Plant physiological influences on the fluxes of oxygenated volatile organic compounds from ponderosa pine trees

Gunnar W. Schade and Allen H. Goldstein

Department of Environmental Science, Policy, and Management,
Ecosystem Sciences Division, University of California, Berkeley, Berkeley, California, USA

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[1] Fluxes of oxygenated volatile organic compounds were measured above a ponderosa pine plantation, adjacent to the Blodgett Forest Research Station (38°53′42.9″N, 120°37′57.9″W, 1315 m elevation), with a fully automated relaxed eddy accumulation system coupled to a dual gas chromatograph-flame ionization detector (GC-FID) system. These measurements were initially reported by *Schade and Goldstein* [2001]. Here we further analyze these data to explore the physiological controls on emissions of 2-methyl-3-buten-2-ol (MBO), ethanol, and acetaldehyde. Measured MBO fluxes were compared to fluxes predicted by a detailed leaf-level emission model. Although the match was very good in general, the model failed to predict a declined emission potential on cooler days following a very cold night. It also consistently overpredicted fluxes in the morning, while underpredicting fluxes in the afternoon, particularly on warm days. We conclude that the ponderosa pine MBO emission potential changes in response to recent environmental temperatures on diurnal and daily timescales, similar to changes reported for isoprene emissions. Though ambient temperature appeared to be the most important driver of ethanol and acetaldehyde fluxes, vapor pressure deficit strongly influenced ethanol emissions from ponderosa pine, suggesting that stomatal opening impacts emissions. Ethanol emissions were also found to increase after high ozone deposition fluxes, which supports the theory that ozone-induced stress may trigger fermentation processes in the leaves. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* VOC emissions, methylbutenol, ethanol, ponderosa pine, physiology

1. Introduction

[2] Little is known about biogenic volatile organic compound (BVOC) emissions and their environmental or plant physiological controls other than for isoprene or monoterpenes. Short-chain oxygenated VOCs such as alcohols, carbonyls, and organic acids are emitted in potentially large amounts from the terrestrial biosphere [*Fall*, 1999], but ambient mixing ratio measurements as well as plant emission studies are limited. However, the potential importance of these oxygenated VOCs (OVOCs) in the atmosphere [*Singh et al.*, 1995; *Folkins and Chatfield*, 2000] warrants further research into their sources and sinks as well as the environmental drivers for their emission. For example, *Fall and Benson* [1996] summarized earlier findings on methanol emissions from plants, showing that stomatal opening affects emissions. However, the exact origin of methanol within the leaf is still unknown. *Kesselmeier et al.* [1997] showed that acetaldehyde emissions from *Pinus pinea* are probably also controlled by stomatal opening. Emissions of organic acids from many plants are low but can contribute to regional atmospheric acidity, in particular in the tropics [*Kesselmeier and Staudt*, 1999]. *Kirstine et al.* [1998] discovered large OVOC emissions from pastures, and *Warneke et al.* [1999] showed that leaf litter could be another substantial source for various OVOCs.

[3] In this publication we will focus on the two OVOCs: 2-methyl-3-buten-2-ol (MBO), an important precursor of acetone in the atmosphere [*Goldstein and Schade*, 2000], and ethanol, a precursor to atmospheric acetaldehyde and known to produce peroxyacetylnitrate, an important "storage" compound of NO_x in the atmosphere. A brief introduction to the current knowledge on these OVOCs follows.

[4] In western North America, MBO has been found to be emitted in large quantities from certain pine trees [*Harley et al.*, 1998]. This C_5, unsaturated alcohol appears to have the same main emission drivers as its close analog, isoprene, namely, photosynthetically active radiation (PAR) and temperature. Initial leaf-level emission measurements from several pine species, *Pinus ponderosa* L. in particular, have been used to model canopy-scale and regional MBO emissions [*Harley et al.*, 1998; *Baker et al.*, 1999; *Schade et al.*, 2000]. By comparing long-term emission measurements with model estimates, *Schade et al.* [2000] showed that the MBO emission potential is probably dependent on the recent ambient temperatures that the investigated ponderosa pine trees experienced, a finding very similar to that for isoprene emissions from a mixed deciduous forest in Canada [*Fuentes and Wang*, 1999].

[5] A plant's changing emission potential for isoprene has been attributed to the activity of the enzyme producing it, that activity being affected by ambient temperature levels [*Silver and Fall*, 1991; *Monson et al.*, 1992; *Kuzman and Fall*, 1993; *Monson et al.*, 1994; *Silver and Fall*, 1995; *Lehning et al.*, 1999; *Geron et al.*, 2000]. The effect manifests itself as a change of the plants basal emission rate (defined as the emission at 30°C and 1000 μmol m^{-2} s^{-1} PAR) and apparently can happen on a diurnal [*Sharkey et al.*, 1999], a weekly [*Fuentes and Wang*, 1999], and a seasonal basis [*Goldstein et al.*, 1998; *Schade et al.*, 2000; *Geron et al.*, 2000].

