allowed for equilibration, and all reported measurements were made after steady state conditions were achieved, as indicated by continuous real-time monitoring of CO_2 and H_2O fluxes.

To quantify the emissions from the enclosed needles, a carefully measured volume of gas, between 400 and 500 cm^3, was slowly withdrawn from the leaf cuvette and cryogenically trapped on a 1 cm^3 stainless steel sample loop packed with glass beads (60/80 mesh, Alltech, Deerfield, Illinois), cooled to liquid nitrogen temperature. The sample was then flash-heated onto a 30 m capillary gas chromatography (GC) column (DB-1, 0.32 mm ID, 1 μm film thickness, J & W Scientific, Folsom, California) and analyzed using a flame ionization detector (FID) (Model 5880, Hewlett-Packard, Avondale, Pennsylvania). The GC/FID was calibrated periodically against a National Institute of Standards and Technology neohexane standard (201 ppbv). Initial identification of the MBO chromatogram peak was made using gas chromatography-mass spectroscopy (GC/MS) (model HP5890 Series II gas chromatograph, model HP5972 mass selective detector, Hewlett-Packard, Palo Alto, California).

Field measurements on ponderosa pine trees were made in a young plantation operated by Sierra Pacific Industries, adjacent to the Blodgett Experimental Forest, El Dorado County, California, at an elevation of approximately 1300 m. Trees were 7 years old and averaged approximately 3 m in height. The gas exchange system described above was also used in the field. Instead of using compressed gases, however, ambient air was scrubbed of hydrocarbons by passing it through an activated charcoal filter (ORBO-32L, Supelco, Bellefonte, Pennsylvania), and passed to the cuvette. Artificial light was provided by a quartz halogen bulb (ELH 120V-300W, General Electric, Cleveland, Ohio) directed at a Tempax cold mirror (Optical Coating Labs, Inc., Santa Rosa, California) mounted at 45° to reflect visible light onto the

cuvette. Projected area was measured for all experimental needles (LI-3000A, Li-Cor, Inc.) which were subsequently oven dried at 60°C for 48 hours and weighed.

Air exiting the cuvette was drawn through the 1 cm^3 sample loop of a portable, isothermal (45°C) gas chromatograph. MBO was separated on a capillary column (DB-1; Alltech Assoc., Deerfield, Illinois) and measured using a reduction gas detector (RGD2, Trace Analytical, Menlo Park, California). Peak integration was accomplished using a commercial integrator (Model 3390, Hewlett-Packard, Avondale, Pennsylvania). The system was calibrated several times daily against a standard cylinder containing 39.2 ppbv MBO.

In order to quantify the sensitivity of the GC/FID to MBO, two gas phase standards of MBO, one humidified and one dry, were analyzed using GC/FID and GC with an atomic emission detector (AED). Whereas FID sensitivity varies with the addition of functional groups, AED response depends only on the number of carbon atoms (J. P. Greenberg et al., Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer, submitted to *Journal of Geophysical Research*, 1998). In analyzing the dry MBO standard, the response of the FID was 10% less than that of the AED; the response of the FID was 3% less than the AED when analyzing the humidified standard. Since all emission samples were humidified, a 3% correction was applied to FID values in calculating emission rates using GC/FID data.

Quantitative analysis of MBO presents several challenges. *Goldan et al.* [1993] indicate that a large fraction of MBO is lost if the sample stream is cooled below -50°C to remove water. In addition, we have observed over 50% conversion of MBO to isoprene through dehydration when a dry MBO standard was transferred through heated stainless steel capillary tubing to the cryogenic preconcentration trap. Humidification of the MBO standards eliminated the dehydration, and emission samples from the cuvette contained enough moisture that there was no conversion of MBO to isoprene.

Although none of the pine emission results reported here were obtained using solid adsorbents, standards were collected on solid adsorbents for introduction into the GC/MS and GC/AED. Solid adsorbent cartridges of several compositions (Carbotrap 200 (80 mg glass beads, 170 mg, 350 mg Carbosieve S-III), Carbotrap 300 (300 mg Carbotrap C, 200 mg Carbotrap B, 125 mg Carbosieve S-III), and Tenax TA (all from Supelco, Inc., Bellefonte, Pennsylvania)) were tested for MBO collection efficiency and quantitative desorption. High percentages of MBO conversion to isoprene were observed when cartridges were dry purged prior to desorption (to remove water vapor collected during sampling) and when cartridges were heated slowly from room temperature to 275°C for desorption (water vapor elutes from the cartridge before MBO, which is then desorbed in a dry gas stream). When cartridges were heated quickly to 275°C by clamping on a desorption heater maintained at 275°C, only slight conversion of MBO to isoprene was observed. There was considerable cartridge to cartridge variability in MBO-isoprene conversion, although Carbotrap 300 formulations gave the highest rates of conversion, while new adsorbents used to formulate Carbotrap 200 multistage adsorbents typically gave approximately 10% conversion. Less than 5% conversion, in most cases, was observed when Tenax TA was desorbed rapidly; although Tenax TA is hydrophobic, the MBO is presumably weakly adsorbed and eluted quickly from

the heated cartridge before significant conversion to isoprene occurs. Given these potential analytical difficulties, literature reports of significant isoprene emission from pine species should be re-evaluated in the context of the analytical techniques used.

