

## Seasonal measurements of acetone and methanol: Abundances and implications for atmospheric budgets

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Received 5 June 2005; revised 13 December 2005; accepted 28 December 2005; published 21 February 2006.

[1] Acetone and methanol have been measured hourly at a rural mountain site in California for a full year, providing a unique data set for analyzing the factors controlling their seasonal cycles. Their mixing ratios showed clear maxima in summer and late spring respectively, and were mostly correlated with atmospheric temperature with highest values during heat waves. Lowest values occurred during winter coincident with the periods of lowest temperature (0.15 ppb for acetone and 0.4 ppb for methanol). The acetone to methanol ratio changed seasonally with a minimum in spring and maxima in late summer and fall, likely reflecting higher springtime methanol emissions. The ratio was highest during fall and winter, probably a result of secondary acetone production from diffuse anthropogenic sources. Large decreases of both gases were observed when frontal passages brought free tropospheric air of Pacific origin to the site as indicated by back trajectory analysis. Neither wet nor dry deposition could explain these periodic decreases. Our results confirm previous assessments showing large acetone and methanol abundances over rural areas indicative of large biogenic sources. Their high degree of correlation at all times suggests a strong link between their biogenic emission sources and only a small influence of anthropogenic sources, at least at this site. The free tropospheric background mixing ratios concur with published measurements from aircraft over the Pacific, and are consistent with a substantial, diffuse source from hydrocarbon oxidation.

**Citation:** Schade, G. W., and A. H. Goldstein (2006), Seasonal measurements of acetone and methanol: Abundances and implications for atmospheric budgets, *Global Biogeochem. Cycles*, 20, GB1011, doi:10.1029/2005GB002566.

### 1. Introduction

[2] Acetone and methanol are oxygenated volatile organic compounds (OVOCs) whose oxidations both lead to significant formation of HO<sub>x</sub> in the upper troposphere [Singh *et al.*, 1994; Folkins and Chatfield, 2000; Mari *et al.*, 2002]. Their abundance is substantial throughout the troposphere owing to lifetimes of approximately 1 month for acetone and 10 days for methanol, together with sources in the terrestrial biosphere [Jacob *et al.*, 2002; Galbally and Kirstine, 2002] and photochemical production from hydrocarbon precursors. Methanol is often the most abundant tropospheric VOC after methane with mixing ratios regularly exceeding 10 ppb in the boundary layer (BL) during summer [Goldan *et al.*, 1995; Riemer *et al.*, 1998; Lamanna and Goldstein, 1999; Schade and Goldstein, 2001; Karl *et al.*, 2003a, 2003b], often followed by acetone with mixing ratios up to 10 ppb.

Unless measured very close to their sources, the mixing ratios of the classic plant emissions isoprene and monoterpenes are generally smaller due to their short atmospheric lifetimes. Only the slightly further oxidized compounds formaldehyde (HCHO), and acetaldehyde (CH<sub>3</sub>CHO), whose atmospheric sources are dominated by secondary formation, sometimes rival the methanol and acetone abundance. While short-chain aldehydes were already quantified in the atmosphere more than 20 years ago, acetone and especially methanol have only been measured and studied in the atmosphere more recently. Presumably this was due to a combination of their uncertain recovery from sampling canisters, low breakthrough volume on hydrophobic activated charcoal cartridges [e.g., Qin *et al.*, 1997] commonly used for VOC collection at room temperature, poor recovery from purge-and-trap systems due to high Henry constants, high polarity making peak resolution during chromatographic separation difficult, and their poor detector responses during flame ionization, the typical VOC detection method after chromatographic separation [Lamanna and Goldstein, 1999]. Some modified and improved sample collection and GC-FID and GC-MS analysis techniques [Singh *et al.*, 1994, 2000; Lamanna and Goldstein, 2001; Apel *et al.*, 2003; Millet *et al.*, 2004], and in particular chemical ionization mass spectrometry [Lindinger *et al.*,

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1998; Karl *et al.*, 2003a, 2003b; de Gouw *et al.*, 2003] have solved these problems.

[3] VOC measurements at Blodgett Forest Research Station (BFRS) have been successfully in operation since summer 1997 [Lamanna and Goldstein, 1999; Schade *et al.*, 1999; Schade and Goldstein, 2001; Goldstein *et al.*, 2004]. In this work, we focus on the nearly continuous measurements of acetone and methanol mixing ratios between April 2000 and March 2001, providing data covering one annual cycle. We analyze the variables driving changes in methanol and acetone abundance, and their relationships (section 3). We also provide a spatial analysis extending our results to the Pacific free troposphere using back trajectories during frontal passages (section 4). Fluxes will be analyzed in a future paper to determine the seasonally changing physical and biological drivers of emissions at the BFRS.

## 2. Location and Measurement Technique

[4] The measurement site is next to the UC Berkeley BFRS (38°53'42.9"N, 120°37'57.9"W, 1315 m elevation) on the western slope of the Sierra Nevada mountains, and has been previously described by Goldstein *et al.* [2000] and Schade and Goldstein [2001, 2003]. Climate at the site is Mediterranean with precipitation between September and May and very little if any rain during the summer months. During winter, frequent snowfall with 3–5 large snowstorms is recorded generally from December through March, with the long-term average snowfall corresponding to 15% of annual precipitation. Snow depths regularly reach up to 100 cm, and continuous snow cover is maintained for 8–10 weeks on average, mostly during January and February. At this elevation, ponderosa pine (*Pinus ponderosa*) plantations dominate the regional vegetation, interspersed with a mixed conifer forest of ponderosa pine, sugar pine (*P. lambertiana*), incense cedar (*Libocedrus decurrens*), douglas fir (*Pseudotsuga menziesii*), black oak (*Quercus kelloggii*), madrone (*Arbutus menziesii*), and canyon live oak (*Quercus chrysolepis*). At lower elevations in the Sierra foothills to the west, oak trees dominate. Higher elevations of the Sierra Nevada to the east include a mixture of firs (*Abies concolor* and *magnifica*) and high elevation pines (*pinus contorta*, *albicaulis*, and *flexilis*). The Sierra Pacific Industries owned measurement location is a typical clear-cut plot planted with *Pinus ponderosa* L. in 1990. Significant amounts of woody litter and stumps can still be found throughout the plantation. The understory is dominated by manzanita (*Arctostaphylos spp.*) and whitethorn (*Ceanothus cordulatus*), which were almost completely cut throughout the plantation during routine shrub removal in spring 1999. In spring 2000, routine thinning was carried out throughout a period of several weeks, which removed two thirds of the trees and half the active green leaf biomass. The process and the effects on monoterpene emissions and ozone deposition in the plantation have been described by Schade and Goldstein [2003] and Goldstein *et al.* [2004].