[6] Another alcohol emitted by plants is ethanol. *Rasmussen et al.* [1994], *Fukui and Doskey* [1998], and, recently, *Holzinger et al.*

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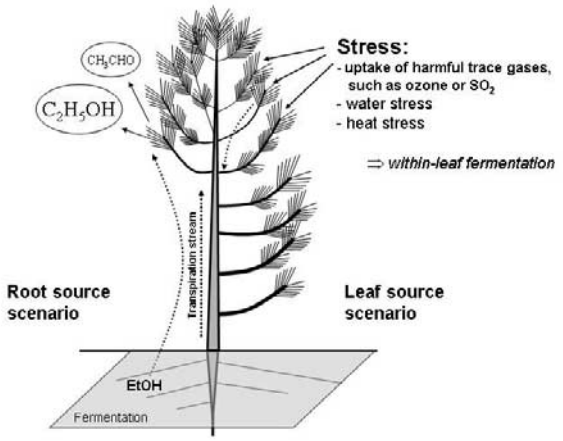

Figure 1. Possible sources of ethanol and acetaldehyde in ponderosa pine trees. Solid arrows denote trace gas fluxes, and dotted arrows denote within-plant transportation. Left-hand side shows the ''flooding scenario'' as described by *Kreuzwieser et al.* [1999], where the roots are the main source of ethanol and its transport to other parts of the plant occurs via the transpiration stream. Right-hand side shows an alternative, the ''stress scenario,'' where ethanolic fermentation is triggered in the leaves directly. Stress factors can include high levels of harmful trace gases, such as ozone [*Kimmerer and Kozlowski*, 1982]. Ethanol found in the stems may be locally produced or transported.

[2000] presented ethanol emissions from flooded trees and grasses that were largely enhanced over those from the nonflooded plants. Flooding also enhanced the emissions of acetaldehyde, apparently linked to the ethanol synthesized during anaerobic respiration in the plant's roots [*Kreuzwieser et al.*, 1999, 2000]. Under the conditions of flooding, acetaldehyde formation was attributed to daytime ethanol oxidation in the leaves [*Kreuzwieser et al.*, 2000]. Ethanol itself can be produced day and night and is probably transported upwards with the plant's transpiration stream. The concept is summarized on the left-hand side of Figure 1. To our knowledge, no research has been carried out to determine whether ponderosa pine in particular responds to root flooding by producing ethanol.

[7] Under ''dry,'' nonflooded conditions, ethanolic fermentation within leaves that are under stress is another possible source of ethanol in plants [*Tadege et al.*, 1999]. Fermentation has been shown to be possible under aerobic conditions as a response to several kinds of stress, such as high levels of harmful trace gases (e.g., O_3 or SO_2) or drought [*Kimmerer and Kozlowski*, 1982; *Kelsey and Joseph*, 2001]. In the Sierra Nevada mountains of California, ponderosa pine trees undergo both drought and ozone stress during the summer months [*Goldstein et al.*, 2000; *Bauer et al.*, 2000]. Their tissues show a higher potential to produce ethanol than other trees [*Kelsey*, 1996; *Kelsey et al.*, 1998a]. However, it is yet unknown whether ethanol is produced in all ponderosa pine tissues or only in one, such as the roots, and then transported to other parts of the tree (left-hand side of Figure 1). We have recently shown that large amounts of OVOCs are emitted from a ponderosa pine plantation in the Sierra Nevada mountains of California [*Schade and Goldstein*, 2001]. *Pinus ponderosa* L. is known to be a strong MBO emitter [*Baker et al.*, 1999; *Schade et al.*, 2000] and also a strong ethanol producer, and we identified the trees at this site to be the dominant source of measured above-canopy MBO and probably also of ethanol fluxes. Acetaldehyde was also emitted from the soil and litter compartments of the plantation [*Schade and Goldstein*, 2001].

[8] In this publication we take a closer look at the canopy-scale fluxes of MBO and ethanol at our field site. We investigate the variability of MBO fluxes compared to a detailed leaf emission model (section 3). We describe several conditions under which the modeled MBO fluxes deviate significantly from the measured canopy fluxes, and we attribute them to plant physiological changes possibly linked to enzyme activity. We also present evidence that daytime fluxes of ethanol depend on stomatal opening (section 4) and may be influenced by ozone deposition.

2. Methods and Database

2.1. Plantation Characteristics

[9] The measurement site near Blodgett Forest Research Station (38°53′42.9″N, 120°37′57.9″W, 1315 m elevation) on the western slope of the Sierra Nevada mountains has been extensively described by *Goldstein et al.* [2000], *Bauer et al.* [2000], and *Schade and Goldstein* [2001]. It consists of a typical clear-cut plot (owned by Sierra Pacific Industries), planted with *Pinus ponderosa* L. in 1990. Large amounts of woody litter and stumps can still be found throughout the plantation. The understory, mostly manzanita (*Arctostaphylos* spp.) and whitethorn (*Ceonothus cordulatus*) bushes, was almost completely cut throughout the plantation during routine shrub removal in spring 1999. Extensive field surveys of the biomass distribution were carried out in summer 1999 and spring 2000. Ponderosa pine ground coverage, tree height, and diameter at breast height (DBH) were measured throughout a 200 × 10 m transect extending from the measurement tower to the southwest, the main daytime wind direction. Leaf area index (LAI) and biomass density for each needle age class was calculated from allometric measurements on 17 cut trees [*Xu*, 2000] and their DBH measurements. Leaf area during summer 1999 was extrapolated from periodic leaf elongation measurements. It reached a maximum of ~4 (all sided) at the end of the growing season. A weighted mean LAI of the transect was used in this study.