3. Results

3.1. Laboratory Study

Measurements of MBO emission from branches of several ponderosa pine trees were made under a uniform set of experimental conditions (30°C air temperature in the cuvette and incident photosynthetically active radiation (PAR)=1000 μmol m^{-2} s^{-1}). All branches examined emitted MBO, with emission rates from needles of potted plants averaging 7.9 μg C g^{-1} h^{-1} (n=5; SE=1.7) Rates of emission from excised branches of two mature trees growing under natural conditions were considerably higher (20.2 and 18.1 μg C g^{-1} h^{-1}) than those from potted plants growing in the greenhouse. Whether this difference is due to variation in tree age or growth environment or is an artifact of the excision procedure itself is unknown, although field experiments described below tend to preclude the latter.

An anonymous reviewer suggested that the high rates of MBO emission reported in this study might be an artifact of needle damage during insertion into the cuvette, analogous to the situation observed for monoterpene emissions from pines [*Juuti et al.*, 1990]. Pines contain specialized storage structures for monoterpenes, which, if mechanically disrupted, empty their contents rapidly, leading to a burst of monoterpene emission, followed by a decline as pools are depleted. In one laboratory experiment, however, we left a set of ponderosa pine needles in the leaf cuvette for 3 days, turning off the light each night, and making measurements periodically during the day under constant conditions (PAR=1000 μmol m^{-2} s^{-1} and leaf temperature=30°C). Except during the first half hour following illumination each day, measured rates over the 3-day period remained essentially constant at 9.3 ± 0.8 μg C g^{-1} h^{-1}, demonstrating that MBO was not escaping from a damaged storage pool. Furthermore, the fact that MBO emissions rapidly fall to near zero in darkness (see below) strongly suggests that MBO is being emitted immediately upon production, rather than stored in specialized structures.

3.2. Ponderosa Pine Plantation Study

Measurements were made on 13 sets of 1-year-old needles from intact branches of ponderosa pine to determine the mean MBO emission potential (determined at 30°C and PAR between 1200 and 1500 μmol m^{-2} s^{-1}). In many situations (including the Eddy Arboretum measurements described below) it is impractical to make measurements on intact branches. To determine whether cutting branches was an acceptable technique, measurements were also made on five sets of 1-year-old needles from cut branches and the results compared to data from intact branches. In an attempt to maintain the transpiration stream during cut branch measurements, branches were cut, immediately placed in a bucket of water and recut under water. Measurements were also made on two-year-old needles and current-year needles of intact
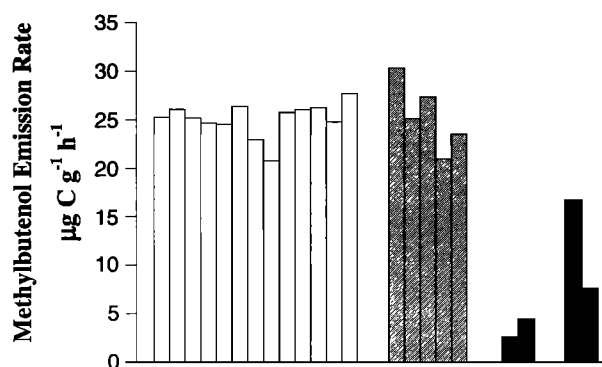
Figure 1. Rates of methylbutenol emission from current-year (immature, solid), 1-year-old (intact branch, open; cut branch, light shading), and 2-year-old needles (dark shading) of ponderosa pine. All measurements were made at 30±0.2°C, with photosynthetically active radiation varying between 1200 and 1600 μmol m^{-2} s^{-1}. Except where indicated, all measurements were made on intact branches.

branches to establish possible effects of needle age on MBO emission rates. Results are presented in Figure 1.

The mean MBO emission rate of the previous years' needles (intact branches) was 25.1±1.7 μg C g^{-1} h^{-1} (n=13) and using cut branches had no apparent effect on MBO emissions (25.5±3.6 μg C g^{-1} h^{-1};n=5). Immature current-year needles (less than 50% of full length) were shown to emit MBO but at substantially lower rates. Two-year-old needles also continued to emit MBO at reduced rates, though whether due to needle age or to more shaded growth environment is unknown.

The influence of incident PAR and needle temperature on both net photosynthesis and MBO emission was determined for field-grown ponderosa pine (Figure 2). MBO emission and photosynthesis responded similarly to irradiance, increasing nearly linearly at low PAR, then leveling off. However, whereas photosynthesis became light saturated at approximately 1000 μmol m^{-2} s^{-1}, MBO emissions continued to increase above 1500 μmol m^{-2} s^{-1}. With respect to varying temperature, photosynthesis and MBO emisson behaved very differently. Photosynthesis was maximal at or below 20°C and declined rapidly as temperature increased. MBO emissions, on the other hand, increased rapidly between 20° and 35°C, reached a maximum at approximately 40°C and declined precipitously above about 42°C.