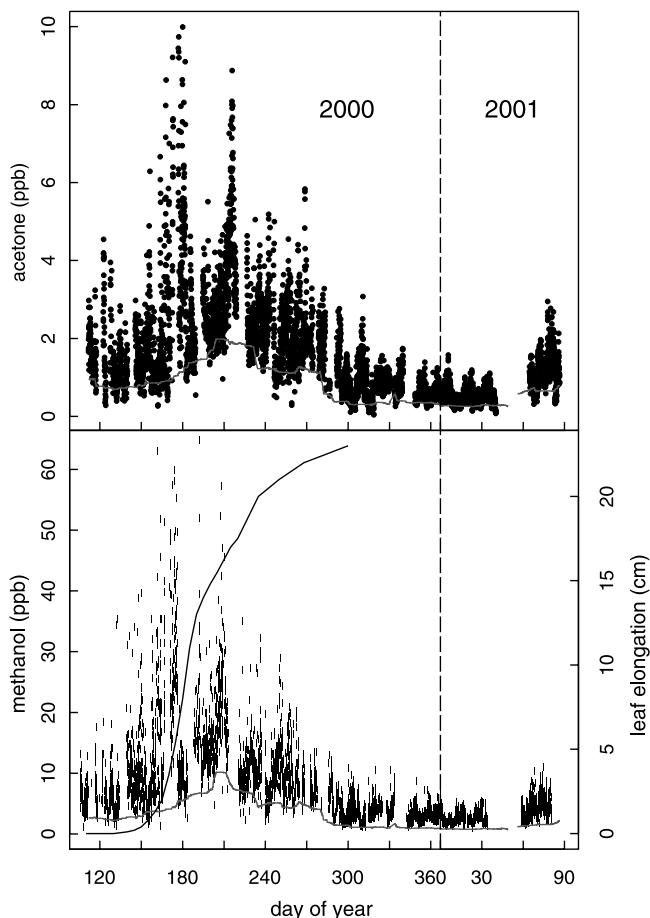
[5] Air was sampled from a 12-m-high walk-up tower erected in 1997. Meteorological data and trace gas mixing ratios and fluxes (CO<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, and VOCs) were measured from approximately twice the average tree height, and

vertical gradients were measured for water, CO<sub>2</sub>, temperature, and wind speed. The VOC measurement technique has been described previously by Lamanna and Goldstein [1999] and Schade and Goldstein [2001]. Only a few changes have been made, which we describe here. Acetone (and other VOC) determination was achieved from ppm standards in N<sub>2</sub> (Scott Marrin Inc., Riverside, California) dilutions into the main air sampling line during relaxed eddy accumulation (REA) sampling into the deadband every 10 hours, recording a complete calibration line from ~0.5–~10 ppb over a few weeks. This resulted in an improved reference, as both channels sample the same air, providing a relative, long-term precision of the acetone mixing ratio measurement of ~5% (calculated from a single calibration line recorded over several months and removing outliers). In contrast, methanol mixing ratios were only measured with a precision of ~30%, as methanol is not resolved completely chromatographically, and its FID response factor is somewhat uncertain. Blank samples did not indicate a consistent background for either acetone or methanol but were highly variable, and often suggested carryover effects, i.e., showing higher blanks after high ambient mixing ratio measurements. Consequently, we did not subtract a fixed blank background from the data but note that the detection limit for a clean chromatographic determination was at best 0.02 ppb for acetone and 0.1 ppb for methanol. As before, methanol was empirically corrected for an assumed methyl ethyl ketone abundance of 1/14 of acetone [Schade and Goldstein, 2001] in both channels.

## 3. Methanol and Acetone Variability

### 3.1. Seasonal and Diurnal Abundances

[6] The complete time lines for acetone and methanol data are shown in Figure 1, along with an onsite measurement of the local ponderosa pine leaf elongation as a measure of regional leaf area index (LAI) development. Running 30-day 0.1 quantiles for both acetone and methanol mixing ratios are included to illustrate the seasonal development of regional background levels [Goldstein *et al.*, 1995], showing maxima during mid-July. Complete quantile ranges for summer 2000 and winter 2000/2001 are listed in Table 1 along with air temperature and relative humidity. Temperature, pressure, absolute humidity, and precipitation seasonalities are shown in Figure 2. Both methanol and acetone mixing ratio seasonalities closely resemble those of temperature and absolute humidity. One third of the daytime variability of acetone and methanol in summer could be explained by air temperature alone assuming a log linear relationship. In addition to their variation with air temperature, a comparison of Figures 1 and 2 shows that both methanol and acetone mixing ratios appear to drop along with or just after clear decreases in pressure, sometimes followed by precipitation. These frontal passages occur frequently in fall and winter (Figure 2), and are analyzed in more detail in section 4. Acetone and methanol exhibited very high mixing ratios during the first heat wave after the last seasonal rainfall in mid-June 2000 (Figure 1). This coincided with the beginning of a rapid growth period of the local ponderosa pine trees that lasted until mid-July,



**Figure 1.** Seasonal cycle of acetone and methanol mixing ratios, along with a 30-day running 0.1 quantile (gray lines). The solid black line in the lower graph depicts weekly measured leaf elongation at the site.

and the intense but more progressed leaf growth in the Sierra Nevada foothills oak belt [Dreyfus *et al.*, 2002] (first leaf-outs in late April). For methanol, higher emissions in the springtime as a result of intensified pectin demethylation during plant/leaf growth have repeatedly been implied as the principal methanol source [Galbally and Kirstine, 2002]. Karl *et al.* [2003a] measured significantly higher relative methanol fluxes during spring as compared to summer and fall at a deciduous forest site in Michigan, dominated by aspen trees, which are also strong isoprene

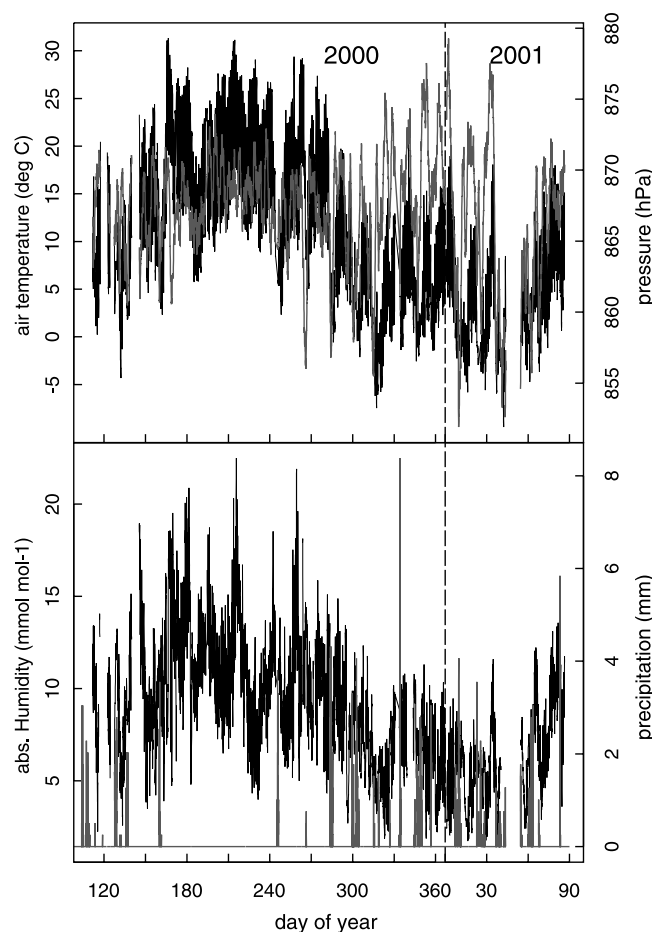
**Table 1.** Quantiles of Summer (June–August) and Winter (December–February) OVOC and Meteorological Data<sup>a</sup>