2.2. Flux Measurements

[10] Meteorological data and trace gas mixing ratios and fluxes (CO_2, H_2O, O_3, and hydrocarbons) were measured from a walk-up tower ~5–6 m above the average tree height [*Goldstein et al.*, 2000; *Bauer et al.*, 2000; *Schade and Goldstein*, 2001]. Leaf temperatures and leaf wetness were measured (using dew sensors from Campbell Scientific, Utah) at three locations on a single tree near the tower. OVOC flux measurements were made continuously from the beginning of July to the beginning of September 1999. The relaxed eddy accumulation flux measurements were carried out using a three-dimensional (3-D) sonic anemometer (Campbell Scientific, Logan, Utah) run by a CR23X data logger and two segregator valve setups (General Valve/Parker, Fairfield, New Jersey). The segregator valves were switched based on a predetermined lag time in the main sampling line. The performance of the system is described in detail by *Schade and Goldstein* [2001]. A comparison of the Campbell anemometer with the main system ATI anemometer (Applied Technologies, Inc., Longwood, Colorado) turbulence measurements showed good agreement for all variables. An automated gas chromatograph with dual flame ionization detectors was used to quantify a series of VOCs and OVOCs as described in more detail by *Lamanna and Goldstein* [1999] and *Schade et al.* [1999].

3. MBO Fluxes

3.1. Flux Model

[11] Fluxes of MBO from western U.S. pine species can, in general, be described in the same way as isoprene emissions from oak species. They show both light and temperature responses that were first described by *Harley et al.* [1998] and were later confirmed by our canopy-scale measurements [*Schade and Goldstein*, 2001]. *Baker et al.* [1999] and *Schade et al.* [2000] used these responses to

Table 1. Input Parameters to MBO Leaf Emission Model

	$D\delta$,[a] g m^{-2}	LAI × δ,[b] m^2 m^{-2}	f	$\varepsilon\delta$, μg g^{-1} h^{-1}
Age 0	70–155[c]	0.7–1.55[c]	0.4	18
Age 1	150	1.25	0.4	16.2
Age 2	120	1	0.4	9
Relative error	10%	10%	20%	5%

[a] Data based on area that the tree covers.
[b] All-sided leaf area index (divide by 3.3 for projected LAI).
[c] Increase (nonlinear) during the measurement period (specific leaf area is 100 g m^{-2} for current year needles and 120 g m^{-2} for 1- and 2-year-old needles).

model MBO emissions from our ponderosa pine plantation, and the latter developed a more detailed leaf emission model to account for the plantation's relatively open structure. Here we further develop our ponderosa pine modeling approach: As described by *Schade et al.* [2000], we model emissions from an individual, representative ponderosa pine tree using its average LAI and biomass in three vertical layers consisting of the three age classes of needles the tree supports at this site (current year, 1 year old, and 2 years old). Light is allowed to strike the tree from all sides. The sunlit portion of leaves is calculated from

$$L_{\text{sunlit}} = \left[1 - \exp\left(-kL_{\text{p}}\Omega\right)\right]/k, \quad (1)$$

where L_{p} is the projected or one-sided LAI (total LAI divided by 3.3 for ponderosa pine [*Schade et al.*, 2000]), k denotes the extinction coefficient, and Ω is the within-shoot clumping factor. The Ω was estimated to be 0.8 for the ponderosa pine trees [*Goldstein et al.*, 2000]. The extinction coefficient k equals 0.5/sin (B) for a spherical leaf angle distribution, with B being the solar elevation angle. Though there are indications for a more vertical distribution, we presumed a spherical distribution as is commonly done in VOC emission modeling [*Guenther et al.*, 1995]. Finally, L_{p} was calculated from the transect LAI estimates and the ponderosa pine ground coverage (40%).

[12] The PAR incident on sunlit leaves was calculated from

$$\text{PAR}_{\text{sunlit}} = \text{PAR}_{\text{direct}}k + \text{PAR}_{\text{shade}}. \quad (2)$$

The direct and diffuse components of PAR were calculated from total above-canopy PAR and algorithms published by *Weiss and Norman* [1985]. Contrary to the model by *Guenther et al.* [1995], shade leaf PAR was estimated directly from above-canopy diffuse PAR applying the "slab" method described by *Norman* [1979] and assuming a leaf reflectance of 0.08 [*Pu et al.*, 1998] and a leaf transmittance of zero in the PAR wavelengths.

[13] The MBO basal emission rate, ε, was adopted to be 18 μg g^{-1} h^{-1} from leaf-level measurements carried out in 1998 (D. Gray, personal communication, 1999) and reported by *Schade et al.* [2000] and was scaled by leaf age. Thus the model already includes a plant physiological response, i.e., leaf age (90% and 50% of current year needle emissions assumed for 1-year-old and 2-year-old needles, respectively), similar to those discussed by *Harley et al.* [1997]. Instantaneous changes in the emission rate according to changes in the light and temperature environment were modeled based on air temperature at tree height and based on above-canopy PAR fluxes. Canopy-scale fluxes, F_{MBO}, were calculated from

$$F_{\text{MBO}} = \varepsilon D\gamma\delta f, \quad (3)$$

where γ represents the light and temperature emission parameters [*Schade and Goldstein*, 2001], D is biomass density, δ scales the emission to leaf age and potential biomass density changes, and f is the ponderosa pine ground coverage. The variation of the model input parameters is shown in Table 1. Note that the trees support a sizable amount of biomass at this age (≤10 years old) and that there was continuing growth during the measurement campaign in July and August 1999.