3.3. Results of Eddy Arboretum Screening

A total of 34 species of pine growing at the Eddy Arboretum were screened for MBO emission. In each case, a 2-3 foot branch was cut and immediately recut under water. Previous experiments on ponderosa pine (Figure 1) indicated that cutting branches did not induce large changes in MBO over the short term and that the technique was suitable for a screening exercise. A single measurement was made on 1-year-old needles on each branch, and species fell into one of three categories: (1) species with emissions below the detection limit of approximately 0.05 μg C g^{-1} h^{-1}, (2) species with detectable emissions less than 1.5 μg C g^{-1} h^{-1}, and (3) species with emission rates greater than 5 μg C g^{-1} h^{-1} (all
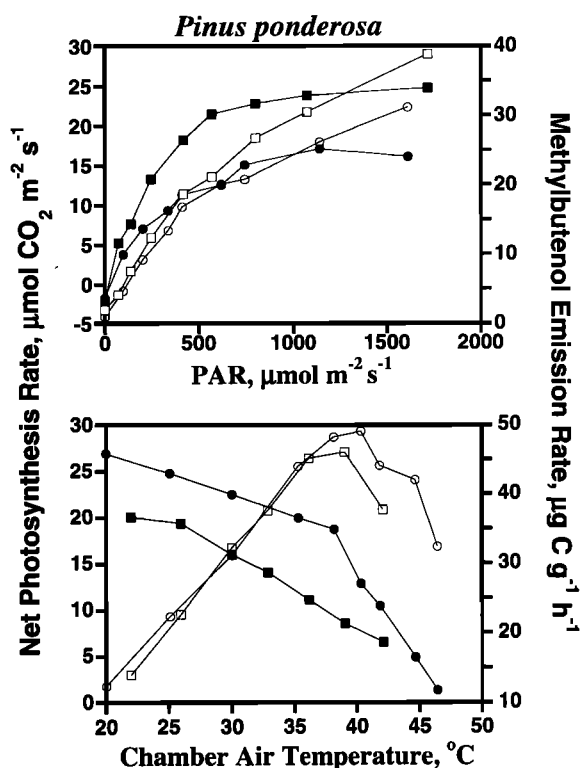
Figure 2. Response of net photosynthesis (solid symbols) and methylbutenol emission (open symbols) to variation in (top) incident PAR and (bottom) air temperature. Measurements were made on two sets of 1-year-old needles of field-grown ponderosa pine, depicted by circles and squares.

except *P. montezumae* had emissions greater than 15 μg C g^{-1} h^{-1}). These results are presented in Table 1, arranged according to a phylogenetic classification of pines [*Little and Critchfield*, 1969].

On the basis of this incomplete survey, detectable MBO emissions within the genus Pinus appear to be restricted to the subgenus Pinus, the so-called yellow or hard pines. And within the subgenus, emitting species are clustered in five subsections of section Pinus. Most of those species found to emit high quantities of MBO, including *P. contorta* var. *latifolia*, *P. coulteri*, *P. jeffreyi*, *P. murrayana*, *P. ponderosa*, *P. sabiniana*, and *P. torreyana* are restricted to western North America. It should be noted that particularly high MBO emission rates were measured in all three members of subsection Sabinianae (*P. sabiniana*-67.0; *P. coulteri*-70.6; *P. torreyana*-37.3 μg C g^{-1} h^{-1}).

4. Discussion

4.1. Modeling Methylbutenol Emissions

Emission of MBO in significant amounts has been demonstrated for several species in the genus Pinus, but has not been found (or looked for extensively) among other coniferous or nonconiferous trees. For those species in Table 1 found to emit MBO in detectable but low amounts, emission rates are similar to typical emission rates of monoterpenes from pines. Those species placed in the high

emission category emit MBO at rates 1 to 2 orders of magnitude greater than typical monoterpene emissions, and in some cases at rates comparable to isoprene emissions from high isoprene emitting tree species. Coupled with high values of foliar mass per unit ground area in pine forests (*Geron et al.* [1994] use a value of 700 g m^{-2} compared with 375 g m^{-2} for deciduous forests), these high emission capacities suggest that MBO could be the major source of reactive carbon in extensive ecosystems dominated by emitting pine species.

MBO has been identified as one component of the pheremone mix from two species of bark beetles, *Ips typographus*, a European species [*Bakke et al.*, 1977] and *Polygraphus rufipennis*, an American species [*Werner and Holsten*, 1995], both of which attack spruce trees. Inclusion of MBO in a trap consisting of a mixture of pheremone attractants for another spruce bark beetle, *Dendroctonus rufipennis*, a competitor of *Polygraphus*, was shown to reduce the number of *Dendroctonus* trapped, suggesting a possible antiattractant role for MBO. Emissions of MBO have also been observed from boreholes of beetles in spruce trees [*Birgersson and Bergström*, 1989], at emission rates quite high relative to the amount of MBO in the guts of *Ips*, implying either an extremely high turnover rate within the insect or an extrainsect source. Given that observation, species of spruce should be screened for MBO emission. Although other members of the genera *Ips* and *Dendroctonus* are important pests on pine, MBO has not been shown to be part of their pheremone complement, nor have experiments been done to demonstrate a potential role for MBO in affecting their behavior.

