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Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation

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Abstract. We present the first canopy-scale, continuous, long-term flux measurements of a suite of oxygenated volatile organic compounds (OVOCs). Fluxes 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 (REA) system coupled to a dual GC-FID system. Quantified OVOCs included 2-methyl-3-buten-2-ol (MBO), methanol, ethanol, acetaldehyde, and acetone. These compounds were the most abundant nonmethane VOCs at this site and were highly correlated with each other, especially during daytime. Fluxes were dominated by MBO and methanol with daytime average emissions of ~1.3 mg C m^{-2} h^{-1}. Ethanol, acetaldehyde, and acetone fluxes were approximately a factor of 5 lower. All fluxes showed diurnal cycles with maxima around noon and minima at night. Temperature and light were the main drivers for MBO emission, and the canopy level flux responses were virtually identical with previously measured leaf level fluxes from ponderosa pine trees at the same site. Ambient temperature appeared to be the most important driver of the other OVOC fluxes, but moisture also played a role, particularly for ethanol and acetone emissions, shown for the first time under field conditions. Soil and litter emissions, measured using a Pyrex glass chamber, contributed significantly to the canopy level fluxes of methanol, acetaldehyde, and acetone, and had a much smaller contribution to the canopy fluxes of ethanol. If the magnitude of these OVOC fluxes is similar in other ecosystems, they will have to be considered a major volatile organic compound emission to the atmosphere and a potentially significant carbon loss from the biosphere.

1. Introduction

Scientific knowledge of biogenic volatile organic compound (BVOC) emissions and their atmospheric chemistry has increased dramatically in the last decade. However, research has focused largely on reactive BVOCs, such as isoprene and terpenes, and still little is known about emissions of oxygenated VOCs (OVOCs) [*Fall*, 1999; *Guenther*, 1999]. OVOCs can constitute a significant amount of total plant emissions [*Arey et al.*, 1991; *Winer et al.*, 1992; *König et al.*, 1995; *Janson et al.*, 1999] or even dominate them [*Harley et al.*, 1998; *Kirstine et al.*, 1998; *Fall et al.*, 1999], and OVOCs such as lower alcohols and acetone are abundant in rural environments [*Ciccioli et al.*, 1993; *Goldan et al.*, 1995; *Riemer et al.*, 1998; *Lamanna and Goldstein*, 1999; *Goldstein and Schade*, 2000]. Plant litter and forage production have also been identified as potentially significant sources of these trace gases to the atmosphere [*Kirstine et al.*, 1998; *Warneke et al.*, 1999; *de Gouw et al.*, 1999; *Schade et al.*, 1999a]. Because of analytical difficulties in measuring these low-molecular-weight, polar compounds in the atmosphere, few published data are currently available. Data on 2-methyl-3-buten-2-ol (MBO) emissions are relatively sparse as well. So far, canopy-scale emissions have only been published on the basis of measurements at our site in the Sierra Nevada [*Harley et al.*, 1998; *Baker et al.*, 1999; *Schade et al.*, 2000].

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The tropospheric abundance of the OVOCs methanol and acetone has received special attention because of their impact on tropospheric chemistry. Acetone photolysis leads to a direct production of HO_x radicals. *Singh et al.* [1995] measured OVOCs at midtropospheric altitudes and concluded that their oxidation could increase HO_x concentrations, which were measured at consistently higher levels than predicted by models. *McKeen et al.* [1997] and *Keim et al.* [1999] showed that models which included acetone chemistry indeed improved the model-measurement HO_x (and NO_x/NO_y) comparison. Acetone can also serve as a temporary sink for NO_x radicals through the formation of peroxyacetyl nitrate (PAN), thereby altering the NO_x to NO_y ratio.

Singh et al. [1994] attributed 51% of the tropospheric acetone sources to the oxidation of anthropogenic hydrocarbons, such as propane or isobutane, and approximately equal amounts to biomass burning and direct biogenic emissions. However, since the discovery of very high acetone abundances in the atmosphere of rural areas [*Goldan et al.*, 1995; *Riemer et al.*, 1998; *Lamanna and Goldstein*, 1999; *Ciccioli et al.*, 1999] and new sources of acetone, such as litter [*Warneke et al.*, 1999] or the oxidation of biogenically emitted methylbutenol [*Ferronato et al.*, 1998; *Goldstein and Schade*, 2000] and monoterpenes [*Reissell et al.*, 1999], the acetone budget now appears to be largely dominated by biogenic sources but remains highly uncertain [*Singh et al.*, 2000; *Goldstein and Schade*, 2000].

Even less information is available about the atmospheric abundances and budgets of methanol, ethanol, and acetaldehyde [*Fall*, 1999]. Ambient mixing ratio correlations with other biogenic VOCs [*Goldan et al.*, 1995; *Lamanna and Goldstein*,

1999] suggest that these OVOCs may have strong biogenic sources as well. It is known that methanol and acetaldehyde are emitted by live leaves [*Kimmerer and MacDonald*, 1987; *Fall and Benson*, 1996; *Kesselmeier et al.* 1997; *Martin et al.*, 1999], and high acetaldehyde fluxes have been measured from orange orchards [*Ciccioli et al.*, 1999]. Furthermore, leaf litter may be a strong source of methanol, possibly accounting for 40×10^{12} g yr^{-1} of emissions globally [*Warneke et al.* [1999]. However, ethanol was not a major emission component of leaf litter emissions [*Warneke et al.*, 1999]. Cutting and drying of grasses and clover also lead to substantial emissions of OVOCs [*Kirstine et al.*, 1998; *de Gouw et al.*, 1999], including methanol, acetaldehyde, acetone, and butanone (methylethyl ketone, MEK).

Ethanol can be produced in plant leaves [*Kimmerer and MacDonald*, 1987], primarily as a product of anaerobic respiration. Ponderosa pine (*pinus ponderosa* L.) is known to be a strong ethanol producer [*Kelsey*, 1996; *Kelsey et al.*, 1998], but no data have been published on how much ethanol they emit to the atmosphere. However, healthy lodgepole pine (*Pinus contorta*), also a strong ethanol producer [*Kelsey*, 1996], emitted between 20 and 60 $\mu g\ m^{-2}\ d^{-1}$ ethanol from its boles [*Gara et al.*, 1993]. During the day, ethanol that was produced in the roots [*Kelsey et al.*, 1998] could get transported with the transpiration stream and is believed to get metabolized to acetaldehyde and acetic acid in the leaves before emission. Therefore it can serve as the main precursor of acetaldehyde emissions [*Kreuzwieser et al.*, 1999; *Kreuzwieser et al.*, 2000], and a strong ethanol producer such as ponderosa pine likely emits acetaldehyde as well.

In this paper, we report emissions of the alcohols 2-methyl-3-buten-2-ol (MBO), methanol, and ethanol, as well as the carbonyls acetaldehyde and acetone, from a ponderosa pine plantation in the Sierra Nevada mountains, California. A new relaxed eddy accumulation (REA) approach, coupled to an automated in situ gas chromatography-flame ionization detector (GC-FID) system, was successfully used to measure these OVOC fluxes at hourly intervals for approximately 60 consecutive days in summer 1999. The measured fluxes are analyzed to elucidate their environmental and physiological drivers.

2. Experimental Methods

2.1. Field Site

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]. The site is characterized by a Mediterranean climate with predominant rainfall between September and May and almost no rain during the summer months. It consists of a typical clear-cut plot (owned by Sierra Pacific Industries, SPI), planted with *Pinus ponderosa* L. in 1990. Large amounts of woody litter and stumps can still be found throughout the plantation. Among the pines there are also a few individuals of douglas fir (*Pseudotsuga menziesii*), white fir (*Abies concolor*), black oak (*Quercus kellogii*), and incense cedar (*Calocedrus decurrens*). The understory was dominated by manzanita (*Arctostaphylos* spp.) and whitethorn (*Ceonothus cordulatus*), which, however, was almost completely cut throughout the plantation during routine shrub removal in spring 1999.