[14] Major uncertainties using this approach are the light transmission model and the ponderosa pine ground coverage. The latter was found to be not uniform, showing a higher tree density closer to the tower (<80 m) than farther away from it (>150 m). In an attempt to improve the model estimate, we scaled both the ground coverage and LAI with the predictions of a fetch model (C.-I. Hsieh, personal communication, 2000) and our transect measurements, which showed that most of the flux is expected to come from distances closer to the tower. However, both the scaled LAI and the ground coverage used in the model presented here were only 5% larger then the average ponderosa pine ground coverage for the daytime fetch area. Minor uncertainties are associated with the leaf biomass, the age scaling of the basal emission rate, the emission parameters, and the mean emission potential of 18 μg g^{-1} h^{-1} (Table 1) for current year needles.

3.2. Flux Anomalies

[15] Daytime fluxes were predicted extremely well by the model (r^2 = 0.91, slope = 1.02), except for a few outliers (Figure 2). The model emissions also predicted diurnal changes in the MBO emission rate well (Figure 3a). However, actual emissions were slightly overestimated in the morning and slightly underestimated in the late afternoon. This trend holds for the complete data set. Figure 3b shows the relative differences between measured and modeled MBO fluxes for the main daylight hours, which account for >95% of total daily MBO emissions. In particular, during hot days the trend from overestimation to underestimation of MBO was prominent, whereas it was less pronounced for cold days (data not shown). For the warm days shown in Figure 3b, afternoon measurement-to-model ratios were significantly higher than in the morning (p = 0.02 at the 95% level). In order to elucidate this systematic model-to-measurement deviation, we carried out a sensitivity analysis. Leaf temperatures instead of air temperatures were used, the model parameters were varied to those based on leaf-level measurements by *Harley et al.* [1998], and the leaf reflectance and transmittance parameters were varied to increase or decrease the amount of diffuse radiation penetration. Neither a single change nor a combination of these changes was able to remove the trends shown in Figure 3. While

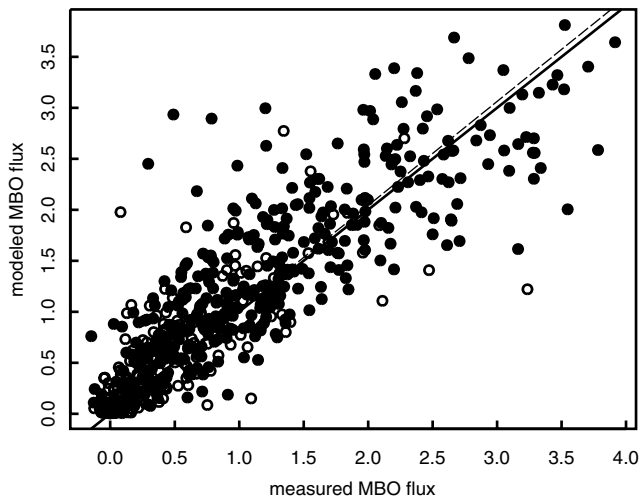

Figure 2. Measured versus modeled emissions of MBO. Dashed line shows the best fit to the main daytime values (solid circles, denoting 1000–1830 LT). Solid line is a 1:1 line.

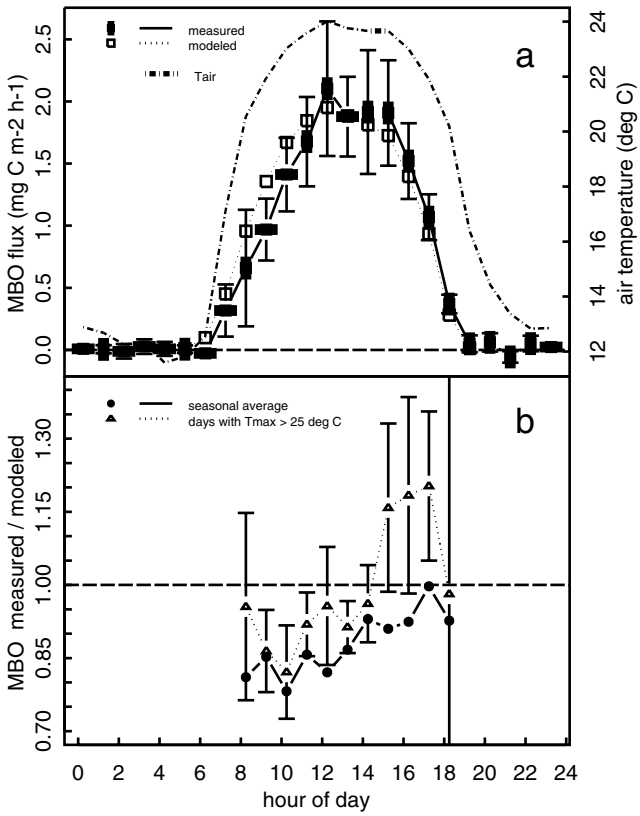

Figure 3. (a) Air temperature (T_{air}, dash-dotted line) and diurnal changes of measured (solid squares) and modeled (open squares) MBO fluxes during a representative week in late July 1999. (b) Mean diurnal changes of the ratio between measured and modeled MBO fluxes. Shown are the average seasonal change and the change during hot days (maximum air temperature (T_{max} is >25°C). Hour of day is local time minus 1 hour. Error bars are standard errors.

they changed the slope of the model-to-measurement intercomparison (Figure 2), the relative morning-to-afternoon trend persisted in all cases. Though the combined errors of modeled and measured values suggest that the observed trend lies within the analytical accuracy, this analysis confirms that it cannot be attributed to the model input parameters.