MBO emission responds to changes in both light and temperature (Figure 2) in a fashion very similar to the well-documented responses of isoprene emission [*Guenther et al.*, 1991, 1993] and light-dependent monoterpene emission [*Loreto et al.*, 1996] from leaves. By analogy, it may be inferred that MBO is emitted immediately upon production and is not stored within the needles. *Guenther et al.* [1993] developed algorithms to describe the light and temperature dependencies of isoprene emission, which have recently been successfully applied to light-dependent monoterpene emissions [*Ciccioli et al.*, 1997]. The light algorithm is as follows:

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1+\alpha^2 L^2}} \tag{1}$$

where C_L is a scalar, correcting for effects of varying PAR, L is incident PAR, and α and C_{L1} are empirical coefficients. Following the procedure of *Guenther et al.* [1993], data in Figure 2 were normalized, such that MBO emissions assumed a value of 1 at PAR=1000 μmol m^{-2} s^{-1} and temperature of 30°C (Figure 3). We fit the data in Figure 3 (top) to (1), determining best fit values of α and C_{L1} using nonlinear least squares regression. The resulting fit and parameter values are shown in Figure 3 (top). Although the algorithm does a reasonable job of fitting the data, it fails to adequately capture the lack of response saturation at high values of PAR. By convention, emission capacities are expressed as the rate assuming PAR=1000 μmol m^{-2} s^{-1}. Since data plotted in Figure 1 were obtained at PAR values between 1200 and 1500 μmol m^{-2} s^{-1}, those values overestimate the emission capacity. Using the relationship plotted in Figure 3, based on (1), we can estimate the emission capacity (PAR=1000 μmol m^{-2} s^{-1})

Table 1. Methylbutenol Emission Within the Genus Pinus

Section	Subsection	Number of Species	MBO Below Detection Limit	MBO Emission <1.5 µg C g^{-1} h^{-1}	MBO Emission >5.0 µg C g^{-1} h^{-1}
			Subgenus Ducampopinus		
Ducampopinus					
	Krempfianae	1	---		
			Subgenus Strobus (White or Soft Pines)		
Strobus					
	Cembrae	5	---		
	Strobi	24	lambertiana strobiformis monticola kwangatungensis		
Parrya					
	Cembroides	15	edulis		
	Gerardianae	2	bungeana		
	Balfourianae	3	---		
	Rzedowskianae	1	---		
			Subgenus Pinus (Yellow or Hard Pines)		
Pinea					
	Leiophyllae	3	leiophylla		
	Pineae	1	pinea		
	Canarienses	2	---		
Pinus					
	Sylvestres	40	sylvestris nigra densiflora halepensis		
	Australes	16	sondereggeri echinata	rigida caribaea taeda	palustris
	Ponderosae	32	engelmannii	pseudostrobus	jeffreyi montezumae ponderosa
	Sabinianae	3			sabiniana coulteri torreyana
	Contortae	8	virginiana	contorta	murrayana contorta var. latifolia murraybanksiana
	Oocarpae	11	patula	radiata	muricata

Measured species are arranged phylogenetically [*Little and Critchfield*, 1969] and placed in one of three categories: (1) emissions below detection limit, (2) emissions <1.5 µg C g^{-1} h^{-1}, or (3) emissions >5 µg C g^{-1} h^{-1}.

for the needles in Figure 1. The mean emission capacity of 1-year-old needles of both intact and cut branches is 25.2 ± 2.3 µg C g^{-1} h^{-1} ($n=18$), although since (1) underestimates the true slope of the light response in the region between PAR=1000 and 1500 µmol m^{-2} s^{-1} (Figure 3), this is probably a slight overestimate.

In order to fit the temperature data in Figure 3 (bottom), we used a temperature algorithm which is equivalent to that of Guenther et al. [1993] but which uses slightly different parameters, that is,

$$C_T = \frac{E_{opt}C_{T2}\exp^{C_{T1}x}}{C_{T2}-C_{T1}(1-\exp^{C_{T2}x})} \qquad (2)$$

where $x = [(1/T_{opt})-(1/T)]/R$, T is leaf temperature (K), R is the gas constant ($=0.00831$ kJ mol^{-1} K^{-1}), E_{opt} is the maximum normalized emission capacity (unitless), T_{opt} is the temperature (K) at which E_{opt} occurs, and C_{T1} and C_{T2} are the

energies of deactivation and activation, respectively (kJ mol^{-1}). Data in Figure 3 (bottom) were fit to (2), determining best fit parameter values using nonlinear least squares regression; the resulting fit and parameter values are shown in Figure 3 (bottom). The temperature algorithm well describes the effects of varying temperature on MBO emission.