	Summer					Winter				
	0%	25%	50%	75%	100%	0%	25%	50%	75%	100%
Acetone, ppb	0.3	1.8	2.4	3.4	10.0	0.1	0.4	0.6	0.9	2.9
Methanol, ppb	0.4	7.8	10.9	16.4	63.9	0.1	1.3	2.0	3.0	10.1
T <sub>air</sub> , °C	2.3	13.3	17.3	23.0	31.3	-9.5	0.4	3.6	7.1	20.4
rH, %	11.4	33.5	52.7	71.8	101.7	11.9	43.2	68.4	93.4	99.6

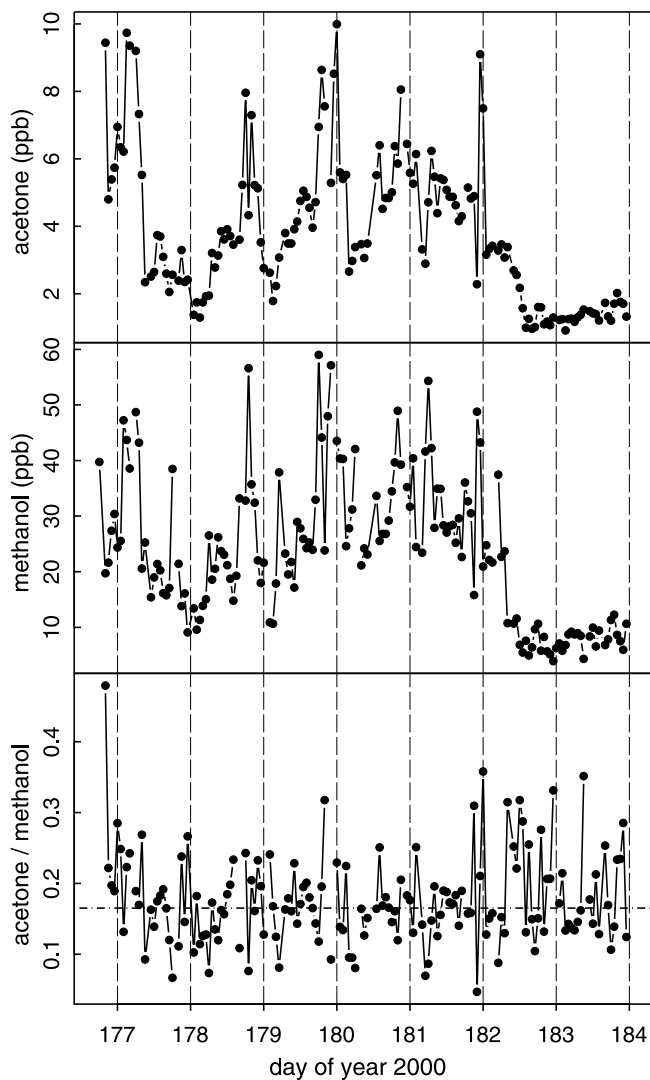
<sup>a</sup>Summer is June–August, and winter is December–February. Data are rounded to one significant digit.

emitters. A similar effect for acetone was not found. Reported mean and maximum mixing ratios of both methanol and acetone were lower in the Karl *et al.* [2003a] study as compared to values at the BFRS. This may be explained by several factors: First, the different kind and lower density of vegetation on a larger spatial scale because the Michigan site is surrounded by the Great Lakes, second, the lower mean and maximum temperatures at the UMBS site in Michigan as compared to the BFRS, and third, an additional source of acetone from 2-methyl-3-butene-2-ol (MBO) in California [Goldstein and Schade, 2000].

[7] Diurnal cycles of acetone and methanol along with pertinent meteorological parameters, depicted in Figures 3 and 4, reveal consistent features, some of them we have reported previously [Schade and Goldstein, 2001]. High mixing ratios are maintained throughout the normal upslope-downslope wind pattern during the summer. During daytime, increasing mixing ratios provide evidence of significant regional emissions into the advected air masses from the Central Valley of California. Sharp increases after sunset driven by a very shallow boundary layer in the early evening confirm these emissions. Both during sunrise and sunset, the acetone to methanol ratio drops below average (0.18), indicating also a smaller local to regional emission



**Figure 2.** Meteorological data for the same period as in Figure 1.



**Figure 3.** A selected period from the end of June 2000 showing diurnal acetone and methanol cycling under typical meteorological conditions, changing on day 182.

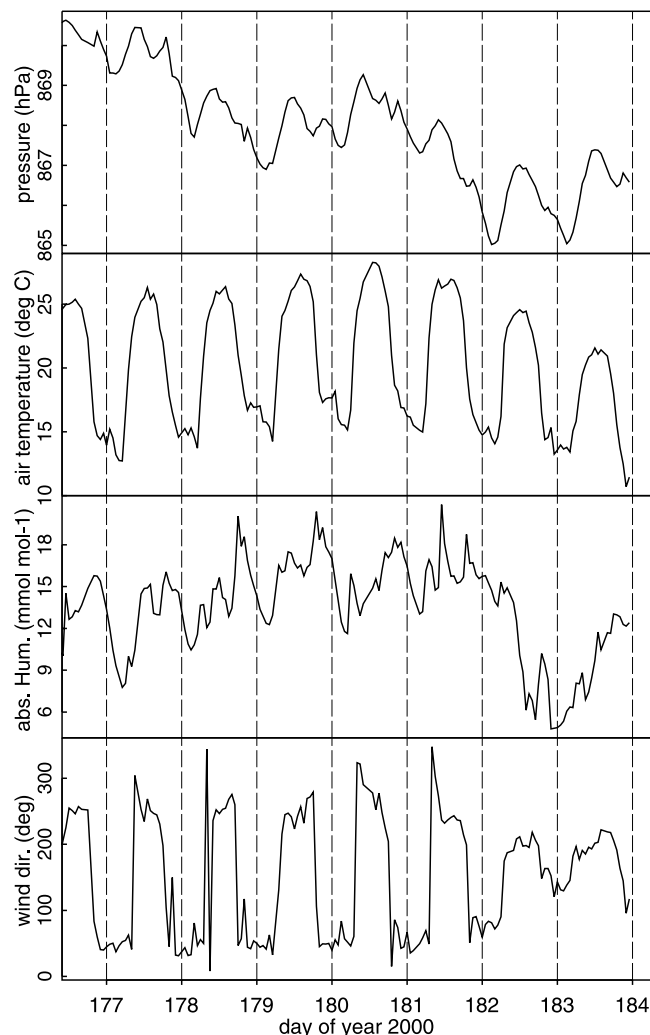
ratio. Later at night, mixing ratios generally decrease owing to cleaner, aged air masses that are advected to the site from higher elevations [Dillon *et al.*, 2002]. These air masses have slightly higher than average acetone to methanol ratios, likely because acetone has a longer atmospheric lifetime compared to methanol ( $\sim 3$  weeks versus  $\sim 1$  week). When low-pressure systems with cooler and dryer air temporarily disturb the usual diurnal cycling of wind direction, a significant drop in VOC abundance occurs. Figure 4 contains a summer example of this scenario, in which a temperature and humidity decrease signaling a change in air mass follows the passage of a low-pressure system. Both acetone and methanol abundances are reduced by two thirds and their ratio becomes less well defined.