A walk-up tower was erected in 1997, when the trees were 6-7 years old and 3-4 meters tall. Meteorological data and trace gas mixing ratios and fluxes (CO_2, H_2O, O_3, and hydrocarbons) were measured approximately 5-6 m above the average tree height [*Lamanna and Goldstein*, 1999; *Goldstein et al.*, 2000; *Bauer et al.*, 2000]. Furthermore, gradients of water, CO_2, and temperature were measured at four heights throughout the canopy. In 1999, leaf temperatures and leaf wetness (Campbell Scientific, Logan, Utah) were measured at four locations on a single tree near the tower. The tower fetch area extends approximately 200 m to the SW during daytime. The nighttime fetch is less well defined but generally lies in the opposite, NE direction. For the REA system, a three-dimensional sonic anemometer (Campbell Scientific), run by a CR23X data logger, was mounted approximately 11 m above ground on a ~2 m beam extending to the SW.

2.2. Hydrocarbon Measurements

An automated gas chromatograph with dual FIDs was used to quantify a series of VOCs and OVOCs as described in detail by *Lamanna and Goldstein* [1999] and *Schade et al.* [1999b]. In 1999, the measurement setup consisted of a 3/8" Teflon perflouroalkoxy (PFA) sampling line, through which ambient air was continuously drawn into a temperature-controlled building next to the tower at a controlled flow of 10 L min^{-1}. Two separate subsamples from the airstream were preconcentrated onto a pair of Silcosteel© microtraps, sequentially filled with a small amount of glass beads, and approximately equal amounts of Carbopack B and Carbosieve SIII (~12 mg, Supelco Inc.). The cold block imbedding the microtraps was reduced in size by a factor of 10 compared to the previous deployments [*Lamanna and Goldstein*, 1999; *Schade et al.*, 1999b] and cooled with two 7.5 A thermoelectric elements (Ferrotec America Corporation, Manchester, New Hampshire). Laboratory tests showed that no breakthrough of the compounds of interest occurred at trap temperatures below -2°C for a sample size of 210 mL. This was done by analyzing dynamic dilutions of ppm standards (see below) into ambient air up to mixing ratios of approximately twice as high as expected at the field site. In the field the cold block temperature was kept between -5° and -10°C during sampling, and the sample size was never larger than 150 mL. After collection the samples were thermally desorbed on-column (250°C for 1.2 min), separated by two 60 m, 1 μm film Rtx-WAX columns with 5 m retention gaps, and detected by two FIDs (a sample chromatogram is given by *Goldstein and Schade* [2000]). The setup was fully automated (HP Chemstation and Campbell Scientific data logger) and measured a pair of 30 min average samples in situ once every hour.

The system was calibrated by automatic dilution of primary ppm level gas standards (Scott Marrin Inc., Riverside, CA) into the tower sampling line every 10 hours to achieve low-ppb and sub-ppb standard additions. The National Center for Atmospheric Research (NCAR) OVOC I standard [*Apel et al.*, 1998] was used to calibrate acetaldehyde and ethanol. Both calibrations were ~30% higher than their molecules theoretical FID responses referenced to isoprene, assuming that the given mixing ratios were correct. Values reported throughout this paper have been calculated using the theoretical FID response factors instead [*Lamanna and Goldstein*, 1999]. Acetone and MBO were calibrated with two Scott-Marrin standards, and their response factors matched the theoretical FID response as referenced to isoprene. Calibration amounts were typically varied over 1-2 week periods between ~0.5 and ~10 ppb. Correlations with r^2 values of better than 0.95 were achieved, and no systematic change in instrument response was observed over time.

Methanol coeluted with MEK and 3-methyl furan and was not successfully calibrated on the WAX columns because the methanol standard also contained MEK. However, methanol separation was achieved for a few samples in June 1999 on a DB-624 column, and the FID response factor (using NCAR OVOC I [*Apel et al.*, 1998]) was consistent with its theoretical response factor, which was thus used for calibration.

OVOC mixing ratios were more precisely determined in 1999 compared to previous measurements with this instrument in 1998 [*Schade et al.*, 2000]. Rapidly switching between sample and zero air in the REA setup greatly improved the chromatography because water, which interferes with the sampling, desorption, and chromatographic processes, was constantly purged from the traps. However, using this setup, methanol coeluted with MEK and 3-methyl furan. We corrected both updraft and downdraft measurements for these biases assuming that the MEK abundance was ~1/14 of that of acetone, based on tight correlations between these compounds in July 1997 and June 1999 at the same site (data not shown), and that the 3-methyl furan abundance was 1/25 of that of isoprene, based on its yield from isoprene photooxidation [*Ruppert and Becker*, 2000] and assuming that its loss rate is similar to that of isoprene. No correction was made for the other OVOCs.

2.3. REA System

A schematic representation of the REA system interfaced with the GC is shown in Figure 1. Similar to the method of *Nie et al.* [1995], a single sampling line (~16 m 3/8" ID Teflon PFA) ran from next to the sonic anemometer to the sampling system inside the temperature-controlled instrument building. Laboratory tests showed that even a high flow of ~30 L min^{-1} taken from beside the anemometer did not influence the wind measurements noticeably. In the field a constant flow of 10 L min^{-1} was set using a flow controller (Figure 1). The residence time in the tubing was 2.3 ± 0.2 s (3 standard deviations, $N = 7$), determined by popping balloons near the anemometer and measuring the lag time between the sonic spike and the onset of the CO_2 response in an infrared analyzer (LICOR 6262). For the REA measurements, updrafts and downdrafts were subsampled from within the main sample stream (Figure 1) and separated with Teflon segregator valves (General Valve/Parker, Fairfield, New Jersey) when the vertical wind speed w exceeded a deadband of $0.6 \times \sigma_w$ [*Oncley et al.*, 1993], using a 5 min running average of w and its standard deviation σ_w [*Guenther et al.*, 1996]. Because of a slightly shorter gas path in the final setup a delay of 2.2 s was input to the data logger that switched the segregator valves. The valves switched between sampling zero air (from a zero air generator, AADCO, Clearwater, Florida) and sampling ambient air by closing a normally open valve and opening a normally closed valve simultaneously. The zero air was sampled in bypass and was adjusted to the tower sampling line pressure (P_1 versus P_2) as shown in Figure 1, using several meters of 1/8" tubing to provide further resistance to a needle-valve-controlled vacuum. Samples were collected onto the microtraps at a flow rate of 15 mL min^{-1} maintained by one flow controller per line. Sample size was determined by summing the times when a segregator valve was "open" during the half-hour period and was typically on the order of order 120 mL (STP) during the day. The standard deviation of the measured flow served as an indicator of potentially unstable sampling due to sudden pressure changes, which could have occurred if sample and zero air pressure were different. Data collected during times when this standard deviation exceeded 0.2 mL min^{-1} (>1%) were discarded.

Systematic differences between the measurement channels can lead to data misinterpretations. We chose the isoprene oxidation product methacrolein (MACR) as a reference for a channel

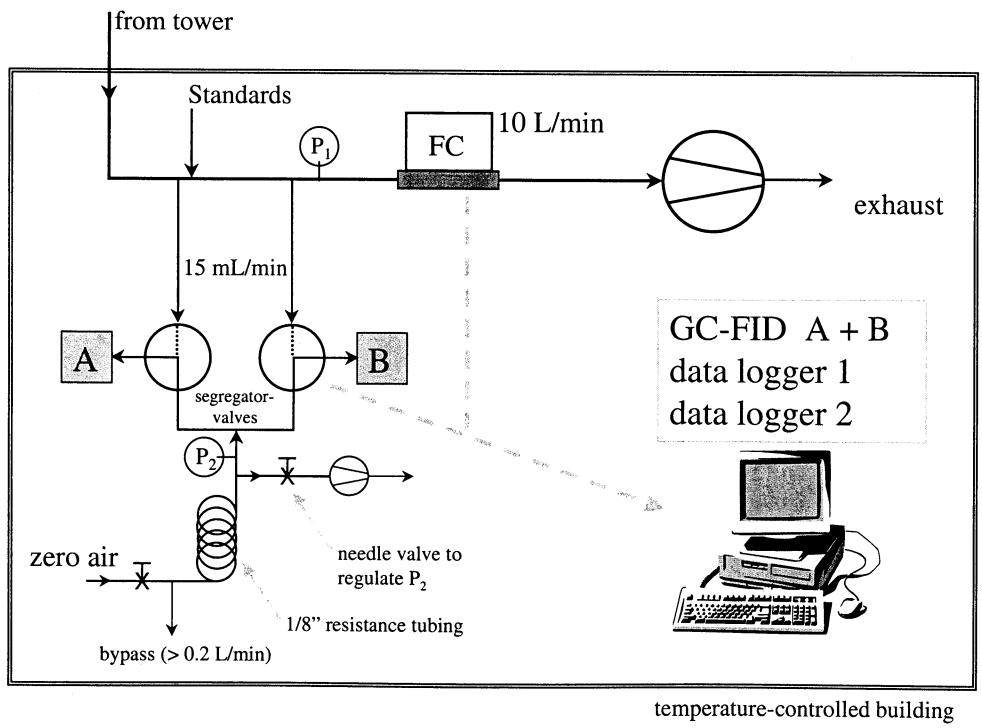

Figure 1. Schematic representation of the REA measurement setup. "A" and "B" represent the up and down samples leading to the two microtraps and GC-FID channels. "FC" stands for flow controller, and "P_1" and "P_2" are pressure sensors used to set the zero air pressure to the sampling line pressure as indicated.