4.2. Implications for Atmospheric Chemistry

The major photochemical sink for MBO during daylight hours is assumed to be reaction with OH. The rate coefficient for the OH reaction with MBO was reported by *Rudich et al.* [1995] to be $k=(8.2\pm1.2)$ x 10^{-12} exp $((610\pm50)/T^{\circ}K)$ cm^3 molecule^{-1} s^{-1}. Recent experiments carried out at $295^{\circ}K$ and 700 torr total pressure [*Ferronato et al.*, 1998] gave a similar value of $k=(6.9\pm1.0)$ x 10^{-11} cm^3 molecule^{-1} s^{-1}. Assuming [OH]=2 x 10^6 molecule cm^{-3}, this implies a relatively short tropospheric lifetime of approximately 2 hours. Given typical
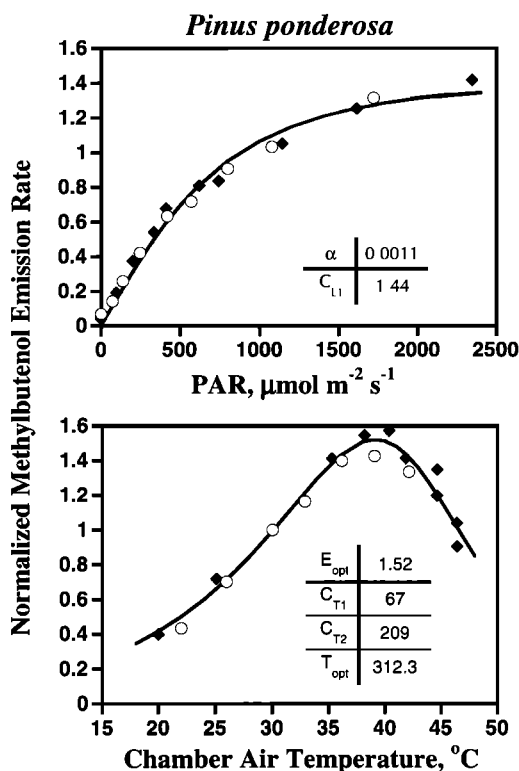
Figure 3. Response of methylbutenol emission to variation in (top) incident PAR and (bottom) air temperature. Measurements were made on two sets of 1-year-old needles of field-grown ponderosa pine. Data from Figure 2 have been normalized, such that emission rate equals 1 at PAR=1000 μmol m^{-2} s^{-1} and air temperature of 30°C. Solid line is a fit to the light and temperature algorithms presented in the text, using parameter values shown on the figures.

atmospheric values of O_3 and NO_3, the rate constants for MBO reaction with O_3 (k=1.00±0.03 x 10^{-17} cm^3 molecule^{-1} s^{-1}) [*Grosjean and Grosjean*, 1994] or with NO_3 (k=(1-2) x 10^{-14} cm^3 molecule^{-1} s^{-1}) [*Hallquist et al.*, 1996; *Rudich et al.*, 1996] imply significantly longer MBO lifetimes with respect to these destruction processes. Recent reaction chamber experiments [*Fantechi et al.*, 1997; *Ferronato et al.*, 1998] indicate that the MBO-OH reaction leads to the production of acetone, glycolaldehyde, formaldehyde, and (presumably) 2-hydroxy-2-methylpropanal. *Ferronato et al.* [1998] found acetone and glycolaldehyde formed in near equal yields of approximately 50%, while the yield of formaldehyde, (and presumably 2-hydroxy-2-methylpropanal) was 35%. They also suggest that organic nitrates may be formed with a yield of approximately 10%. The reaction of MBO with O_3 appears to yield the same major products, though in different proportions [*Grosjean and Grosjean*, 1995; *Fantechi et al.*, 1997].

In order to establish whether ambient concentrations of MBO observed by *Goldan et al.* [1993] are consistent with these measured enclosure rates of MBO emission, we carried out a simple modeling exercise. Landscape average emission rates, F (mg C m^{-2} h^{-1}), of MBO, isoprene, and monoterpenes for a 10,000 km^2 area in the Rocky Mountains, west of Boulder, Colorado, were calculated as

$$F = \varepsilon\, D\, \gamma \qquad (3)$$

where ε is a landscape average emission potential (mg C g^{-1} h^{-1}), D is the total foliar density (g m^{-2}), and γ is an emission activity factor that accounts for sensitivity of emissions to variations in PAR and temperature, described by (1) and (2). An emission potential is the emission rate of a specific VOC expected for a particular plant species at a temperature of 30°C and PAR of 1000 μmol m^{-2} s^{-1}. The landscape average emission potential ε is the weighted average, that is, $\Sigma(\varepsilon_i$ x $D_i)$, of emission potentials representative of various tree species (i) where D_i is the fraction of the total foliar density composed of each species.

Forest biomass and species composition data were derived using the method of *Geron et al.* [1994]. Forests cover 75% of the region and the average total foliar density of forests in this region (734 g m^{-2}) results in a total foliar density of 550 g m^{-2}, dominated by lodgepole pine (336 g m^{-2}). Ponderosa pine (62 g m^{-2}), subalpine fir (45 g m^{-2}), Douglas fir (45 g m^{-2}), aspen (39 g m^{-2}), Englemann spruce (16 g m^{-2}), and blue spruce (6 g m^{-2}) also comprise a significant fraction of the total biomass. These foliar densities were used to weight the MBO emission capacities determined in this study (25 μg C g^{-1} h^{-1} for lodgepole and ponderosa pine and 0 for all other species) and the isoprene and monoterpene emission capacities reported by *Guenther et al.* [1994] for each species. The resulting landscape average emission capacity (at 30°C and PAR=1000 μmol m^{-2} s^{-1}) of 14.5 mg C m^{-2} h^{-1} is comprised of 69% MBO, 21% isoprene, and 10% mono-terpenes. Using the canopy environment model described by *Guenther et al.* [1995] and the light and temperature relationships described above, for a typical summer day in this region (temperature=22 °C, PAR=1500, Sun angle = 56°) we calculate a total VOC emission rate of 4.6 mg C m^{-2} h^{-1} (64% MBO, 20% isoprene, and 16% monoterpenes).