### 3.2. Acetone-Methanol Ratio

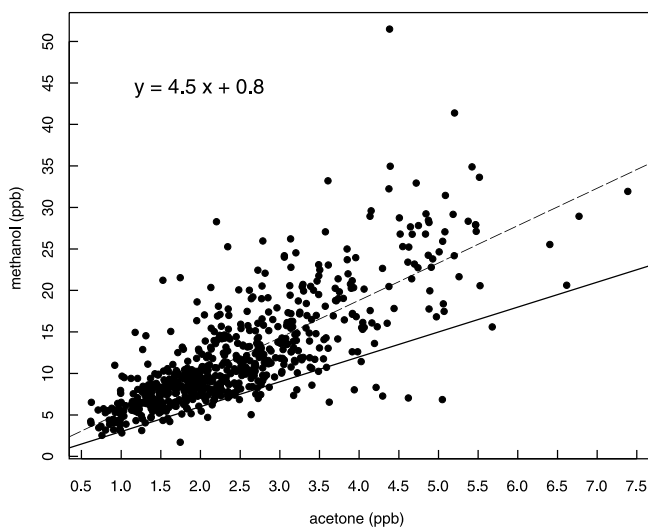
[8] A scatterplot of acetone versus methanol for the summer months is shown in Figure 5. During daytime a

ratio of approximately 0.2 (slope = 0.22) is maintained with an  $r^2$  of 0.66. This is in good agreement with previous results reported by Riemer *et al.* [1998] and Karl *et al.* [2003a], who measured slopes of 0.21 and 0.23, respectively, and somewhat lower than a slope of 0.27 measured by Goldan *et al.* [1995]. Unfortunately, Karl *et al.* [2003a] did not report on a seasonal change or physical drivers of the acetone to methanol ratio. However, such changes may reveal consistent features to support or undermine current assumptions of acetone or methanol atmospheric cycling.

[9] The lower bound to the methanol data seen in Figure 5 suggests that at least three times as much methanol compared to acetone is permanently present at this site in summer, setting a lower limit to the regional emission ratio. Part of the variability in the ratio is due to changing air masses, both on a diurnal and seasonal basis. The mean and the background ratio though have to be driven by the regional emissions and subsequent atmospheric chemistry. We investigated the seasonal changes to the first using a local regression model with a coarse resolution (2–3 week) for smoothing. Significant changes were detected ranging from a low early summer ratio of 0.17 increasing to a late



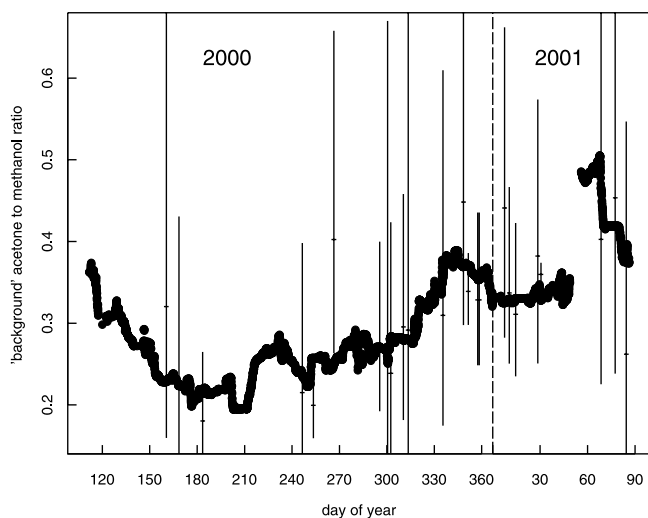
**Figure 4.** Meteorological data for the period in Figure 3.



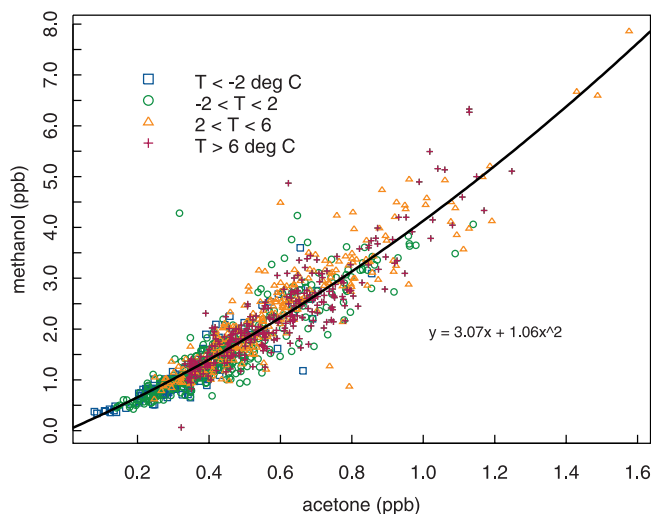
**Figure 5.** Summertime acetone-methanol relationship. Solid line has a slope of 3.

summer and fall ratio up to 0.3. An even clearer seasonality was detected for the background ratio calculated from the gray lines in Figure 1, and shown in Figure 6. Decreasing from early spring values above 0.35, a broad minimum around 0.2 is observed in late spring followed by a slow increase to 0.3 throughout the summer then another more rapid increase to almost 0.4 throughout the fall leaf dropping period. With snow on the ground, values returned to a ratio of 0.33. Maximum values up to 0.5 however were observed during the early 2001 springtime snowmelt, rapidly decreasing to values below 0.4, inline with values during the previous year.

[10] Seasonal cycling of the acetone-methanol ratio is consistent with growth-correlated emissions of methanol peaking in June then decreasing throughout summer, and assuming that acetone emissions do not show such a growth



**Figure 6.** “Background” acetone to methanol ratio as calculated from the 0.1 quantiles shown Figure 1. Vertical bars show measured (mean, minimum-maximum) ratios after the passage of fronts (see text).