intercomparison on a measurement basis. We could detect neither emission nor deposition of MACR in our ecosystem; it elutes from the WAX column without interference and is generally present at mixing ratios above 0.2 ppb in summer. Measurements in 1998 showed no systematic differences between the channels with a r^2 of 0.96. During extended parts of the measurement period in summer 1999, systematic differences between the MACR peaks occurred that were later identified as an improperly shutting valve on one of the segregator valve setups. Data were corrected for this dilution with zero air by using MACR as a reference peak, that is, by multiplying the measured mixing ratios of the diluted channel by the ratio of the MACR mixing ratios between the two channels for each sample. The adjustment was applied to the complete data set and ranged from 0.6 up to a factor of 4 with an 0.1-0.9 quantile range of 0.8-1.8.

The major advantages of this analytical system include its full automation, enabling unattended sampling over several day periods (not possible with existing cartridge REA systems), its having no electronic or valve equipment exposed to the elements, and its one-dimensional automated in situ chromatography for the OVOCs. The lag time was extremely stable because we controlled the flow through the main sampling line. Because of the potential "smearing" of smaller eddies inside a long sampling line like ours [*Lenschow and Raupach*, 1991], a dead band was used to reduce sampling of small eddies.

2.4. Soil and Litter Efflux Measurements

In order to estimate the OVOC flux contribution from the soil compartments of the ecosystem we carried out a limited set of enclosure measurements. A Pyrex glass chamber covered with light-transparent Teflon foil [*Schade et al.*, 1999a] was placed on the ground near the measurement tower. A spot that was in full sunlight throughout most of the day was chosen in order to monitor a range of different temperatures inside the chamber. That temperature was measured with a thermocouple placed inside the litter layer or in the topsoil (upper 1 cm).

The chamber was flushed with the same zero air used for the FIDs and to run instrument blanks. Flow to the chamber was mechanically regulated to approximately 8 L min^{-1} under ambient conditions, and chamber air was extracted at 1-2 L min^{-1} by moving the sampling line from the measurement tower to the soil chamber. Excess air escaped the chamber mostly through small holes in the cover foil [*Schade et al.*, 1999a], and the chamber was set for much higher inflow than sample flow to avoid turbulent mixing of air from outside with chamber air. Subsamples of 150 mL were preconcentrated over 30 min periods from the main sample stream onto the hydrocarbon microtraps and analyzed in the same manner as described above. OVOC fluxes were calculated from the difference in mixing ratio between chamber blanks and original samples, multiplied by the flow through the chamber, and referenced to the chamber ground area. Chamber blanks were measured by covering the ground with another sheet of Teflon foil during sampling. Only small differences could be found between these chamber blanks and direct measurements of the zero air, except for methanol, for which a larger carry-over effect occurred after very high mixing ratios in the chamber.

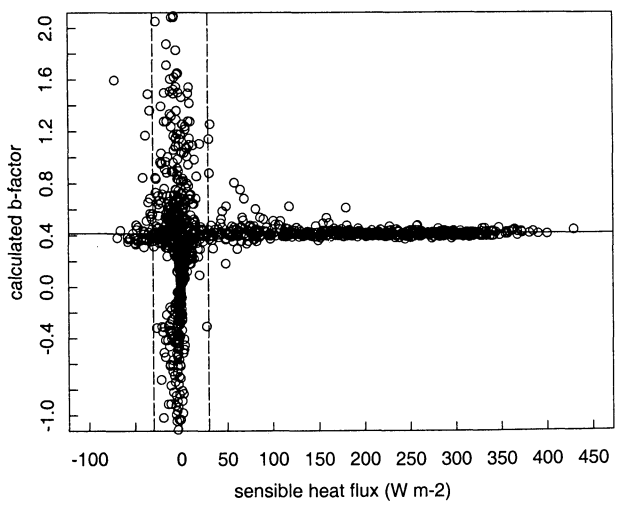

Figure 2. Variation of the calculated REA *b*-factor with sensible heat flux. The vertical dashed lines bracket the measurements for which the *b*-factor was set to its mean (horizontal solid line).

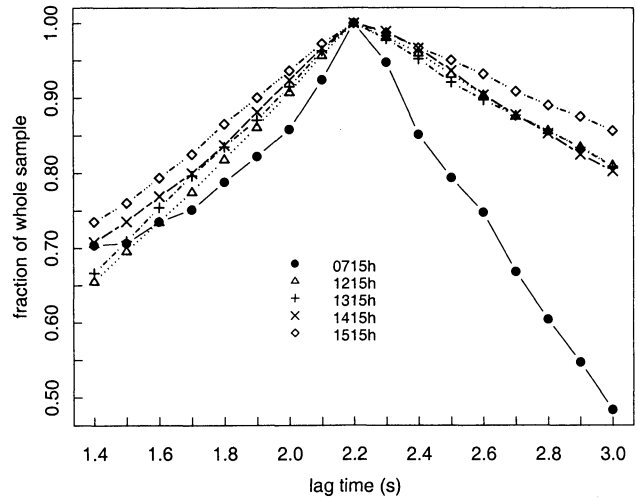

Figure 3. Theoretical variation of the *b*-factor with a changing lag time for different times of the day. The fraction on the *y* axis corresponds to the minimum *b*-factor, which represents the maximum sampling efficiency, divided by the individual *b*-factor. Each curve represents a single 30 min measurement period.

3. Results and Discussion

3.1. REA Data

Individual (O)VOC fluxes, F, were calculated from

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

where b was determined from measurements of sensible heat flux and air temperature [*Bowling et al.*, 1998], σ_w is the standard deviation of the vertical wind speed, and C_u and C_d are the (O)VOC mixing ratios in the updrafts and downdrafts, respectively. As shown in Figure 2, this method has a higher uncertainty for small fluxes of sensible heat, usually occurring during times of reduced turbulence at night and the transition periods when the sensible heat flux changes sign in the morning and evening. As b was remarkably stable when sensible heat flux was not small, we replaced the calculated value by its mean (0.41) for sensible heat fluxes within ±30 W m^{-2} of zero. In addition, values outside a ±0.2 interval of the mean b were discarded. We also filled in a small amount of missing daytime

sonic data (2% of the data) with the mean b-factor and values for σ_w measured on another sonic anemometer, used to determine the CO_2, water, and ozone fluxes. Fluxes of sensible heat and momentum from the two anemometers showed very good agreement (for sensible heat, slope equals 1.05 and r^2 equals 0.99; for momentum, slope equals 0.87 and r^2 equals 0.98).

Possible systematic errors in b were investigated in two ways. First, its dependence on the chosen lag time between the sample entering the line and it being segregated was analyzed using air temperature as measured by the sonic anemometer. A subset is shown in Figure 3. During the daylight hours with high turbulence, b was indeed optimized by our chosen lag-time. However, even if the chosen lag-time had been off by as much as 0.5 s, the maximum daytime systematic error would generally have been less then 20%. The potential error grows larger during the transition periods (0715 Pacific standard time (PST)). Under low turbulence conditions at night, b generally does not show a distinct minimum at the lag time. However, as shown in Figure 2, air temperature from the sonic anemometer is not a good predictor in this case, because many nighttime sensible heat fluxes are too low. Under these conditions, sampling occurs more erratically with fewer and shorter eddies being large enough to exceed 0.6 σ_w. - Second, the calculated b-factors were plotted versus the atmospheric stability parameter z/L (z is the measurements height, L is the Monin-Obukov length). No dependence on z/L was obvious except maybe for the transition periods ($z/L \rightarrow 0$), when the calculated b-factors should be viewed with caution because of small sensible heat fluxes.