Using this calculated VOC flux, we estimated above canopy hydrocarbon concentrations using a simple box model [*Guenther et al.*, 1996]. The model is based on a mixed-layer scalar conservation equation and assumes that turbulent horizontal fluxes and mean vertical advection are negligible, the vertical flux profile is linear, the mean concentration has reached steady state and is homogeneous in space, and that entrainment flux is negligible. We used the OH and O_3 reaction rate coefficients reported by *Atkinson* [1990] for isoprene and monoterpenes (assuming that the monoterpene flux is 50% α-pinene and 50% β-pinene), the MBO+OH coefficients of *Ferronato et al.* [1998] and the MBO+O_3 coefficients of *Grosjean and Grosjean* [1994] to estimate lifetime τ. Assuming conditions typical of midday in June in this region in the Rocky Mountains (O_3=40 ppb, OH = 4 x 10^6 molecules cm^{-3} [*Mount et al.*, 1997] and z_i = 1500 m, modeled mixed layer concentrations are about 925 parts per trillion (ppt) MBO, 330 ppt isoprene, and 100 ppt monoterpenes. *Guenther et al.* [1996] estimate the uncertainty associated with attempting to estimate a surface flux based on ambient concentration measurements in the mixed layer and arrive at an uncertainty of about ±50%, due primarily to uncertainty in the OH concentration. Here we attempt to estimate mixed layer isoprene concentrations from modeled surface fluxes, and the uncertainty in the surface flux model adds considerably to the overall uncertainty in mixed layer predicitions. Although the predicted ratio of MBO to isoprene is almost 3, isoprene, due to its greater reactivity, contributes about 29% and MBO contributes 58% of the total

OH sink due to these biogenic hydrocarbons. Using the ratios between surface layer and mixed-layer concentrations observed by *Guenther et al.* [1996], we estimate surface layer concentrations of about 1.5 ppb MBO and 0.5 ppb isoprene. Given the expected large variations in surface concentrations due to local sources, these estimates, though quite uncertain, are in reasonable agreement with the ambient concentrations observed by *Goldan et al.* [1993] (1-3 ppb MBO and 200-500 ppt isoprene) at a site, dominated by lodgepole pine, within our model domain.

The reported rate constant of the MBO-OH reaction is quite high, comparable to that of the isoprene-OH reaction (k=9.88 x 10^{-11} cm^3 molecule^{-1} s^{-1} at 300 K [*Atkinson*, 1990]) and the contribution of MBO oxidation to tropospheric O_3 formation is likely to be substantial, possibly dominating O_3 production in pine forests of western North America. Secondary O_3 production from oxidation of the products of the MBO-OH reactions is likely to be less than in the case of isoprene, due to the relatively long lifetime of acetone (10-30 days in summertime [*Singh et al.*, 1994]), a major stable product of MBO oxidation.

In addition to contributing to regional tropospheric O_3, oxidation of MBO may be a significant source of acetone to the atmosphere, at least on a regional scale. *Singh et al.* [1995] have pointed out the potential importance of acetone photolysis as a source of HO_x radicals in the free troposphere. *Ferronato et al.* [1998] indicated that acetone is a major product not only of MBO oxidation but probably of the oxidation of 2-hydroxy-2-methylpropanal as well. Assuming 100% conversion of the latter to acetone, the total acetone yield from MBO oxidation by OH could approach 85%, with the production of 0.6 g acetone per gram of MBO destroyed. Whether the amount of acetone produced by the oxidation of MBO from pines comprises a significant fraction of the global source strength, estimated at 40-60 Tg annually [*Singh et al.*, 1995], depends largely on the global distribution of pine species which emit significant amounts of MBO.

4.3. Phylogenetic and Geographical Patterns of Emissions

There are clear phylogenetic and geographical biases in the data collected at Eddy Arboretum (Table 1). Of 34 species examined, only six are among the white or soft pines in subgenus Strobus. None of these was found to emit MBO, however, and until there is evidence to the contrary, it seems reasonable to assume that all MBO-emitting species are found in subgenus Pinus. Within that subgenus, all emitting species were found in five subsections of section Pinus, but more data are necessary to prove whether this is uniformly the case. Of 34 species examined, only seven are Eurasian and of the 27 North American species, 21 are restricted to western North America. Despite the sampling bias, it is striking that all species of pine found to emit MBO are of North American origin. All emitting species were found in section Pinus, containing six subsections. Subsection Sylvestres is almost entirely Eurasian, the single significant exception being *P. resinosa*, the Red Pine of eastern North America (not sampled). Subsection Australes consists entirely of eastern North American species, of which several were found to emit MBO, but only one, *P. palustris*, emitted in large amounts. The final four subsections of section Pinus are restricted to western North America and Mexico, and the large majority of those species emitted MBO in significant quantities. More

data are necessary to verify these generalizations, but unless new evidence to the contrary arises, it seems likely that MBO is a significant emission only in North America and primarily in western North America (including Mexico, which though not well represented in the sample, contains many species in the emitting groups).

