



Quantifying biogenic and anthropogenic contributions to acetone mixing ratios in a rural environment

Allen H. Goldstein*, Gunnar W. Schade

Ecosystem Sciences Division, Department of Environmental Science Policy and Management, University of California at Berkeley, 151 Hilgard Hall, Berkeley, CA 94720-3110, USA

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Abstract

Acetone was one of the most abundant volatile organic compounds (VOCs) observed in the Sierra Nevada Mountains (California, USA). Mixing ratios were measured hourly above a ponderosa pine plantation using an automated in situ dual-channel GC-FID system throughout July 1997, from July through October 1998, and fluxes were measured with a relaxed eddy accumulator from July through September 1999. Acetone mixing ratios ranged from 1.4 to 7.8 ppb in July 1997, 1.1 to 7.8 ppb in July 1998, and 1.0 to 8.0 ppb in July 1999, and were correlated with compounds of biogenic and anthropogenic origin. During sunny periods in 1997 ($\text{PAR} > 1300 \mu\text{mol cm}^{-2} \text{s}^{-1}$) acetone was correlated with methylbutenol (biogenic emission from ponderosa pine, $r^2 = 0.48$). Under the same conditions, acetone was also correlated with acetylene (anthropogenic emission, $r^2 = 0.52$), yet acetylene and methylbutenol were not correlated with each other ($r^2 = 0.06$). A linear combination of $1.34 \times \text{methylbutenol} + 9.64 \times \text{acetylene}$ was highly correlated with acetone mixing ratios ($r^2 = 0.80$), suggesting that the quantity of biogenic and anthropogenic contributions to the observed acetone could be determined using this correlation. Based on this method, 45% of the observed acetone could be attributed to biogenic sources, 14% to anthropogenic sources, and 41% to the regional background level. Comparison with direct emission ratios from tailpipe exhaust showed that the anthropogenic contribution to acetone mixing ratios could be attributed almost completely to secondary photochemical production (99%), with only a minor contribution from direct fuel combustion emissions (1%). Based on direct measurements of ecosystem scale fluxes, the biogenic contribution to acetone mixing ratios could be attributed to direct emissions (35%), methylbutenol oxidation (63%), and monoterpene oxidation (2%). © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Acetone is present in the global troposphere at mixing ratios that make it an important source for HO_x radicals and a temporary sink for NO_x radicals through formation of peroxy acetyl nitrate in the upper troposphere (Singh et al., 1994, 1995; Jaegle et al., 1997; Wennberg et al., 1998). Identified acetone sources include primary

emissions from both biogenic and anthropogenic origins, secondary emissions from oxidation of biogenically and anthropogenically emitted volatile organic compounds (VOCs), and biomass burning. The atmospheric budget of acetone remains highly uncertain, however Singh et al. (2000) estimate a global source of 56 (37–80) Tg yr^{-1} ($1 \text{ Tg} = 10^{12} \text{ g}$).

Direct biogenic emissions of acetone have been measured from trees (Isodorov et al., 1985), pastures (Kirstine et al., 1998) and dead plant matter (Warneke et al., 1999). Acetone production during oxidation of biogenically emitted VOC compounds has also recently been quantified; OH oxidation of α - and β -pinene yields 8–15%

*Corresponding author. Tel.: +1-510-643-2451; fax: +1-510-643-5098.

E-mail address: ahg@nature.berkeley.edu (A.H. Goldstein).

acetone (Aschmann et al., 1998; Reissell et al., 1999), and OH oxidation of 2-methyl-3-buten-2-ol (methylbutenol) yields 50% acetone (Alvarado et al., 1999; Ferronato et al., 1998). Singh et al. (2000) estimate more than half of the global acetone source is biogenic, including 11 (7–15) Tgyr⁻¹ from oxidation of monoterpenes and methylbutenol, 15 (10–20) Tgyr⁻¹ from primary biogenic emissions, and 6 (4–8) Tgyr⁻¹ from decaying plant matter.

Elevated mixing ratios of acetone have been observed in many forested regions and it has been suggested that local biogenic emissions were responsible (Goldan et al., 1995; Riemer et al., 1998; Lamanna and Goldstein, 1999). However, no attempt has been made to quantify how much of the local acetone is derived from anthropogenic versus biogenic sources, or from primary versus secondary production. In this paper we report observations of acetone mixing ratios and direct biogenic emission rates measured above a ponderosa pine plantation in the Sierra Nevada Mountains, ~ 75 km downwind of a major urban and industrial center (Sacramento, CA). We use observations of acetone mixing ratios and biogenic emission rates, along with biogenic and anthropogenic trace gases, to quantify the percentage of observed acetone which originates from primary biogenic, secondary biogenic, primary anthropogenic and secondary anthropogenic sources.