3.2. Ambient Mixing Ratios

Mixing ratios ranged from 1.1 to 41 ppb for methanol, from 0.1 to 9.6 ppb for ethanol, from 0.1 to 5.8 ppb for acetaldehyde, from 0.3 to 11 ppb for acetone, and from 0 to 7.0 ppb for MBO (all updraft data) (Figure 4). Measured ambient OVOC mixing ratios were in accordance with earlier observations at this and other rural sites for methanol, acetone, acetaldehyde, and MBO [*Goldan et al.*, 1995; *Slemr et al.*, 1996; *Solberg et al.*, 1996; *Frost et al.*, 1998; *Riemer et al.*, 1998; *Apel et al.*, 1998; *Lamanna and Goldstein*, 1999; *Schade et al.*, 2000] but were higher for ethanol. For comparison, both isoprene and MVK mixing ratios ranged from the detection limit up to approximately 4 ppb, while the sum of the major monoterpenes [*Schade et al.*, 1999b] rarely exceeded 1 ppb. Mean diurnal mixing ratio cycles for the OVOCs during a two-week period in July 1999 are shown in Figure 5. Increases in mixing ratio during times of limited vertical mixing are indicative of local sources and are clearly visible in the evening hours. While MBO showed a typical diurnal cycle with larger mixing ratios during the day and decreasing mixing ratios at night, methanol and acetone were more variable with no distinct diurnal pattern. Acetaldehyde and ethanol showed weak diurnal cycles with generally higher mixing ratios at night, when vertical mixing rates were reduced. In addition, we observed higher ethanol than acetaldehyde mixing ratios at night and the opposite during the day.

Particularly during the daylight hours, but also at night, all OVOC mixing ratios were highly correlated with each other, as shown in Figure 6 for selected compounds. This suggests a common transport or direct emission source and/or common drivers to these OVOC emissions, such as temperature. We estimated biogenic and anthropogenic contributions to the methanol, ethanol, acetaldehyde, and acetone mixing ratios using correlations to compounds of known origin, as described by

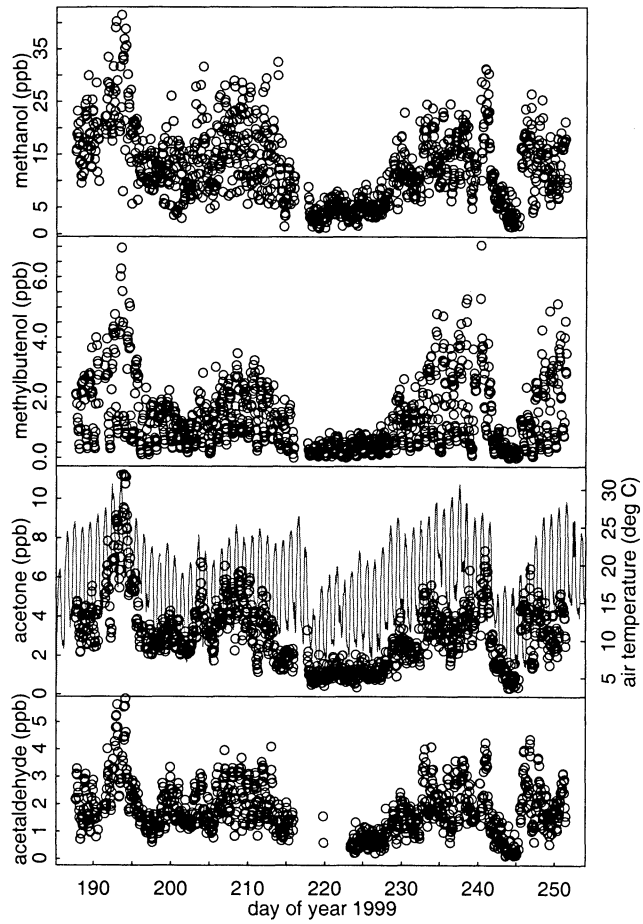

Figure 4. Mixing ratios of four OVOCs, as well as air temperature during the entire measurement period from July to September 1999 (updrafts).

Goldstein and Schade [2000]. OVOC mixing ratios under sunny conditions (PAR > 1300 μmol m^{-2} s^{-1}) were correlated with tracers of both anthropogenic and biogenic sources. We used methyl tertiary butyl ether (MTBE) as a tracer of anthropogenic [*Squillance et al.*, 1997; *Stationary Source Division*, 1997], and MBO as a tracer of biogenic sources [*Harley et al.*, 1998]. The overall determination coefficient from a multilinear regression and estimates of the biogenic and anthropogenic contributions to the individual OVOC mixing ratio are shown in Table 1. Calculated "backgrounds" are based on the intercepts plus the slopes times the local background of MTBE, estimated from the MTBE measurements to be at the detection limit of ~0.005 ppb. Average biogenic and anthropogenic contributions to the total mixing ratio were calculated from the slopes times the median MBO or MTBE mixing ratios, divided by the sum including background. No anthropogenic contribution was assumed for ethanol because of a slope with MTBE that was insignificantly different from 0. Note that our estimate of the "anthropogenic" contribution does not discriminate between primary emission and secondary production. It has to be viewed as an upper limit because the local transport scheme with upslope winds during the day not only advects anthropogenic hydrocarbons to the site, such as MTBE, but also biogenic hydrocarbons, such as isoprene, at the same time. That, for example, results in a correlation between MTBE and isoprene oxidation products, which most probably do not come from the same source. Therefore we cannot exclude the

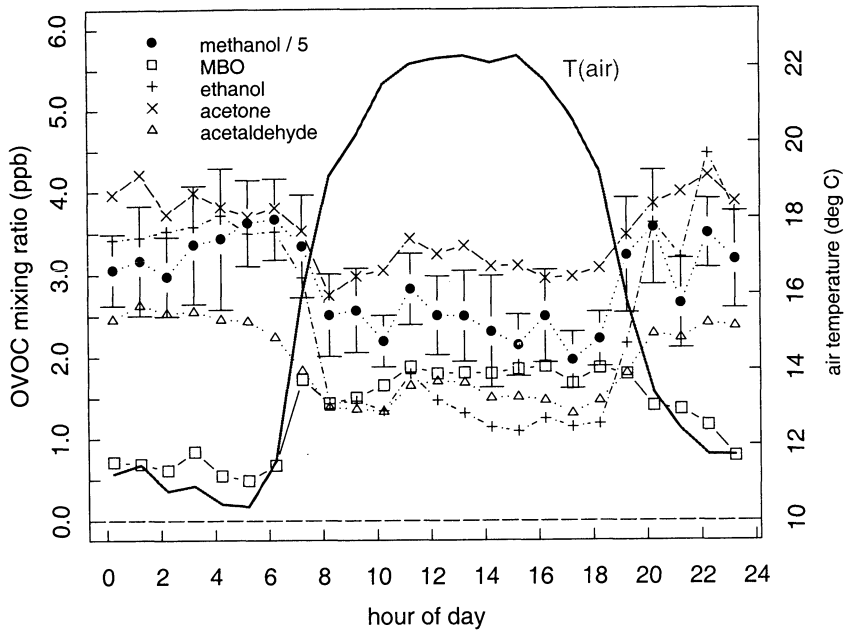

Figure 5. Mean diurnal mixing ratio cycles of five OVOCs during July 20 to August 2, 1999. Points are averages of 10-14 measurements; error bars are 90% confidence levels.

possibility that some amount of the OVOC correlation with MTBE presented here is simply a result of coadvection. Note also that the values in Table 1 are average values for the whole data set and that they can change with weather conditions and time of day, as discussed below.

We can group the OVOCs measured in this work roughly into three classes according to their atmospheric lifetimes (Table 2): MBO as shorter-lived, acetaldehyde and ethanol as medium-lived, and methanol and acetone as longer-lived trace gases. However, despite these lifetime differences the OVOCs showed remarkably strong daytime intercorrelations.