Ponderosa pine, in terms of abundance and range, is a dominant tree of western North America, growing from northern Mexico to southern British Columbia, and from sea level to 2800 m [*Elias*, 1980]. Lodgepole pine, often a colonizer of burned-over sites and found in pure stands, also ranges from Baja California to Alaska, increasing in abundance in the northern Rocky Mountains and Pacific Coast regions [*Elias*, 1980]. Other MBO emitting species occupy much more restricted geographical ranges. Based on Forest Inventory and Analysis data from the U.S. Department of Agriculture Forest Service and using methods of *Geron et al.* [1994], the percentage of forest crown area occupied by high MBO emitting species (primarily ponderosa and lodgepole pine, with a smaller contribution from Jeffrey pine) ranges from 10.5% in Utah to over 37% in Wyoming, averaging slightly under 24% for the 13 westernmost United States (excluding Nevada). Using these fractions and forest density estimates based on satellite data [*Zhu and Evans*, 1994], MBO emitting pine species cover approximately 0.18 x 10^6 km^2. Assuming foliage density of 700 g m^{-2}, an average MBO emission capacity of 25 µg C g^{-1} h^{-1}, and incorporating canopy effects and effects of seasonal variation in PAR and temperature using the current Biogenic Emissions Inventory System [*Pierce and Waldruff*, 1991; *Geron et al.*, 1994], we calculate annual emissions of 2.2 Tg MBO. If we further assume 0.6 g acetone produced for each gram of MBO destroyed [*Ferronato et al.*, 1998], pines in the western United States may represent an annual source of acetone of the order 1.3 Tg. Inclusion of western Canada and Mexico in the analysis would raise this estimate somewhat. However, given the apparently limited geographical extent of MBO emissions from pines, and despite the importance of MBO emitting pines in western North America, it is unlikely that production of acetone by MBO oxidation constitutes a large percentage of the global source.

References

Arey, J., A. M. Winer, R. Atkinson, S. M. Aschmann, W. D. Long, and C. L. Morrison, The emission of (Z)-3-hexen-1-ol, (Z)-3-hexenylacetate and other oxygenated hydrocarbons from agricultural plant species, *Atmos. Environ.*, 25, 1063-1075, 1991.

Atkinson, R., Gas-phase tropospheric chemistry of organic compounds: A review, *Atmos. Environ.*, 24, 1-41, 1990.

Bakke, A., P. Froyen, and L. Skattebol, Field response to a new pheremonal compound isolated from *Ips typographus*, *Naturwissenschaften*, 64, 98-99, 1977.

Birgersson, G., and G. Bergström,   Volatiles released from individual spruce bark beetle entrance holes, *J. Chem. Ecol., 15,* 2465-2483, 1989.

Chameides, W., R. Lindsay, J. Richardson, and C. Kiang, The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, *Science, 241,* 1473-1475, 1988.

Ciccioli, P., et al., Use of the isoprene algorithm for predicting the monoterpene emission from the Mediterranean holm oak *Quercus ilex* L.: Performance and limits of this approach, *J. Geophys. Res., 102,* 23,319-23,328, 1997.

Elias, T. S., *The Complete Trees of North America,* Times Mirror Mag., Inc., New York, 1980.

Fantechi, G., N. R. Jensen, J. Hjorth, and J. Peeters, Mechanistic study of the atmospheric degradation of isoprene and MBO, in *Proceedings of EUROTRAC Symposium 1996,* edited by P. M. Borrell et al., pp. 397-402, Comput. Mech. Billerica, Mass., 1997.

Ferronato, C., J. J. Orlando, and G.S. Tyndall, The rate and mechanism of the reactions of OH and Cl with 2-methyl-3-buten-2-ol, *J. Geophys. Res.,* in press, 1998.

Geron, C. D., A. B. Guenther, and T. E. Pierce, An improved model for estimating emissions of volatile organic compounds from forests in the eastern United States, *J. Geophys. Res., 99,* 12,773-12,791, 1994.

Goldan, P. D., W. C. Kuster, F. C. Fehsenfeld, and S. A. Montzka, The observation of a C5 alcohol emission in a North American pine forest, *Geophys. Res. Lett., 20,* 1039-1042, 1993.

Graedel, T. E., Terpenoids in the atmosphere, *Rev. Geophys., 17,* 937-947, 1979.

Grosjean, E., and D. Grosjean, Rate constants for the gas-phase reactions of ozone with unsaturated aliphatic alcohols, *Int. J. Chem. Kinet., 26,* 1185-1191, 1994.

Grosjean, D., and E. Grosjean, Carbonyl products of the ozone-unsaturated alcohol reaction, *J. Geophys. Res., 100,* 22,815-22,820, 1995.

Guenther, A., R. Monson, and R. Fall, Isoprene and monoterpene emission rate variability: Observations with eucalyptus and emission rate algorithm development, *J. Geophys. Res., 96,* 10,799-10,808, 1991.

Guenther, A., et al., Isoprene and monoterpene emission rate variability: Model evaluation and sensitivity analysis, *J. Geophys. Res., 98,* 12,609-12,617, 1993.

Guenther, A., P. Zimmerman, and M. Wildermuth, Natural volatile organic compound emission rate estimates for U.S. woodland landscapes, *Atmos. Environ., 28,* 1197-1210, 1994.

Guenther, A., et al., A global model of natural volatile organic compound emissions, *J. Geophys. Res., 100,* 8873-8892, 1995.

Guenther, A., et al., Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements, *J. Geophys. Res., 101,* 1345-1359, 1996.