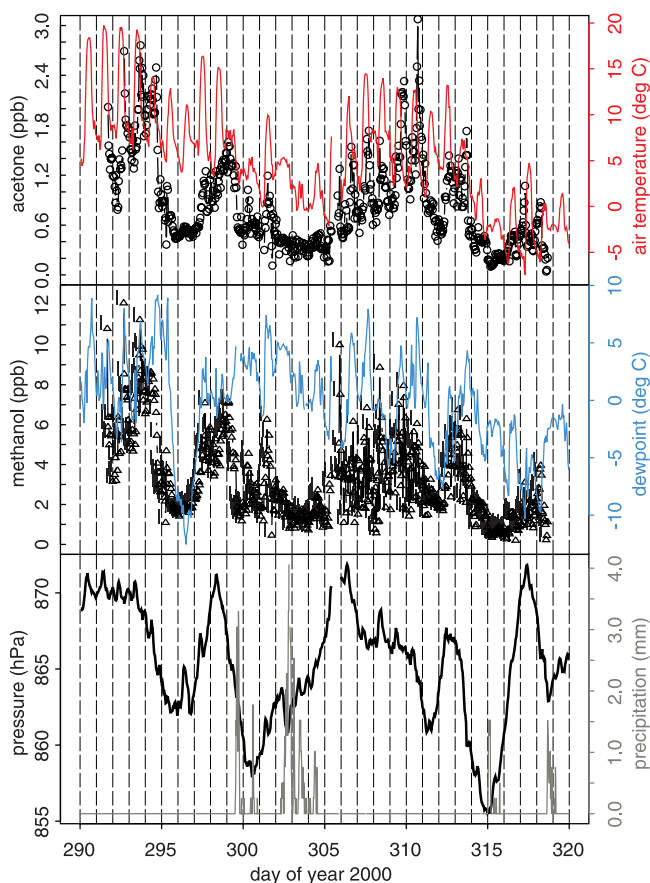


**Figure 7.** Wintertime acetone-methanol relationship. Data points are grouped to show the temperature dependence.

correlation. Increasing values throughout the summer may be driven by decreasing methanol emissions and/or increasing acetone production from increasing MBO emissions. On the basis of our earlier analyses of biogenic and anthropogenic contributions to the local mixing ratios of acetone and methanol at the BFRS [Goldstein and Schade, 2000; Schade and Goldstein, 2001], a spring to fall drop in methanol emissions by a factor of 3–4 could explain the observed ratio change, while an additional acetone input from MBO oxidation alone could not. Neither of these processes though can explain the observed ratio swings in the late fall and early spring. They might instead indicate significant acetone emissions from degrading plant matter [Warneke et al., 1999], possibly suppressed by the regional snow cover during much of the wet season. With snow on the ground in January 2001, the acetone to methanol ratio was much less variable than during the growing season and showed a slight dependence on abundance (Figure 7). The ratio changed in favor of acetone as abundances dropped, as expected due to acetone’s longer atmospheric lifetime compared to methanol. Our analysis showed that neither acetone nor methanol were correlated with anthropogenic tracers ( $r^2 < 0.1$ ; data not shown) and their ratio did not depend on air mass age as calculated from anthropogenic hydrocarbon ratios. Instead acetone and methanol were correlated with MBO which is emitted by the local and regional pine forests. Higher MBO abundances were related to ambient temperature as expected for this biogenically emitted compound (Figure 7). This suggests that even in winter, when biogenic emissions are often assumed to be negligible, the abundances of both acetone and methanol can be dominated by biogenic sources. This is further corroborated by the factor analysis in section 3.4.

### 3.3. Temperature Dependence

[11] Ambient temperature explains at least one third of the acetone and methanol variability. This finding mimics observations from both the ROSE and SOS study sites indicating the dominance of temperature dependent sources,



**Figure 8.** Acetone and methanol variability with meteorological parameters on a regional and synoptic scale.

probably mostly biogenic, at all three sites. Daytime summer dependences given for the SOS site were  $0.969e^{0.084T}$  ( $\ln(\text{VOC}) = a + \beta T$ ) for methanol and  $0.865e^{0.053T}$  for acetone [Riemer *et al.*, 1998]. For methanol at Blodgett we observed a summer (June–August) daytime relationship of  $2.2e^{0.068 \pm 0.004T}$ , and for acetone of  $0.52e^{0.064 \pm 0.004T}$  (standard error each,  $N = 670$ ). While the site differences may not be statistically significant, we observed a significant seasonal change. In winter the temperature dependence factors ( $\beta$ ) decreased to 0.053 and 0.037 at Blodgett, respectively suggesting more of a decrease in temperature-dependent sources from summer to winter for acetone compared to methanol, with other acetone sources gaining relative importance.

### 3.4. Other Drivers

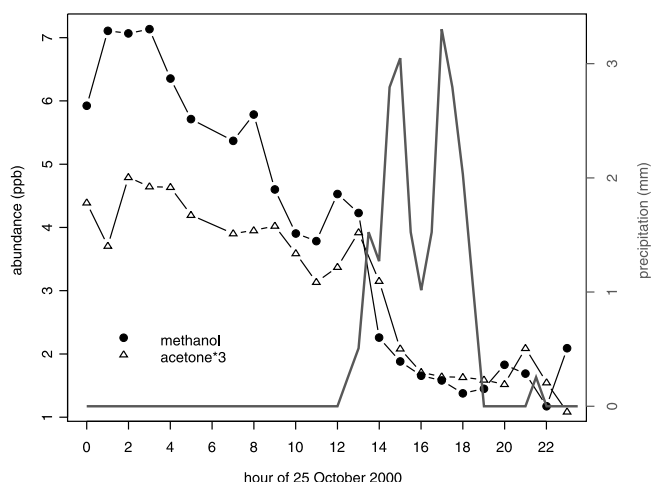
[12] We have previously analyzed the influences of different sources on methanol and acetone mixing ratios at the BFRS site [Goldstein and Schade, 2000; Schade and Goldstein, 2001]. Here we briefly revisit two features: The correlation with other VOCs and CO using factor analysis, and the effect of rain events. For the first, we carried out a separate factor analysis for June–August 2000 and for January 2001. The number of compounds measured during the winter was reduced to incorporate the results into the summer matrix. The outcome is shown in Table S01

(auxiliary material<sup>1</sup>). Very similar to our previous results [Lamanna and Goldstein, 1999; Goldstein and Schade, 2000; Schade and Goldstein, 2001], this analysis (1) interprets acetone abundances as a mixture of biogenic emissions, anthropogenic emissions, and secondary production, (2) suggests that methanol can be interpreted as a mixture of a significant background and direct biogenic emissions only, (3) shows that anthropogenic contributions to acetone and methanol variability at this rural site are negligible in winter, and (4) shows a previously unrevealed covariance between known biogenic emissions and these OVOCs in winter that provides evidence of ongoing emissions outside the dominant growing season.