Mixing ratios of longer-lived trace gases, such as methanol and acetone, did not have strong diurnal cycles, such as that of MBO. Changes in the overall abundance of methanol and acetone occurred on longer time scales, associated with changes in regional weather conditions. For example, a dramatic decrease in mixing ratios at the beginning of August (Figure 4) was coincident with unusually cold weather. During August 7-18, daytime temperatures stayed below 20°C, and minimum acetone mixing ratios dropped well below 1 ppb, which we had defined earlier as the regional background under summer conditions [*Goldstein and Schade*, 2000]. A similar change was encountered for all OVOCs in August 1999 and again in late September 1999. This strongly suggests a dominance of biogenic over anthropogenic sources, as the anthropogenic sources are less dependent on temperature. The background values given in Table

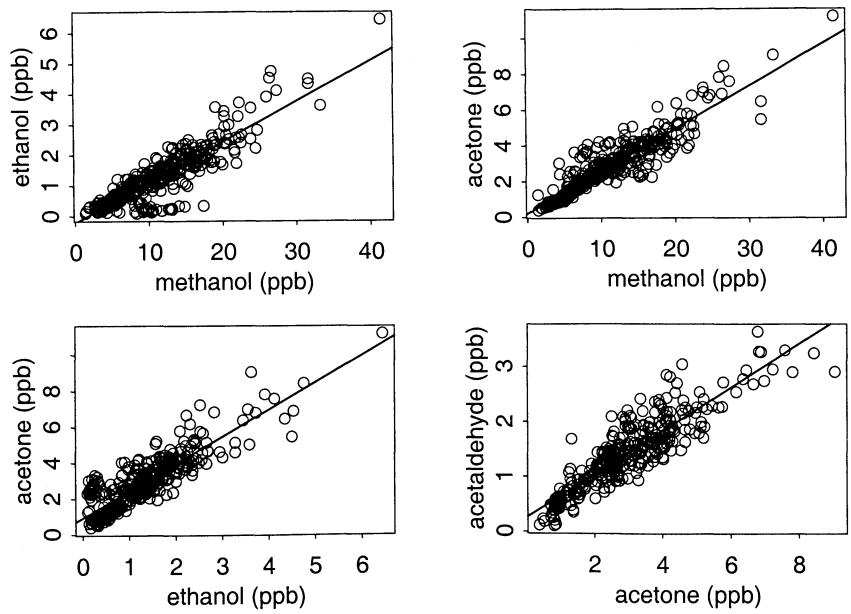

Figure 6. Daytime correlations between the OVOC mixing ratios (updrafts).

Table 1. Results of a Multilinear Regression Analysis of Ambient OVOC Mixing Ratios[a]

	Intercept, ppb	Slope MTBE	Slope MBO	r^2	"Background" ppb	Contribution[b]	
						Percent Biogenic	Percent Anthropogenic
Methanol	2.70	34.1	3.42	0.39	2.87	34.8	20.0
Ethanol	0.19	-0.48	0.51	0.29	0.18	85.6	NA
Acetaldehyde	0.28	6.65	0.41	0.80	0.31	37.7	34.5
Acetone	0.35	17.41	1.17	0.81	0.43	45.7	38.1

[a] The r^2 denotes the overall determination coefficient, NA, not applicable.
[b] Above background.

1 represent mixing ratios measured during the cold weather regimes encountered. Compared to our earlier analysis for acetone [*Goldstein and Schade*, 2000], these background levels are significantly lower, leading to a higher estimate for the average anthropogenic contribution compared to more typical summer weather conditions. We repeated the OVOC budget analysis for different temperature regimes. The biogenic contribution increased with temperature and above 25°C was roughly 50% higher for both acetone and methanol compared to the average values given in Table 1.

The medium lifetime OVOCs acetaldehyde and ethanol showed small diurnal cycles similar to those of the monoterpenes [*Schade et al.*, 1999b]. Mixing ratios were slightly lower during the day than at night. A main difference between acetaldehyde and ethanol mixing ratios is their contribution of sources: While acetaldehyde sources were explained as partially biogenic and partially anthropogenic by the tracer approach (Table 1), ethanol mixing ratios appeared to be of almost completely biogenic origin. The biogenic contributions to the acetaldehyde mixing ratios were only enhanced by 25% during hot days, compared to 50% for acetone and methanol. The respective anthropogenic contribution changed only slightly, possibly because of enhanced secondary photochemical production from anthropogenic hydrocarbons at higher temperatures.

Ethanol was the only compound without a significant correlation with MTBE, which might be due to the fact that ethanol is used as an alternative fuel oxygenate, and generally not used in combination with MTBE in California. We presume the ethanol sources to be almost completely biogenic. As ethanol was not strongly emitted from the soil or litter, the ponderosa pine trees were likely the dominant regional source. The higher mixing ratios of ethanol at night were probably driven by substantial emissions into a shallower nighttime boundary layer, and concentrations decreased as vertical mixing increased in the morning.

Table 2. OVOC Lifetimes in Hours[a]

OVOC	OH	Photolysis
MBO	2.1	-
Acetaldehyde	8.8	~92[b]
Ethanol	84	-
Methanol	288	-
Acetone	1272	~2500[c]

[a] A 12 hour daytime average OH abundance of 2×10^6 molecules cm^{-3} was assumed [*Atkinson*, 2000].
[b] From *Warneck* [2000].
[c] From *Gierczak et al.* [1998].

3.3. Fluxes

Fluxes were highest for MBO and methanol and showed diurnal cycles for all compounds, depicted in Figures 7a and 7b. Shown are means (median for the methanol data) for each hour over the whole measurement period, whereby the number of available samples per hour ranged from 38 (1415 PST) to 51 (1915 PST). Average daytime and nighttime OVOC fluxes are summarized in Table 3, and α-pinene has been included for reference. Based on the minimum detectable difference (95% confidence level) between updrafts and downdrafts, calculated for each OVOC from channel intercomparisons, only methanol and ethanol fluxes were statistically different from zero at night (2200-0500 PST; $p = 0$ for methanol and ethanol). However, nighttime mean fluxes of acetone and acetaldehyde were also slightly above zero.

Air temperatures throughout the measurement period ranged from 4°C at night to a maximum of 32°C during the day and

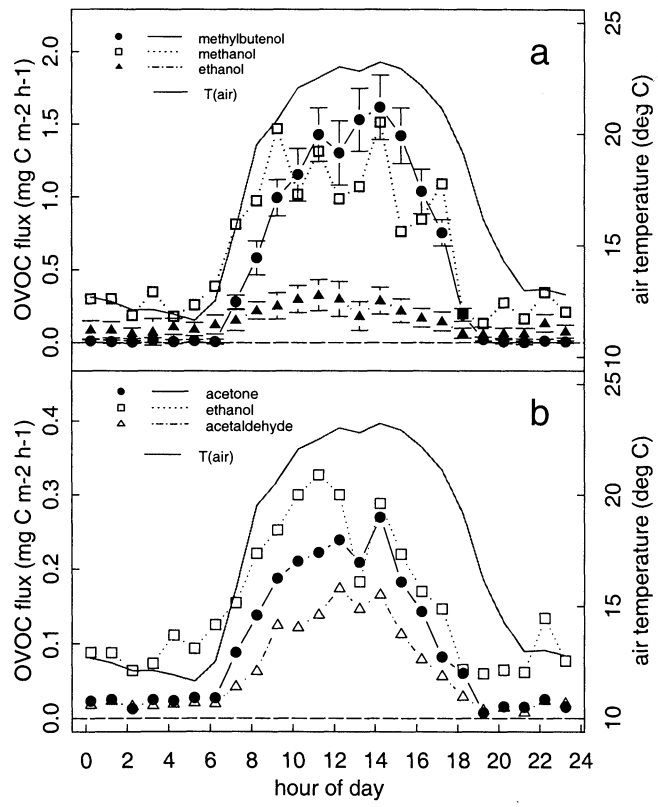

Figure 7. Diurnal variation of OVOC fluxes for (a) MBO, methanol, and ethanol, and (b) acetone, acetaldehyde, and ethanol. Error bars are 90% confidence levels.