Hallquist, M., S. Langer, E. Ljungstrom, and I. Wangberg, Rates of reaction between the nitrate radical and some unsaturated alcohols, *Int. J. Chem. Kinet., 28,* 467-474, 1996.

Juuti, S., J. Arey, and R. Atkinson, Monoterpene emission rate measurements from a Monterey Pine, *J. Geophys. Res., 95,* 7515-7519, 1990.

Kesselmeier, J., et al., The BEMA-Project: Emission of short chained organic acids, aldehydes and monoterpenes from *Quercus ilex* L. and *Pinus pinea* L. in relation to physiological activities, carbon budget and emission algorithms, *Atmos. Environ., 31,* 119-133, 1997.

Knudsen, J. T., L. Tollsten, and L. G. Bergstrom, Floral scents: A checklist of volatile compounds isolated by head-space techniques, *Phytochemistry, 33,* 253-280, 1993.

König, G., M. Brunda, H. Puxbaum, C. N. Hewitt, and S. C. Duckham, Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agricultural and natural plant species, *Atmos. Environ., 29,* 861-874, 1995.

Little, E. L., and W. B. Critchfield, Subdivisions of the genus Pinus

(Pines). Misc. Publ. 1144. U.S. Dep. of Agric. Forest Service, 1969.

Loreto, F., P. Ciccioli, A. Cecinato, E. Brancaleoni, M. Frattoni, and D. Tricoli, Influence of environmental factors and air composition on the emission of α-pinene from *Quercus ilex* leaves., *Plant Physiol., 110,* 267-275, 1996.

MacDonald, R. C., and R. Fall, Acetone emission from conifer buds, *Phytochemistry, 34,* 991-994, 1993a.

MacDonald, R.C. and R. Fall, Detection of substantial emissions of methanol from plants to the atmosphere, *Atmos. Environ., 27A,* 1709-1713, 1993b.

Monson, R. and R. Fall, Isoprene emission from aspen leaves. Influence of environment and relation to photosynthesis, *Plant Physiol., 90,* 267-274, 1989.

Mount, G. H., et al., Measurement of tropospheric OH by long-path laser absorption at Fritz Peak Observatory, Colorado, during the OH Photochemistry Experiment, fall 1993, *J. Geophys. Res., 102,* 6393-6413, 1997.

Nemecek-Marshall, M., R. C. MacDonald, and R. Fall, Methanol emission from leaves: Enzymatic detection of gas-phase methanol and relation of methanol fluxes to stomatal conductance and leaf development, *Plant Physiol., 108,* 1359-1368, 1995.

Pierce, T., and P. Waldruff, PC-BEIS: A personal computer version of the biogenic emissions inventory system, *J. Air Waste Manage. Assoc., 41,* 937-941, 1991.

Rudich, Y., R. Talukdar, J. B. Burkholder, and A. R. Ravishankara, Reaction of methylbutenol with hydroxyl radical: Mechanism and atmospheric implications, *J. Phys. Chem., 99,* 12,188-12,194, 1995.

Rudich, Y., R. Talukdar, R. W. Fox, and A. R. Ravishankara, Rate coefficients for reactions of NO3 with a few olefins and oxygenated olefins, *J. Phys. Chem., 100,* 5375-5381, 1996.

Sharkey, T., and F. Loreto, Water stress, temperature and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves, *Oecologia, 95,* 328-333, 1993.

Singh, H. B., and P. B. Zimmerman, Atmospheric distribution and sources of nonmethane hydrocarbons., in *Gaseous Pollutants: Characterisation and Cycling,* edited by J. O. Nriagu, pp. 177-235, John Wiley, New York, 1992.

Singh, H. B., et al., Acetone in the atmosphere: Distribution, sources, and sinks, *J. Geophys. Res., 99,* 1805-1819, 1994.

Singh, H. B., M. Kanakidou, P. J. Crutzen, and D. J. Jacob, High concentrations and photochemical fate of oxygenated hydro-carbons in the global troposphere, *Nature, 378,* 50-54, 1995.

Talbot, R. W., et al., Sources and sinks of formic, acetic and pyruvic acids over Central Amazonia, 2,. Wet season, *J. Geophys. Res., 95,* 16,799-16,811, 1990.

Trainer, M., E. Williams, D. Parrish, M. Buhr, E. Allwine, H. Westberg, F. Fehsenfeld, and S. Liu, Models and observations of the impact of natural hydrocarbons on rural ozone, *Nature, 329,* 705-707, 1987.

Werner, R. A., and E. H. Holsten, Current status of research with the spruce beetle *Dendroctonus rufipennis,* in *Application of Semiochemicals for Management of Bark Beetle Infestations: Proceedings of an Informal Conference,* pp. 23-29, U.S. Dep. of Agric. For. Serv. Intermountain Res. Stn., Ogden, Utah, 1995.

Zhu, Z., and D. L. Evans, U.S. forest types and predicted percent forest cover from AVHRR data, *Photogramm. Eng. Remote Sens., 60,* 525-531, 1994.

V. Fridd-Stroud, J. Greenberg, A. Guenther, P. Harley, and P. Vasconcellos, Atmospheric Chemistry Division, National Center for Atmospheric Research, 1850 Table Mesa Drive, Boulder, CO 80307-3000. (e-mail: harley@acd.ucar.edu)