[13] Winter measurements have the additional benefit of establishing a timeline through changing humidities. It has previously been suggested that lower methanol levels after precipitation may be due to deposition to wetted surfaces or rainout [Fall, 1996; Riemer *et al.*, 1998], as methanol has a relatively high Henry constant ( $220 \text{ M atm}^{-1}$  at 298 K). However, as we will show here and in the next section, lower methanol mixing ratios during rain events are most likely not caused by the rain itself but by the fact that an air mass change occurs prior to or during the rain event. Consider the examples depicted in Figure 8. The first rain event began around noon of day 299 (25 October) and was in fact preceded by dropping mixing ratios of acetone and methanol. Both OVOCs dropped by 70–80% in the course of that day and were highly correlated ( $r^2 > 0.85$ ). The parallel drop already suggests that deposition did not dominate as this effect would be expected to be different for acetone and methanol. Nevertheless, the drop was accelerated from  $0.03$  ( $0.26$ )  $\text{ppb h}^{-1}$  for acetone (methanol) to an initial  $0.3$  ( $1.2$ )  $\text{ppb h}^{-1}$  1 hour after the onset of the rain (Figure 9). As acetone wet removal is insignificant and methanol rainout could at most remove 10–20% of its abundance [Crutzen and Lawrence, 2000], another process must be responsible for the observed rapid change. One possibility to explain this decrease would be reactive uptake into the liquid phase at the surface during the rain, and this possibility is further considered here. Starting with an acetone (methanol) mixing ratio of 1 (2.3) ppb, time constants of  $3.3 \times 10^{-5} \text{ s}^{-1}$  and  $2.5 \times 10^{-5} \text{ s}^{-1}$  were calculated with relative errors of approximately 30% each. To put this in perspective, photochemical removal by the OH radical at  $1 \times 10^6 \text{ molecules OH cm}^{-3}$  is 2–3 orders of magnitude slower. If an air column of several 100 m depth were depleted via deposition (i.e., from the base of the clouds to the ground), the determined removal rate would correspond to a deposition velocity larger than  $1 \text{ cm s}^{-1}$ . While this is not impossible, it appears highly unlikely, especially when compared to recent measurements [Karl *et al.*, 2004; Carpenter *et al.*, 2004].

[14] Rain events are associated both with a downward moving air mass and advection. Typically, these events are also associated with large temperature decreases and increased wind speed and thus dilution of boundary layer air with air from aloft. Therefore, if instead of deposition we

<sup>1</sup>Auxiliary material is available at <ftp://ftp.agu.org/apend/gb/2005GB002566>.



**Figure 9.** Acetone and methanol abundances during a rain event on 25 October 2000.

consider the mixing ratio drop to be a dilution or replacement with a different air mass containing lower mixing ratios, we can apply the simple model

$$\frac{dc_a}{dt} = -K \times (c_a - c_a^{bg}), \quad (1)$$

where  $K$  is a mixing constant, and  $c_a^{bg}$  is the “background” mixing ratio that dilutes the initial, ground level mixing ratio measured at the beginning of the drop.  $K$  can be independently estimated using VOCs that likely do not deposit and that are not emitted locally, such as most anthropogenic VOCs. We assumed that the mixing ratios of toluene and MTBE can be used for this purpose and that their diluting abundance was one half of their mixing ratio measured at the end of the rain event. Using equation (1) in its integrated form with  $c_a^{bg} = 0.01 (\pm 0.005)$  ppb for both toluene and MTBE we calculated a combined  $K$  of  $0.5 \pm 0.15 \text{ h}^{-1}$ . While this may appear high, a comparison with the other rain events in Figure 8 shows that similarly sharp mixing ratio drops did not occur on a regular basis (in fact, during the rains on days 302 and 303 no significant changes in acetone or methanol mixing ratio occurred at all, and during the day 304 rain, both acetone and methanol mixing ratios actually increased along with temperature). So assuming the calculated  $K$  value is correct, we next calculated that the respective backgrounds for acetone and methanol must have been between 0.34–0.5 ppb, and 0.9–1.3 ppb, respectively. These mixing ratios are consistent with the values in Figure 9 and may reflect the fact that acetone and methanol have longer atmospheric lifetimes than toluene and MTBE and are therefore relatively “enhanced” in the cleaner air mass, including a higher acetone to methanol ratio.

[15] Further arguments against reactive wet surface uptake but in favor of the dilution effect can be found in the observations that mixing ratio drops also occurred without precipitation, such as on days 294/295, 311, or 314, which were days on which air mass changes were signified via

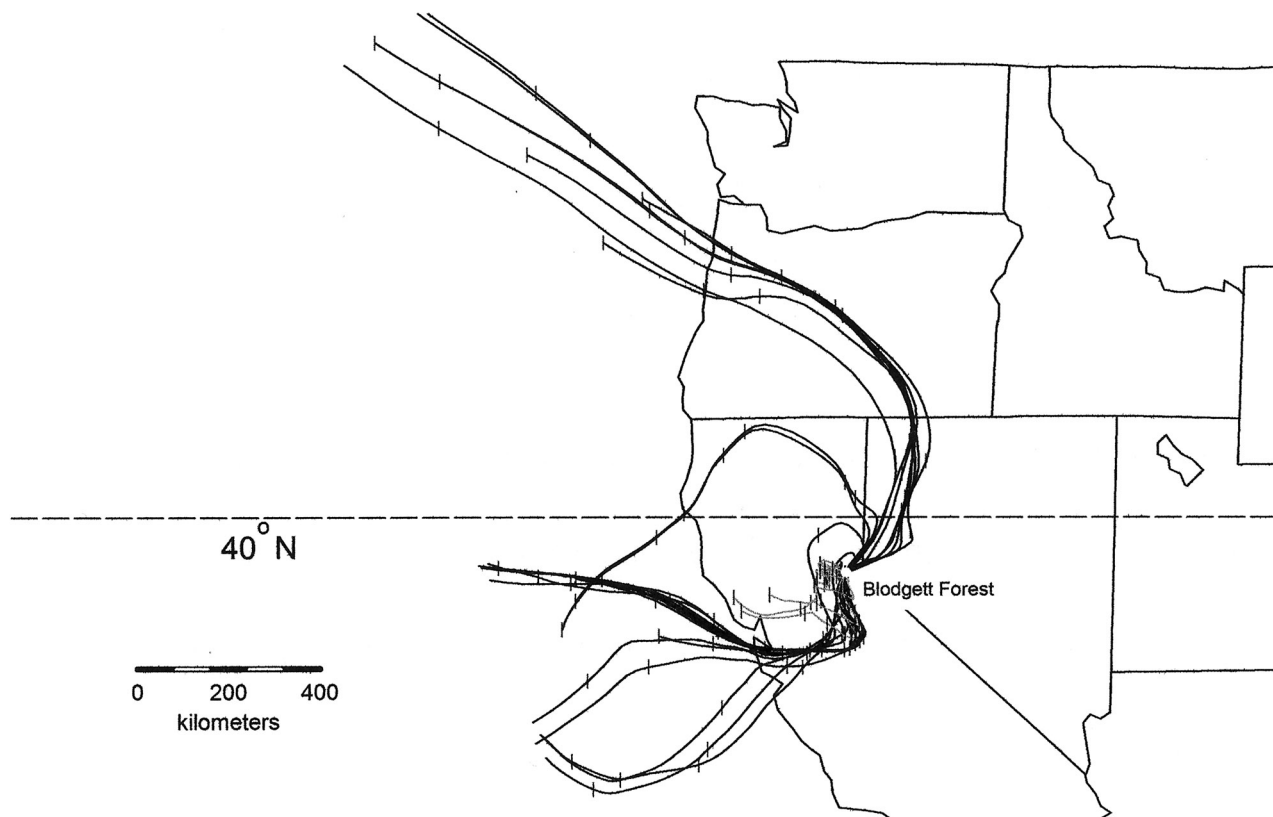
strong horizontal temperature, pressure, and humidity gradients (Figure 8). Furthermore, the reactive uptake conjecture is inconsistent with the observation that snow on the ground after day 315 did not prevent increasing mixing ratios after the snowfall.