[16] The diurnal discrepancy between measurements and model could be explained by a changing emission potential throughout the day. *Sharkey et al.* [1999] recently showed that the isoprene basal emission rate of oak leaves at Harvard Forest increased dramatically during two summer days with temperatures over 30°C. The measured relative increase is of the same magnitude as our diurnal change in the measurement-to-model ratio (~50% increase), which is equivalent to an increase in basal emission rate. Depending on temperature, the emission potential at 30°C and 1000 μmol m^{-2} s^{-1} PAR flux could be 50–70% higher in the late afternoon compared to morning or midday values on hot summer days. A temperature-driven change of the basal emission rate is most probably also the explanation for the difference in values reported for the MBO basal emission rate from ponderosa pine by *Harley et al.* [1998] and those by D. Gray at the same site (reported by *Schade et al.*, [2000]). While the value of 25 μg g^{-1} h^{-1} reported by *Harley et al.* [1998] was acquired during a limited number of hot days in early summer 1997, 18 μg g^{-1} h^{-1} was found as the mean under variable climatic conditions in 1998 (D. Gray, personal communication, 1999).

[17] A more reliable statement about changes in the emission potential on the basis of our canopy-scale fluxes can be made on a day-to-day comparison rather than an hour-to-hour comparison. An obvious deviation between measurement and model data occurred after day 218 (6 August), shown in Figure 4. A sudden drop in ambient temperatures, with nighttime values down to 5°C, was followed by an unusually cold week. During (and partially after) this time, marked by vertical dotted lines in Figure 4, the model drastically overestimated measured MBO fluxes (Figure 5) by up to a factor of 2. The model-to-measurement intercomparison improved only after maximum temperatures had been higher than 22°C for several days. This behavior was repeated, though more briefly, at the beginning of September (day 243) when temperatures dropped again. Presumably, the rapid recovery of ambient temperatures played a role here. In particular, nighttime air temperatures had dropped below 10°C for only four nights.

[18] Another interesting period, marked by the vertical dashed lines in Figure 4, occurred following two hot summer days (24 and 25 August). For three out of the four subsequent days, measured fluxes were significantly higher than modeled fluxes. Nighttime temperatures were among the highest measured throughout the summer. Again, this could be interpreted as a temporary but significant change in the trees' emission potential, increasing as a response to high ambient temperatures. A respective change did not occur following the two hot days in mid-July (days 193 and 194, Figure 4). The major differences between these hot periods were that the July period had lower vapor pressure deficits, higher soil moisture, and higher ozone deposition [*Bauer et al.*, 2000] while the trees were still developing current year needles. We cannot assess if any one or several of these factors together are responsible for the differences. However, it appears that the trees were more drought stressed in late August as compared to mid-July and that this along with partial stomatal closure in the August period might have triggered an increased MBO emission capacity as a stress response, similar to the one found for isoprene in other plants [*Fang et al.*, 1996; *Loreto et al.*, 1998].

4. Ethanol Fluxes

[19] Ethanol fluxes from this ponderosa pine plantation were most probably dominated by emissions from the trees rather than from the soil or litter compartments [*Schade and Goldstein*, 2001]. Following the shrub removal in spring 1999, little living understory, potentially contributing to the fluxes, was left during the measurement period in 1999. Having one dominating source reduces

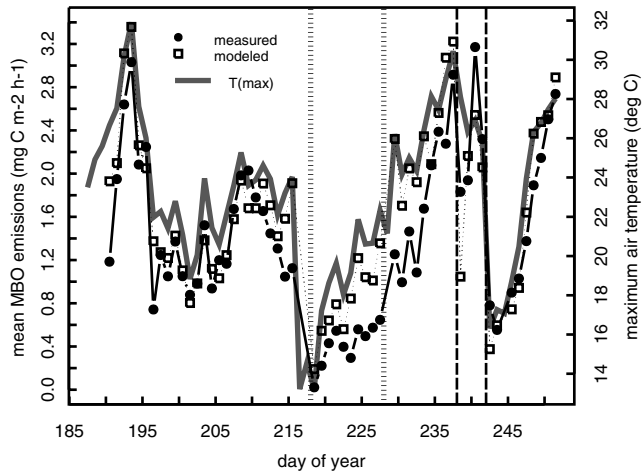

Figure 4. Mean daytime (1100–1730 LT, given as Pacific standard time (PST) in graph (hour of day is local time minus 1 hour)) measured (circles) and modeled (squares) MBO emissions throughout the measurement period from 6 July to 2 September 1999. Vertical dashed and dotted lines mark episodes discussed in text.