Table 3. Average Daytime (1000–1730 PST), and Nighttime (2200–0530 PST) OVOC Fluxes From the Canopy-Scale Measurements[a]

	Daytime	Nighttime
MBO	1.37	0.01
α-pinene	0.10	0.01
acetaldehyde	0.14	0.02
acetone	0.21	0.02
methanol	1.09	0.25
ethanol	0.27	0.10

[a] Fluxes are in mg C m^{-2} h^{-1}.

therefore allowed us to analyze temperature as a most likely driver of the OVOC fluxes. All fluxes were aggregated into 2°C intervals. MBO fluxes were also analyzed for light dependence by aggregating fluxes measured at 25 ± 2°C into PAR intervals of 100 μmol m^{-2} s^{-1} (Figures 8a and 8b). MBO light and temperature responses were virtually identical to the leaf level measurements presented by *Harley et al.* [1998] for trees at the same site. The remarkable match implies that there were no major systematic errors in our canopy-scale flux measurements. The temperature response of canopy-scale MBO fluxes was slightly steeper than measured from the leaf level and was more so if leaf temperatures were used instead of air temperature (data not shown). However, since no tower flux data were obtained above 32°C, no systematic deviation from the published leaf level temperature response [*Harley et al.*, 1998] should be inferred from our data.

Flux dependencies on temperature for the other OVOCs were analyzed on the basis of the inferred algorithm

$$F_{OVOC} = F_{ref} \exp[\beta \times (T - T_{ref})] \quad T_{ref} = 303 \text{ K}. \qquad (2)$$

Beta factors and fluxes at 303 K were calculated from trimmed logarithmic regressions to the aggregated data, and are summarized in Table 4. Again, α-pinene has been included as reference for a monoterpene emitted from this ecosystem. The data and curves for the OVOC temperature responses are shown in Figures 9 and 10.

Besides temperature, there were obviously other factors influencing the OVOC fluxes. We note here that methanol fluxes were significantly correlated with light at 25 ± 2°C ($r^2 = 0.45$, $p = 0.003$, $N = 17$) similar to MBO (Figure 8a), which is expected on the basis of leaf level measurements [*Nemecek-Marshall et al.*, 1995]. Acetone and ethanol fluxes were both influenced by humidity, acetone exhibiting increased fluxes with higher humidity levels during certain periods, and ethanol fluxes varied as a function of ambient humidity levels (Figure 11). Furthermore, the apparent discontinuity of the temperature response for methanol, ethanol, and acetaldehyde emissions at the highest temperatures (Figures 9 and 10) is a result of only five measurements being averaged, of which the three lowest were obtained during the lowest absolute and relative humidities (RH) measured (<17% RH). They may not be representative for the general temperature response, but were most probably impacted by humidity effects on plant physiology, such as afternoon stomatal closure [*Goldstein et al.*, 2000].

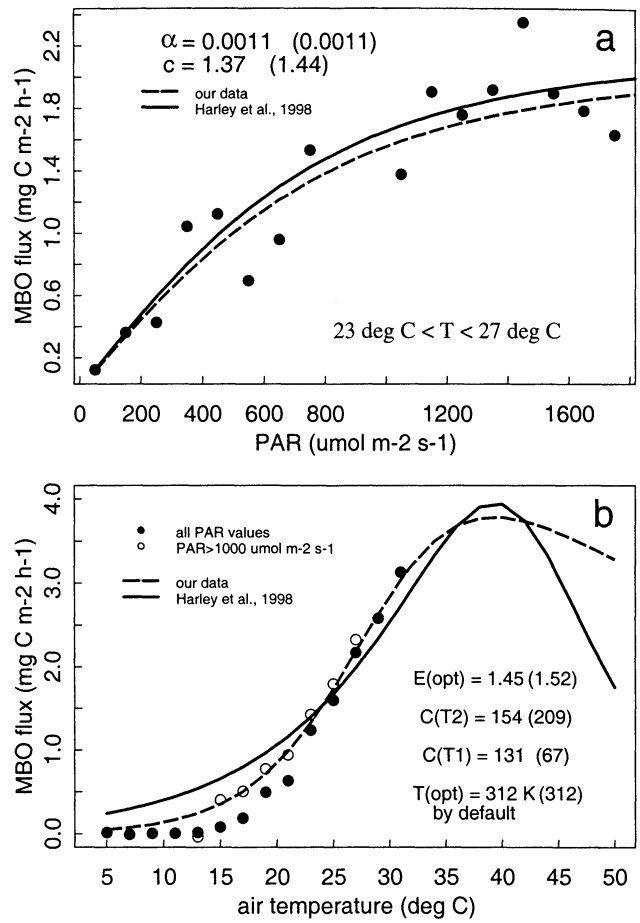

Figure 8. (a) Light and (b) temperature dependence of the measured MBO fluxes. The model equations used are $C_L = \alpha\, c\, \text{PAR}\, \{1 + \alpha^2 (\text{PAR})^2\}^{-1/2}$, and $C_T = E_{opt}\, C_{T2} \exp(C_{T1}\, x)\, \{C_{T2} - C_{T1}(1 - \exp[C_{T2}\, x])\}^{-1}$, with $x = [(1/T_{opt}) - (1/T)]\, R^{-1}$, where T is temperature, R is the ideal gas constant, E_{opt} is the maximum emission capacity that occurs at T_{opt}, and C_L and C_T stand for the respective MBO emission. The numbers in parentheses next to our own model parameter calculations represent the parameters calculated from the leaf level response by *Harley et al.* [1998].

Table 4. Emission Factors for the Canopy and Bare Soil OVOC Emissions

	Canopy-Scale Emissions			Soil Emissions[a]	
	F_{ref}[b]	β	r^2	β	r^2
Methanol	2.87	0.11	0.94	0.03	0.70
Ethanol	0.64	0.14	0.86	NA[c]	NA
Acetone	0.37	0.11	0.98	0.02	0.78
Acetaldehyde	0.20	0.13	0.92	0.05	0.96
α-pinene	0.19	0.12	0.91	NA[c]	NA

[a] Based on topsoil temperatures.
[b] In mg C m^{-2} h^{-1} (at 30 °C).
[c] No systematic variation with temperature (ethanol), or no emissions (α-pinene).

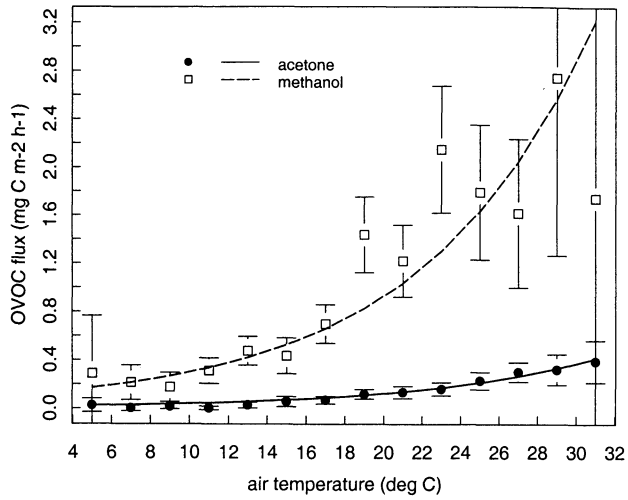

Figure 9. Temperature dependence of acetone and methanol fluxes. Error bars represent 95% confidence levels.

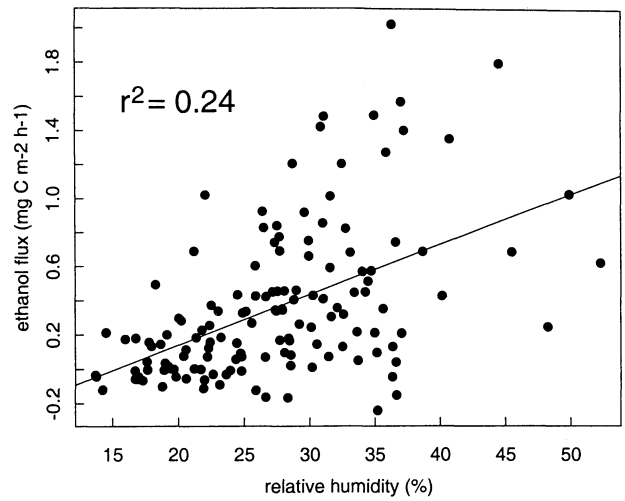

Figure 11. Correlation of ethanol fluxes with ambient relative humidity for measurements at 25° ± 2°C.