[16] In summary, a closer investigation reveals that regular drops in OVOC abundance are most likely not caused by an irreversible deposition to wet surfaces, but rather by a change in air mass, replacing aged emissions-affected air by clean air, likely from aloft. This leads to the conclusion that measurements during such events allow observation of air masses that are much less affected by local emissions and more representative of the free troposphere.

#### 4. Back Trajectory Analysis

[17] Back trajectories from June 2000 throughout March 2001 were calculated using HYSPLIT (R. R. Draxler and G. D. Rolph, HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model, 2003, access via NOAA ARL READY Website (<http://www.arl.noaa.gov/ready/hysplit4.html>)), version 4.7. Simultaneously, we evaluated our meteorological data together with archived U.S. weather maps ([http://weather.unisys.com/archive/sfc\\_map/](http://weather.unisys.com/archive/sfc_map/)) to determine the timing and type of frontal passages. Trajectories started at  $38.89^\circ\text{N}$  and  $120.6^\circ\text{W}$  at 100 m above ground level using model vertical velocity and meteorological data output along the trajectory, and were generally run backwards for 48 hours. Latitude/longitude data were analyzed to determine if and when the trajectory passed from the Pacific Ocean over land within these previous 48 hours. Accumulated precipitation along the trajectory as well as the number of hours over land and the related subset of hours within the land boundary layer (BL) were investigated, the latter by relating trajectory height above ground to model BL height plus a 100 m safety margin. Figure 10 shows two ensembles of “Pacific” back trajectories that were associated with very low acetone and methanol mixing ratio data, together with one ensemble of trajectories from just a day before a frontal passage. The latter corresponds to day 293 in Figure 8 showing a typical cycle of lower nighttime and higher daytime mixing ratios due to local biogenic emissions and transported anthropogenic emissions from the California Central Valley. Though the model resolution (80 km) is generally not high enough to determine small-scale flows like the western Sierra Nevada upslope-downslope wind pattern, it clearly captures the change from a regional (California) air mass (days 290–293) to a “clean background” air mass (days 295–296) established after a cold front passage on 21 October 2000 (day 294), and depicted by the North Pacific trajectory ensemble in Figure 10. A similar VOC pattern and back trajectory origin change occurred between days 307–310 and days 311/312 (Figure 8), not plotted in Figure 10 for clarity.

[18] In total, 27 frontal passages were identified between 1 June 2000 and 28 March 2001. As shown in Table 2, not all of these had Pacific origins within the 48 hours analyzed. However, almost all the identified passages were associated with decreasing acetone and methanol mixing ratios. Table 2 also lists the established mixing ratios after the frontal



**Figure 10.** Back trajectories (with markers every 6 hours) for two typical “Pacific” origin periods (black lines), and one regional origin period (gray lines).

passages. The fall and winter events are coincident with the lowest mixing ratios measured during the entire field campaign. There was neither a significant correlation with the accumulated precipitation along the trajectory, nor with the estimated average time the trajectories spent in the land BL. While the former confirms that wet deposition is insignificant for acetone and methanol atmospheric mixing ratios, the latter appears surprising when taking into account that most sources lie in the land BL. The explanation may lie in the fact that with the passage of a front usually a colder air mass gets established at the ground and the daytime upslope air mass transport to the site is perturbed. Both effectively lead to a large reduction of the source input into the BL at our site with the result that even “land-origin” air masses often have low mixing ratios. The only correlating quantities to those low mixing ratios were time and air temperature along the trajectory, the latter correlation largely driven by the few summer values. Again, this is not too surprising as emissions are exponentially related to temperature [Schade and Goldstein, 2001], and temperature decreases seasonally with progression into fall and winter.

[19] The above analysis suggests that acetone and methanol mixing ratios in the free troposphere undergo very similar seasonal cycles as in the boundary layer, which reconfirms the dominance of ground level sources over atmospheric sources to their global budgets. However, the atmospheric sources can dominate the background in remote areas, and the mixing ratios measured after cold front

passages with Pacific origin may reflect the Pacific tropospheric background. For both acetone and methanol the lowest measured mixing ratios (methanol  $< 1$  ppb) are consistent with Pacific free tropospheric measurements by Singh *et al.* [2003, 2004] for winter/spring 2001. We also found a slight dependence on mean trajectory height, consistent with the Singh *et al.* [2003] finding of a gradient toward the marine BL, suggesting slow ocean uptake.

[20] The ratio of acetone to methanol after the frontal passages is comparable to the running 0.1 quantile ratio shown in Figure 6. Except for one case all quantile values were within calculated minimum and maximum ratios from the values measured after frontal passages, which encourages the usage of low quantiles to describe the regional background at this measurement location.