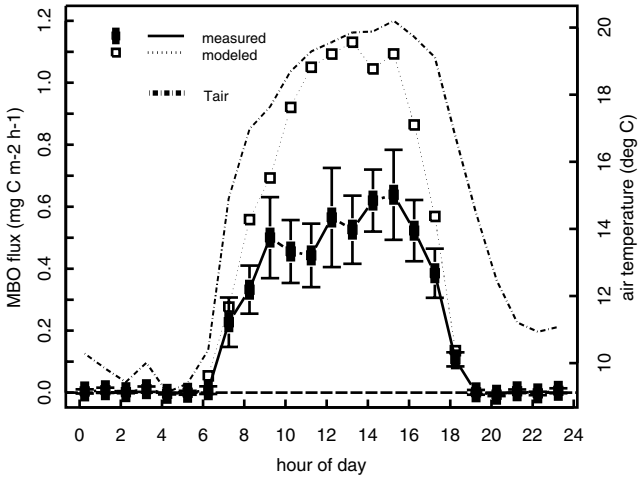

Figure 5. Discrepancy between measured (solid squares) and modeled (open squares) MBO emission during the cold episode in the beginning of August 1999 (days 218–229). Hour of day is local time minus 1 hour. Error bars are standard errors.

complication in the flux measurements and facilitates analysis. To investigate whether the ponderosa pine trees were the dominant source of ethanol, we took some core samples from live stems, rotting stumps, and woody biomass left over from the logging operation 10 years ago. The stem samples showed ethanol concentrations of $\sim$0.04 μmol g^{-1} dry weight of sapwood, very similar to those reported by *Kelsey et al.* [1998b]. Concentrations were generally larger in the phloem/inner bark and were generally lower toward the base of the trees, consistent with results from ponderosa pine trees in Oregon (R. Kelsey, USDA Forest Service, Corvallis, Oregon, personal communication, 2000). The rotting stumps and woody biomass had slightly lower ethanol concentration than the live stems but might contribute to the observed nighttime fluxes of ethanol [*Schade and Goldstein*, 2001]. Only daytime fluxes, however, were investigated in the following analysis.

4.1. Influence of Stomatal Opening

[20] We have shown previously that ethanol fluxes increased exponentially with temperature but were also correlated with ambient humidity levels [*Schade and Goldstein*, 2001]. The variability of fluxes with increasing temperature and their dependence on ambient humidity suggests a possible plant physiological influence. A closer analysis, depicted in Figure 6, revealed that ethanol fluxes at a certain temperature decreased with vapor pressure deficit (VPD), which can serve as a proxy of stomatal opening in summer-dry ecosystems [*Bauer et al.*, 2000]. A similar correlation was found when latent heat fluxes were used instead of VPD (data not shown). That and the fact that diurnal fluxes maximize around noon, then start decreasing before the daytime maximum temperature is reached [*Schade and Goldstein*, 2001], imply that ethanol emissions are at least under partial stomatal control.

[21] Impacts of stomatal opening have also been found on methanol emissions from plants [*MacDonald and Fall*, 1993; *Nemecek-Marshall et al.*, 1995]. Both methanol and ethanol are very polar VOCs. However, as far as is currently known [*Fall*, 1999], they do not share a common origin in the plant. Nevertheless, our daytime canopy-scale methanol and ethanol fluxes were highly correlated (r^2 = 0.66, slope = 0.22). When the methanol, acetaldehyde, and acetone fluxes from our plantation were analyzed in the same way as ethanol, the correlations with VPD (or ozone deposition) were less clear than for ethanol. This is most probably a result of the fact that methanol, acetone, and acetaldehyde were also emitted from the soils and the accumulated onsite litter [*Schade and Goldstein*, 2001] and that both these and the tree emissions are driven by temperature. However, emissions from the soil and litter compartments probably do not follow the same drivers that trigger stomatal opening. In fact, soil and litter temperature, and soil wetting as a result of light rain, were stronger drivers of these emissions [*Schade and Goldstein*, 2001]. The above-canopy fluxes of these OVOCs were therefore a mixture of at least two different, similar-size sources and can be expected to show a higher variability than ethanol fluxes, which were dominated by the ponderosa pine trees.

[22] In summary, in spite of a high variability of the measured ethanol fluxes, there is indirect evidence to conclude that stomatal opening significantly influences daytime ethanol fluxes, and potentially the other OVOC fluxes as well.

4.2. Other Influencing Factors

4.2.1. Connection between ethanol emissions and ozone deposition. [23] Instantaneous ethanol emissions were correlated with both ozone deposition flux and ozone deposition velocity at warm temperatures during the day. Ozone deposition velocity can be considered as another indicator of stomatal opening in this summer-dry ecosystem [*Bauer et al.*, 2000]. It is therefore difficult to separate the effect of ozone uptake on plant OVOC emissions from a mere covariation of fluxes due to a simultaneous control by stomatal opening. However, the correlation of ethanol emissions with actual ozone deposition fluxes was higher than that for ozone deposition velocity. The correlation was further improved when ethanol emissions were plotted against ozone deposition fluxes from the preceding hour, depicted in Figure 7. Ethanol fluxes generally increased with the amount of ozone deposited at a given temperature, for temperatures higher than 20°C in particular. No further improvement in correlation was achieved when a 2-hour lag time between ozone deposition flux and ethanol emission was investigated. In addition to the correlation of instantaneous fluxes, an analysis of the integrated daytime ozone deposition showed a good correlation with integrated daytime ethanol emissions (r^2 = 0.66 before day 215, r^2 = 0.44 after day 215, $p < 0.0001$ in both cases). Significantly higher ethanol emissions at similar temperatures occurred earlier in summer