Daytime patterns of OVOC fluxes were slightly different between the alcohols and carbonyls. Whereas methanol and ethanol emissions increased earlier and more gradually in the morning, fluxes of acetaldehyde and acetone increased later but more sharply. The lag time between acetaldehyde and ethanol at this time of the day could be due to low plant levels of acetaldehyde, which can be produced from ethanol before being emitted to the atmosphere [*Kreuzwieser et al.*, 2000]. The respective precursor for acetone in plants is not known yet. However, assuming that the acetone fluxes were dominated by the ponderosa pine trees, their diurnal cycle suggests that, similar to acetaldehyde, there are no large acetone pools available. This conclusion may be valid throughout the day. In the afternoon, when fluxes drop off gradually, they appear to precede the temperature drop by at least an hour. Such diurnal behavior is consistent with a flux control by stomatal opening in drought-stressed Mediterranean ecosystems [*Goldstein et al.*, 2000].

The overall error in F was estimated from (1) as follows: Assuming a relative uncertainty in the determination of σ_w and b of a maximum of 10% each, the total error for an individual flux measurement is dominated by the OVOC mixing ratio measurement accuracy in the updrafts and downdraft samples. Except for methanol, which coeluted with MEK and 3-methyl-furan, the precision for each compound, based on multiple calibration lines, was better then 10%, and the overall accuracy, including random errors computed from channel intercomparisons, was better than 15%. Therefore, the total random error for a single flux measurement was less than 25%. Higher errors have to be inferred for methanol because of its occasional abundance in blank samples [*Lamanna and Goldstein*, 1999] and the uniform correction of its mixing ratios applied to each individual sample. On the basis of the latter the potential systematic error for the methanol fluxes was estimated from the error of the acetone to MEK correlation measured in July 1997 and June 1999 ($r^2 > 0.9$) plus the error in the 3-methyl-furan yield from isoprene (± 35%) to be 30-55% (median to 0.9 quantile) at

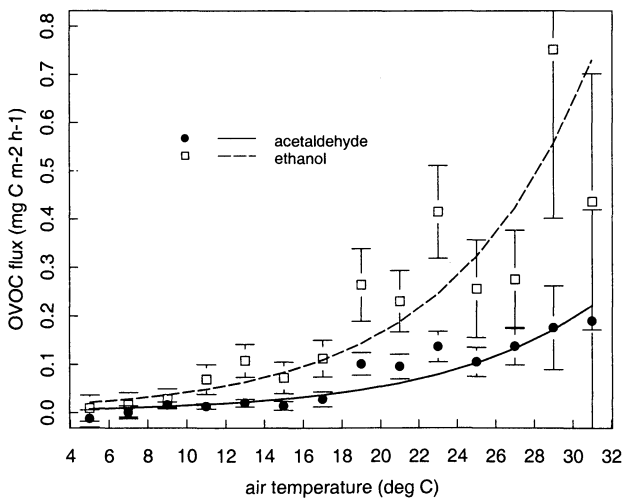

Figure 10. Temperature dependence of acetaldehyde and ethanol fluxes. Error bars represent 95% confidence levels.

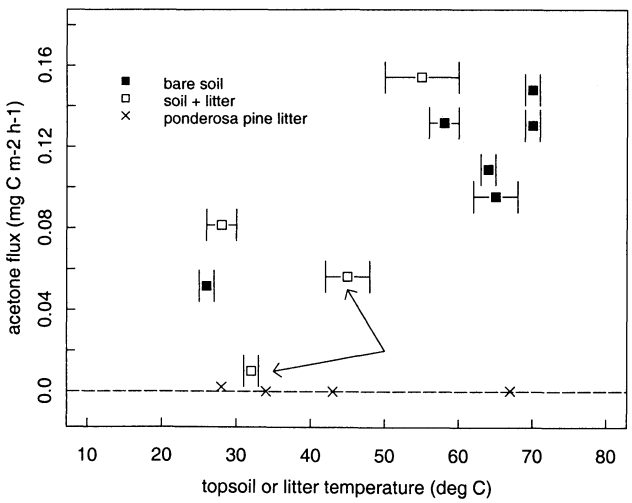

Figure 12. Acetone fluxes measured with chamber experiments. No significant acetone fluxes were measured when ponderosa pine litter alone was in the chamber, and the arrows mark the measurements where ponderosa pine litter covered the soil. The error bars represent the measured range during the half-hour sample period.

most. The mean and maximum relative corrections applied were approximately 10% and 30% of both channels, dominantly inferred from MEK.

3.4. Soil and Litter OVOC Emissions

We carried out a limited number of chamber flux measurements on "bare soil", "soil plus litter", and "only litter", mostly under completely dry conditions for both the soil and litter compartments. In general, similar OVOC distributions were encountered in all enclosure samples compared to the atmosphere. OVOCs clearly dominated the emissions, as demonstrated before by *Warneke et al.* [1999]. The main OVOCs emitted were acetone, acetaldehyde, and methanol or MEK (as we do not have soil emission measurements on a column other than the Rtx-WAX, we cannot assess how much of the methanol peak was actually MEK). Smaller emissions were observed for ethanol, isopropanol (tentatively), pentanal, hexanal, butanal, and three unidentified compounds. No monoterpenes were emitted from bare soil, but fresh ponderosa pine litter emitted large quantities of monoterpenes as an exponential function of temperature (data not shown); 1 year old litter still emitted monoterpenes but at much lower levels. However, neither fresh nor old ponderosa pine litter had large OVOC emissions, in contrast to leaf litter from manzanita bushes, which exhibited large emissions of acetaldehyde and methanol.

Figure 12 shows acetone emissions measured throughout the summer from two different soil locations. Fluxes depended on topsoil temperature and were lower than bare soil fluxes in cases where the ponderosa pine litter obviously shaded and cooled the soil beneath it. The range of temperatures shown in Figure 12 was commonly observed throughout the plantation. Bare soil surface temperatures in full sunlight routinely reached values higher than 60°C, and litter layer temperatures, also in full sunlight, higher than 55°C.

Two points, which showed enhanced soil OVOC emissions, have been omitted from Figure 12. These occurred from a wetted soil surface after a minor rain event during the night of August 26-27, 2000. Acetone fluxes were a factor of 3-4 higher that morning compared to the data shown in Figure 12, while the increase in emissions of methanol and acetaldehyde was smaller, though still prominent.

An overnight measurement of the major OVOCs emitted from the soil in October 1999 is shown in Figure 13. Methanol, acetaldehyde, and acetone were emitted throughout the night as inferred from their peak areas compared to chamber blanks, and all compounds showed a strong response to increasing topsoil temperatures after sunrise. Using all our flux measurements and topsoil temperature, we calculated β-factors for the major OVOC fluxes according to (2). They are included in Table 4 and are in general lower than the ones calculated from the canopy-scale REA flux measurements and air temperatures. That is likely due to the strong temperature gradients through the soil profile and our use of topsoil temperatures.

The soil chamber measurements shown in Figure 13 demonstrated that a small flux of methanol, acetaldehyde and acetone was maintained at night. Assuming that these OVOC fluxes were of biogenic origin, and would therefore probably have a compensation point (such as found, for example, for ammonia [*Schjoerring et al.*, 1998]), they could be an artifact due to the use of zero air in the chamber tests. If the measured fluxes were of nonbiogenic origin, we can infer that the measured nighttime canopy-scale fluxes given in Table 3 were real. For ethanol, nighttime fluxes were obviously dominated by the ponderosa pine trees, as ethanol emissions from the soil were very low. The picture is less clear for methanol because of its high variability and the possible systematic error in its flux determination due to its coelution with MEK.

It is clear from these results that a significant percentage of the total fluxes could have derived from the on-site soil and litter. In particular, the underbrush clearing in June 1999 left large amounts of manzanita litter on the ground, which probably contributed especially to the methanol, acetaldehyde, and acetone

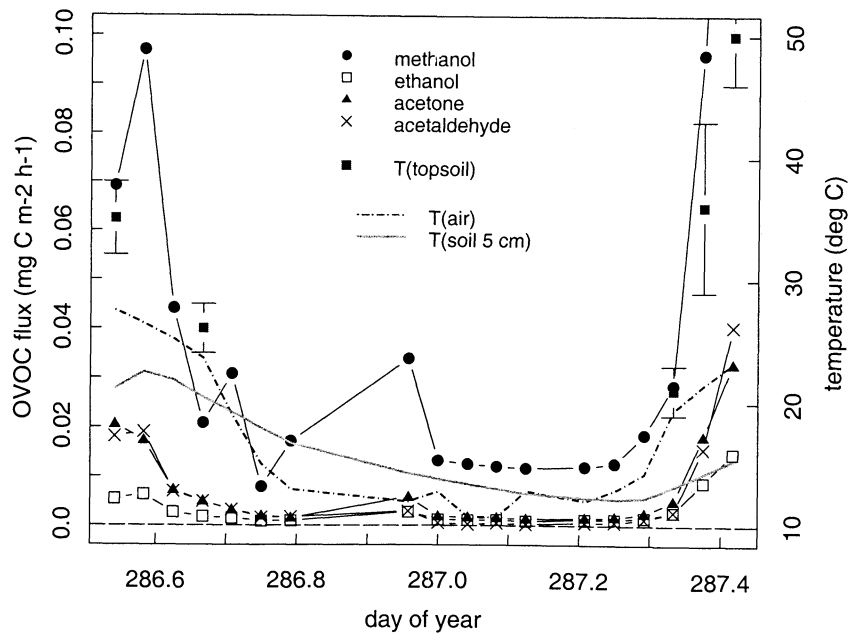

Figure 13. OVOC fluxes measured during an overnight chamber experiment from noon, October 13, to noon, October 14, 1999. Note the large difference between topsoil and soil temperatures at 5 cm depth after sunrise.