## 5. Conclusions

[21] Our acetone and methanol measurements at the BFRS established an interesting seasonality of these important atmospheric OVOCs, that allows some general conclusions about their sources and sinks in the atmosphere. In general, mixing ratio seasonalities followed the temperature curve with more frequent additional variability occurring during the wet season as a result of frontal passages that bring lower mixing ratio air masses from higher in the troposphere to the surface measurement site. Higher methanol to acetone ratios are found in the atmosphere during the



**Table 2.** Timing of Frontal Passages and Characteristics of Associated Back Trajectories (BT) Calculated Using HYSPLIT<sup>a</sup>

Frontal Timing	Mean BT Height, m	Hours in the BL	Mean Temperature, K	Pacific Origin	Mean Acetone $\pm$ SD, <sup>b</sup> ppb	Mean Methanol $\pm$ SD, <sup>b</sup> ppb
June 8	16	25	287	Y	1.0 $\pm$ 0.2	3.1 $\pm$ 1.6
June 16	45	48	291	Y	0.9 $\pm$ 0.3	4.2 $\pm$ 1.4
July 1	15	31	289	N	1.3 $\pm$ 0.2	7.0 $\pm$ 1.4
Sept 2	93	46	288	N	1.1 $\pm$ 0.2	5.2 $\pm$ 1.8
Sept 9	737	15	291	N	2.2 $\pm$ 0.2	10.8 $\pm$ 1.4
Sept 22	187	46	285	Y	1.6 $\pm$ 0.2	3.9 $\pm$ 1.1
Sept 28	38	36	289	Y	NA	NA
Oct 10	69	37	286	Y	NA	NA
Oct 21	419	28	276	Y	0.5 $\pm$ 0.1	1.9 $\pm$ 0.4
Oct 26	37	48	284	N	0.7 $\pm$ 0.2	2.3 $\pm$ 1.0
Oct 28	180	43	281	N	0.3 $\pm$ 0.1	1.5 $\pm$ 0.5
Nov 5	1108	9	275	Y	0.7 $\pm$ 0.2	2.2 $\pm$ 0.4
Nov 8	464	27	278	Y	0.3 $\pm$ 0.1	1.0 $\pm$ 0.6
Nov 27	1382	6	278	N	0.8	3.9
Nov 30	419	17	279	Y	0.5 $\pm$ 0.1	1.7 $\pm$ 0.7
Dec 13	337	16	283	Y	0.4 $\pm$ 0.1	0.8 $\pm$ 0.2
Dec 16	1238	3	266	Y	0.4 $\pm$ 0.0	1.3 $\pm$ 0.1
Dec 22	18	49	280	N	0.3 $\pm$ 0.0	0.9 $\pm$ 0.1
Dec 23	196	36	277	N	0.3 $\pm$ 0.0	0.9 $\pm$ 0.1
Jan 8	275	35	279	N	0.4 $\pm$ 0.1	0.9 $\pm$ 0.1
Jan 11	265	22	280	Y	0.3 $\pm$ 0.0	0.8 $\pm$ 0.2
Jan 15	570	18	269	Y	0.2 $\pm$ 0.0	0.8 $\pm$ 0.1
Jan 24	256	32	279	Y	0.4	1.6
Jan 29	30	49	276	N	0.3 $\pm$ 0.1	0.7 $\pm$ 0.1
Jan 31	969	11	266	Y	0.3 $\pm$ 0.0	1.0 $\pm$ 0.0
March 10	488	28	274	Y	0.5 $\pm$ 0.1	1.2 $\pm$ 0.4
March 19	1004	10	278	Y	1.2 $\pm$ 0.3	2.6 $\pm$ 1.0
March 26 <sup>c</sup>	48	36	286	Y	0.5 $\pm$ 0.1	1.9 $\pm$ 0.7

<sup>a</sup>BT, back trajectories; Y, yes; N, no. Note that not all trajectories with a Pacific origin have low acetone and methanol abundances. In summer, trajectories always passed through California's Central Valley.

<sup>b</sup>Where no SD is given, only a single measurement was available.

<sup>c</sup>This was seemingly not a front but two cold, dry air intrusions from aloft.

late spring and early summer, likely reflecting peak methanol emissions during the intensive plant growth period and decreasing methanol emissions alongside peak acetone photochemical production during mid to late summertime, when the methanol to acetone ratio decreases. Acetone is additionally influenced by anthropogenic primary emissions and secondary production from anthropogenic precursors while such an influence was not found for methanol. The strong correlation between these OVOCs at our site at all times suggests that (1) their direct biogenic emissions are correlated, (2) these biogenic emissions significantly contribute to atmospheric abundances even in winter, and (3) their secondary production in or their removal from the atmosphere may be correlated as well. The temperature dependence of their atmospheric abundance changes from summer to winter in a way consistent with several acetone but likely no methanol precursors diminishing. This seasonal change can be explained by the fact that biogenic MBO, monoterpene, acetone and methanol emissions are all strongly temperature dependent, but the secondary production of acetone by the oxidation of regionally emitted MBO and monoterpenes is strongly reduced in winter. Wintertime relationships are in accord with a higher acetone than methanol atmospheric lifetime, and Pacific air mass back trajectories carry acetone and methanol abundances in agreement with marine tropospheric measurements.

[22] Established minimum background levels at the BFRS site, approximately 0.4 ppb for methanol and 0.15 ppb for acetone, may reflect limits that are maintained dominantly

by the oxidation of long-lived hydrocarbons in the atmosphere. Using the GEOS-CHEM CTM model, *Jacob et al.* [2002] calculated a hydrocarbon source of  $21 \pm 5$  Tg per year as acetone, sustaining more than 50% of measured mixing ratios at selected sites in winter. The resulting tropospheric background mixing ratio assuming a winter acetone atmospheric lifetime of 25 days would be approximately 0.14 ppb. For methanol, *Jacob et al.* [2005] calculated a model background of 0.2–0.4 ppb for a global source of  $38 \text{ Tg yr}^{-1}$  from methane oxidation. In both cases, the model results match our observations fairly well, assuming that the lowest measured levels represent true tropospheric background. Note also that *Jacob et al.* [2005] conclude that their model source is likely underestimating the true source strength from methane oxidation, which would bring the model tropospheric background closer to the observations in the remote marine troposphere, and also closer to our measured background levels. However, more measurements and more detailed model calculations appear necessary to establish what can be learned from winter methanol abundances about fundamental tropospheric methane chemistry.

[23] Assuming that any variability above the background at the BFRS is dominated by biogenic inputs as determined in this study, and further assuming that the lifetime ratio of acetone to methanol is 2 in winter, we calculate a molar biogenic emissions ratio of 0.7–1 from Figure 7. This can be compared with a ratio of approximately 1.1 ( $\sim 100 \text{ Tg yr}^{-1}$  methanol and  $\sim 25 \text{ Tg yr}^{-1}$  acetone) using the GEOS-

CHEM model and other results [Galbally and Kirstine, 2002; Jacob et al., 2002, 2005], which is consistent with the measurements within the estimated errors of the budget terms. The comparison improves when accounting for the observation that the biogenic methanol emissions correlate with plant growth and should be lower in winter.

[24] As our measurement site lies over land, the data explain biogenic influences much better than background issues. For both acetone and methanol the biogenic sources clearly dominate at the BFRS site. These will be the focus of the second part of this analysis in a future publication.

[25] **Acknowledgments.** The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model on the READY website (<http://www.arl.noaa.gov/ready.html>) used in this publication. This research was supported by the California Air Resources Board (award 98-328), the U.S. Department of Energy (contract DE-AC03-76SF0009), and the University of California Agricultural Experiment Station. We thank Megan McKay and Meredith Kurpius for helping maintain the experimental site and for providing the meteorological data. We also thank Bob Heald and the Blodgett Forest crew for their invaluable support, and SPI for allowing us to carry out this research on their property.

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