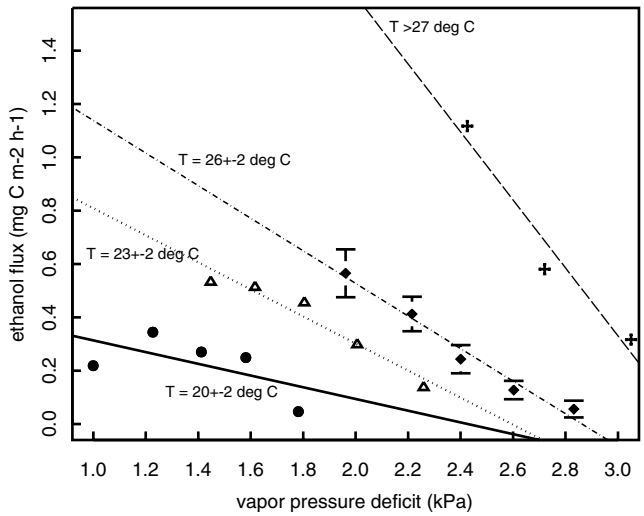

Figure 6. Dependence of daytime (1000–1930 LT, given as PST in graph) ethanol fluxes on ambient air temperatures and vapor pressure deficit (VPD). Note that the response to VPD increases with increasing ambient temperatures as expected for a response of stomatal opening to VPD. Error bars are standard errors.

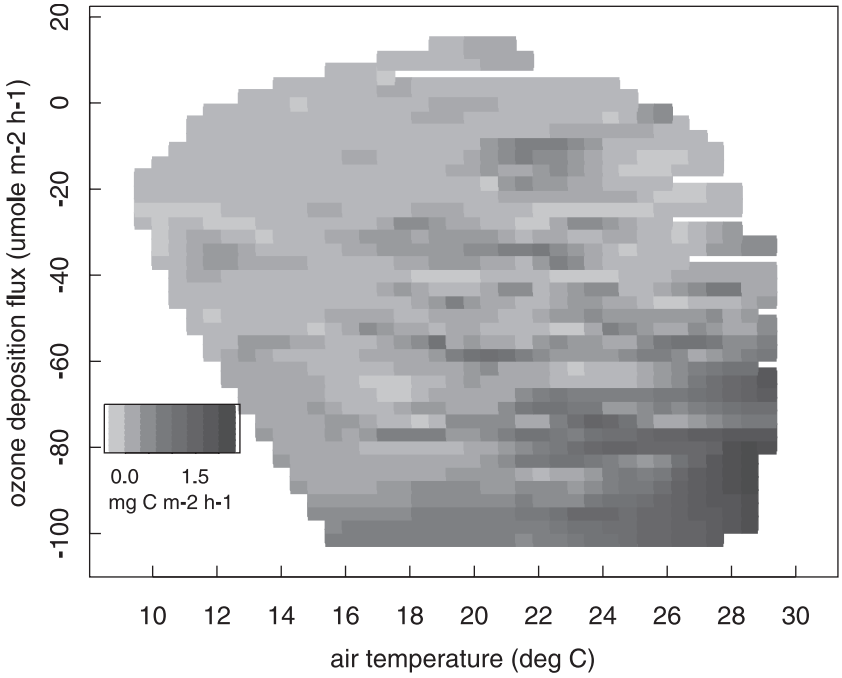

Figure 7. Two-dimensional representation of daytime (1000–1930 LT, given as PST in graph (hour of day is local time minus 1 hour)) ethanol fluxes as dependent on ambient air temperatures and the preceding hour ozone deposition flux. See color version of this figure at back of this issue.

when the current year needles were still growing rapidly, which is consistent with a higher sensitivity to ozone deposition of these needles [*Bauer et al.*, 2000].

[24] In conclusion, our data indirectly support the finding that plants exposed to ozone respond with ethanol production in their leaves [*Kimmerer and Kozlowski*, 1982], followed by emission to the atmosphere. That stress response appears to be correlated with the ozone uptake rather than simply with ozone exposure and appears to occur with a lag time on the order of 1 hour.

4.2.2. Possible connections to acetaldehyde fluxes and soil moisture. [25] If the presence of ethanol in leaves were only due to transport, such as from the roots (Figure 1), any observed acetaldehyde emission would probably be due to ethanol oxidation in the leaves during photosynthetically active times [*Kreuzwieser et al.*, 1999]. Hence, assuming the supply of ethanol is stable, the ratio of ethanol to acetaldehyde fluxes should decrease during the day as compared to at night and possibly scale with PAR. We found the presumed day-night change (data not shown) in the flux ratio. However, the observed diurnal change in the ratio could simply be driven by the different source distribution and strength, i.e., a smaller nighttime soil acetaldehyde source compared to the nighttime ethanol source [*Schade and Goldstein*, 2001]. Whether the presumed relationship exists under field conditions will have to be tested under more controlled conditions with leaf- or branch-chamber experiments.

[26] An argument against the root transport scenario is the dry conditions at our site in summer. High soil moistures could lead to oxygen-depleted conditions similar to flooding, thereby inducing anaerobic fermentation in roots. Soil moisture at our site has been measured since 1997 [*Goldstein et al.*, 2000], and data at 50 cm depth showed a decrease from 21 to 17.4% by volume (time domain reflectometry sensor, Campbell Scientific Inc., Logan, Utah) during the measurement period in summer 1999. It is unlikely that anaerobic soil conditions existed at these moisture levels anywhere in the plantation. That does not preclude that soil moisture might have had a significant impact; however, any such influence was too small to be elucidated from the observed ethanol fluxes throughout such a small range of observed soil moistures. A longer measurement period including higher soil moisture regimes would be necessary to conclude whether an influence of soil moisture is important in this ecosystem.