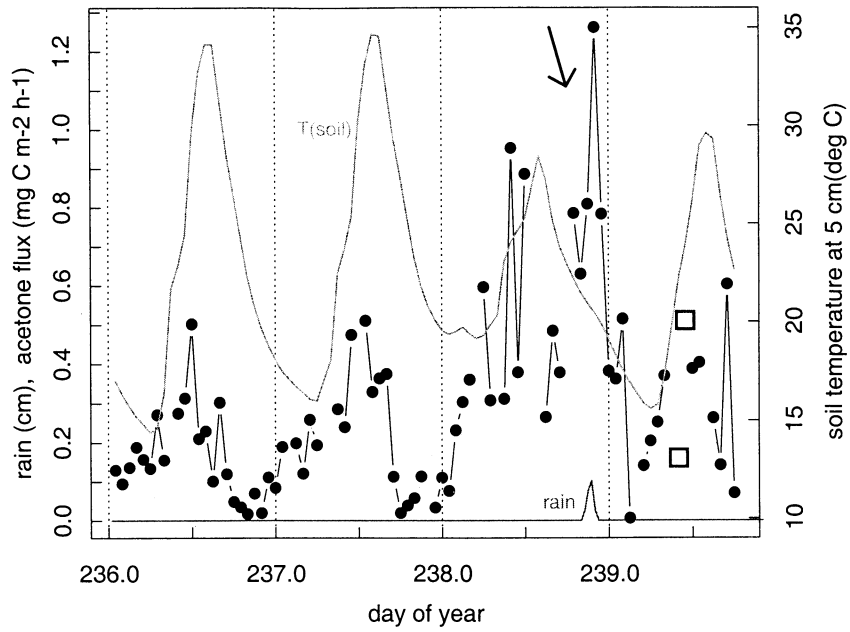

Figure 14. Canopy-scale (closed circles) and soil chamber (large open squares) acetone fluxes before and after a minor rain event during the evening of August 26, 1999 (marked by an arrow). The two soil efflux samples had topsoil temperatures of 24° and 40°C.

fluxes. However, as shown by our bare soil flux tests, large amounts of litter were not a necessary requirement for OVOC emissions. We estimate that if the average topsoil temperature in the fetch area during daytime was between 30° and 50°C, 20-40% of the methanol, 30-45% of the acetone, and 20-65% of the acetaldehyde canopy-scale emissions could have come from the soil. The relative contribution probably changed when the soil got wet from rain or dew, as occurred during August 26-27, 2000: As shown in Figure 14, the acetone fluxes increased dramatically during the rain. The following morning, when the topsoil was still wet, canopy-scale acetone fluxes were elevated, and soil acetone fluxes were elevated compared to dry soil samples, though the soil temperatures were similar to those of the days before. Fluxes of methanol and acetaldehyde were also elevated during the rain event but much less so compared to acetone. As the canopy-scale fluxes during the rain were consistent with the results from the respective chamber tests the next morning, we infer that the increase in emissions was mainly a result of wetting the soil surface. The effect of wetting as well as the dominance of acetone in the OVOC soil emissions are very similar to the results of *Warneke et al.* [1999] but had not been shown under field conditions before. We also note that our observed fluxes of pentanal and hexanal correspond to the masses 87 and 101 measured by *Warneke et al.* [1999].

4. Implications and Conclusions

Oxygenated VOCs make up a major part of atmospheric reduced carbon at our site, and the emissions of these OVOCs are predominantly of natural origin. However, the relative impact of biogenic and anthropogenic emissions was different for each individual OVOC. That difference was also apparent in the flux data, showing higher emissions for MBO and methanol than for ethanol or the carbonyls. Assuming that similar flux magnitudes are confirmed in other ecosystems, methanol emissions must be considered a major VOC emission and a significant plant carbon loss on a global basis [*Guenther et al.*, 1995]. In comparison, fluxes of ethanol may not be as significant globally, because not all tree species are considered to be high ethanol producers, like ponderosa pine. However, both ethanol and methanol oxidation in the atmosphere lead to the production of aldehydes that can be photolyzed and can therefore contribute to HO_x production. Because of their lifetimes, effects of ethanol emissions on HO_x chemistry would be only regional whereas methanol is transported globally and to the upper troposphere, where its effects on HO_x may be substantial and more widespread [*Singh et al.*, 1995]. As a possibly significant source of acetaldehyde and, subsequently, PAN, ethanol may play a more significant role in the long-range transport of NO_x, and it may be worthwhile to study ethanol emissions from trees in more detail in the future.

Acetone fluxes measured from this ponderosa pine plantation leave us with many interesting questions. There are only a few published reports on acetone emissions in addition to our own work. One focused on conifer buds [*MacDonald and Fall*, 1993], and one referred to leaf surface ozonolysis as the main source of acetone [*Fruekilde et al.*, 1998]. We analyzed our acetone flux data in search of a relation to either ozone mixing ratios or measured ozone deposition [*Bauer et al.*, 2000] but found no evidence for a possible connection to either. Nevertheless, assuming no other significant live plant sources at our site besides ponderosa pine, the trees still contributed more than 50% to the canopy-scale fluxes (daytime: 0.23-0.39 $\mu g\ g^{-1}\ h^{-1}$). The leaf level fluxes reported by *Martin et al.* [1999] and *Janson et al.* [1999] for a number of spruce, fir, and pine species were similar to this range, which implies that acetone emissions are a common feature at least among the coniferous species. However, as there is little knowledge as to how acetone is produced inside the leaves, what regulates its emissions, and how much is emitted on a day-to-day basis [*Fall*, 1999], more research is needed in this area. We present canopy-scale acetone fluxes and show that temperature was the main regulating parameter but also that moisture could play a significant role. At times, acetone fluxes

may be dominated by soil and litter emissions, which were clearly elevated by wetting. *Warneke et al* [1999] demonstrated that Maillard-type reactions can produce large amounts of acetone in decaying organic matter by a process of heating and wetting. Such processes can occur especially in Mediterranean-, savanna-, and grassland-type ecosystems, possibly also in tropical rain forests. In the Sierra Nevada, where little rain falls in summer, the first rain in fall might produce a large pulse of acetone, and we have shown the effect in Figure 14. Significant acetone production in organic matter to produce such a pulse may strongly depend on temperature, which is often higher in ecosystems without or with an open overstory.

Besides their effect on atmospheric chemistry, OVOCs may also represent a significant carbon loss to the ecosystem. Fluxes of oxygenated VOCs dominated non-CO_2 carbon fluxes from this environment. The approximately 10 year old plantation lost on average 1.3% (range 0.8-3.1 % for 15° to 30°C) of its daytime net ecosystem carbon exchange to OVOCs. Though this may appear rather small, it is important to recognize that the trees in this plantation are growing rapidly compared to a mature stand [*Goldstein et al.*, 2000].

In summary, emissions of oxygenated VOCs, largely underrepresented in field and laboratory measurements so far, are a substantial component of total biogenic VOC fluxes. Our measurements, and the analytical tools we have developed, will allow improvement of earlier estimates of their emissions [*Guenther et al.*, 1995], but more laboratory and field measurements are necessary before broad-scale conclusions should be drawn. Also, more investigations into litter and soil emissions are needed to determine which ecosystem components are dominating the OVOC emissions and how they respond to environmental drivers.

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