5. Conclusions

[27] Further analysis of our flux measurement data set on oxygenated VOCs revealed several ways that plant physiology plays a significant role in the control of their emissions to the atmosphere. Similar to the isoprene emissions measured over a boreal forest [*Fuentes and Wang*, 1999], the MBO emission potential was reduced after and during a low-temperature episode. A series of hot days triggered a higher MBO emission potential during the following days although ambient temperature levels were dropping. Our data also suggest that the emission potential may change on a diurnal basis, similar to that reported for isoprene emissions from *Quercus alba* and *Quercus rubra* [*Sharkey et al.*, 1999]. Leaf-level measurements at the same site in 2000 (D. Gray, personal communication, 2000) confirm that the basal emission rate of MBO from ponderosa pine can change with temperature throughout the day. These findings lead to the conclusion that reporting a single "basal emission rate" (at 30°C and 1000 μmol m^{-2} s^{-1} PAR) may not be a completely accurate representation of a plant's potential emission rate (for MBO or isoprene). It may be more appropriate to report a range of values along with the ambient temperature conditions the plants experienced before and during the measurements, similar to *Zhang et al.* [2000], or to report the actual seasonality in basal emission rates as presented by *Geron et al.* [2000] for isoprene and *Staudt et al.* [2000] for monoterpenes.

[28] We also presented indirect evidence that emissions of ethanol from our plantation were influenced by stomatal opening. This was probably true for other OVOCs, such as methanol, acetaldehyde, and acetone, as well. However, analysis of these other canopy-scale OVOC fluxes was complicated by the fact that they were emitted from both the ground and the trees [*Schade and Goldstein*, 2001], whereas only the tree source was impacted

by plant physiological controls. Ethanol fluxes were also correlated to the deposition of ozone, hence our data supports the theories that ozone-induced stress can enhance ethanol production in the leaves, consequently leading to higher emission rates. Future measurements and analyses should focus on whether ozone and ethanol fluxes simply covary because of their mutual dependence on stomatal opening or whether ethanol production in response to ozone stress is indeed the source of the elevated ethanol emissions.

[29] The magnitude of ethanol and methanol fluxes from this plantation was similar to that of the monoterpenes and MBO, respectively, on a mass carbon basis. This, as we pointed out earlier [*Schade and Goldstein*, 2001], would translate to substantial global emissions, if these compounds were found to be emitted as ubiquitously as isoprene. Because of their long lifetimes, OVOCs can be transported over large distances and into the free troposphere, where they can contribute to ozone formation and influence the oxidative capacity of the upper troposphere [*Singh et al.*, 1995; *Folkins and Chatfield*, 2000; *Brühl et al.*, 2000]. Therefore further analysis of their sources and their respective environmental and physiological drivers is warranted.

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A. H. Goldstein and G. W. Schade, Department of Environmental Science, Policy, and Management, Ecosystem Sciences Division, University of California, Berkeley, 151 Hilgard Hall, Berkeley, CA 94720-3110, USA. (ahg@nature.berkeley.edu; gws@nature.berkeley.edu)

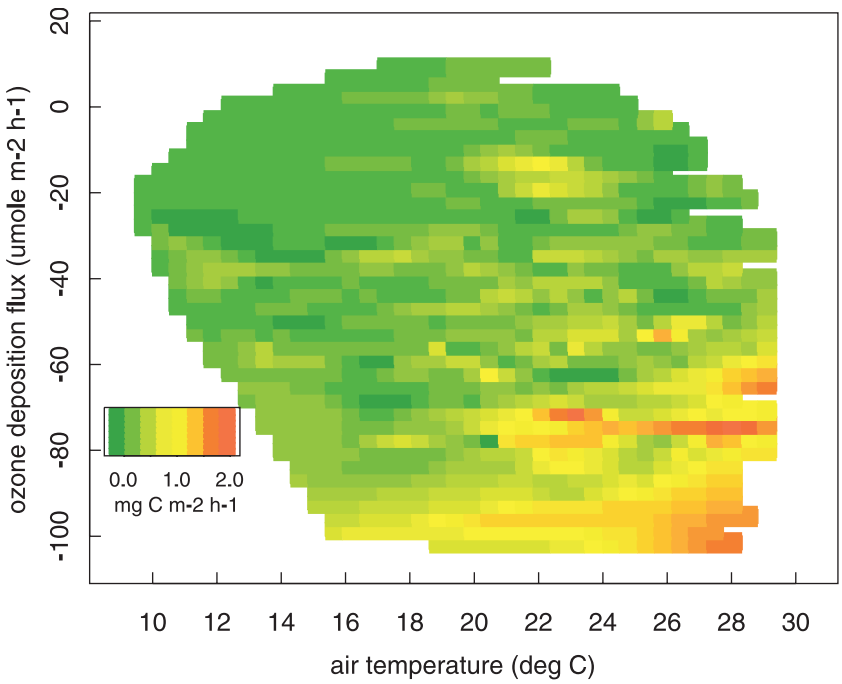

Figure 7. Two-dimensional representation of daytime (1000–1930 LT, given as PST in graph (hour of day is local time minus 1 hour)) ethanol fluxes as dependent on ambient air temperatures and the preceding hour ozone deposition flux. See color version of this figure at back of this issue.