2. Experimental

Hydrocarbon measurements were made continuously throughout July 1997, from July to October 1998, and from June through October 1999 above a ponderosa pine (*Pinus ponderosa* L.) plantation at approximately hourly intervals. The measurements were part of a larger field experiment at the Blodgett Forest Research Station on the western slope of the Sierra Nevada mountains (38°53'42.9"N, 120°37'57.9"W, 1315 m elevation) to study biosphere-atmosphere exchange of trace gases and energy and its impact on regional atmospheric chemistry (Lamanna and Goldstein, 1999; Schade et al., 1999; Goldstein et al., 2000). Meteorological measurements included wind speed and direction, net radiation, photosynthetically active radiation (PAR), air temperature and relative humidity, rain, soil heat flux, soil temperature, soil moisture, and needle temperature. The pine plantation (owned by Sierra Pacific Industries, SPI) consisted of even aged trees (6–9 years old) that were 3–5 m tall. Among them were a few individuals of douglas fir (*Pseudotsuga menziesii*), white fir (*Abies concolor*), black oak (*Quercus kelloggii*), and incense cedar (*Calocedrus decurrens*), and the understory was dominated by manzanita (*Arctostaphylos* spp.) and whitethorn (*Ceanothus cordulatus*). The site is characterized by a Mediterranean climate, with the majority of precipitation falling between September and May, and little or no rain during the

summer. The predominant daytime wind direction is upslope from the Sacramento valley to the west. At night, the site receives downslope flow from the Sierra Nevada mountains to the east.

VOCs containing up to 10 carbon atoms were quantified using a fully automated two-channel GC-FID system without using liquid cryogen (Lamanna and Goldstein, 1999). This instrument was designed to be used in three different sample collection schemes, and was deployed using a different scheme in each of the three measurement years: ambient mixing ratio measurements (1997), gradient flux (1998), and relaxed eddy accumulation (REA) flux (1999). In 1997, the system was configured to measure ambient mixing ratios of the widest possible suite of C₂–C₁₀ VOCs. Measurements were made continuously from a single height (9 m above the ground, ~ 6 m above the forest canopy) and the two measurement channels had different pretreatment systems and chromatography columns. The front column was a PLOT Rt-Alumina 0.32 mm × 60 m (Restek, Bellefonte, PA) and the rear column was a DB-WAX 0.32 mm × 60 m × 0.5 μm film thickness (J&W Scientific, Folsom, CA) for the separation of non-polar and polar compounds, respectively. Samples were collected for both channels at 20 ml min⁻¹ STP (MKS Instruments, Andover, MA) for 20 min on Silcosteel micro-traps filled sequentially with glass beads, Carboxpack B, and Carbosieve SIII, at - 80°C, resulting in 400 ml samples (STP) at 40 min intervals (Lamanna and Goldstein, 1999). The measurements in 1997 included a wide variety of anthropogenically emitted compounds such as acetylene, and these data will be used to differentiate between the biogenic and anthropogenic impacts on observed acetone mixing ratios.

In 1998, VOC mixing ratios and vertical gradients were quantified for compounds containing up to 10 carbon atoms using two identical DB-WAX columns (0.32 mm × 60 m × 0.5 μm film thickness, J&W Scientific, Folsom, CA). Two samples were obtained simultaneously from approximately 2.5 and 4.5 m above the tree height and preconcentrated on the Silcosteel micro-traps at - 25°C. Samples were collected at 10 ml min⁻¹ STP for 30 min, resulting in 300 ml samples at 60 min intervals (Schade et al., 1999).

In 1999, VOC mixing ratios and fluxes were measured with a newly developed REA system using a Campbell Scientific (Logan, UT) 3D Sonic anemometer and data logger (CR23X) interfaced with the two-channel GC-FID system. The two GC channels had identical Rtx-WAX columns (0.53 mm × 60 m × 0.5 μm film thickness, Restek, Bellefonte, PA) each equipped with a 5 m retention gap. A real air sample chromatogram (Fig. 1) from 1999 shows the compounds quantified using these columns. Ambient air was drawn from 11 m height beside the sonic anemometer through a single 3/8" PFA tube at a controlled rate of 10 l min⁻¹ to segregator valves

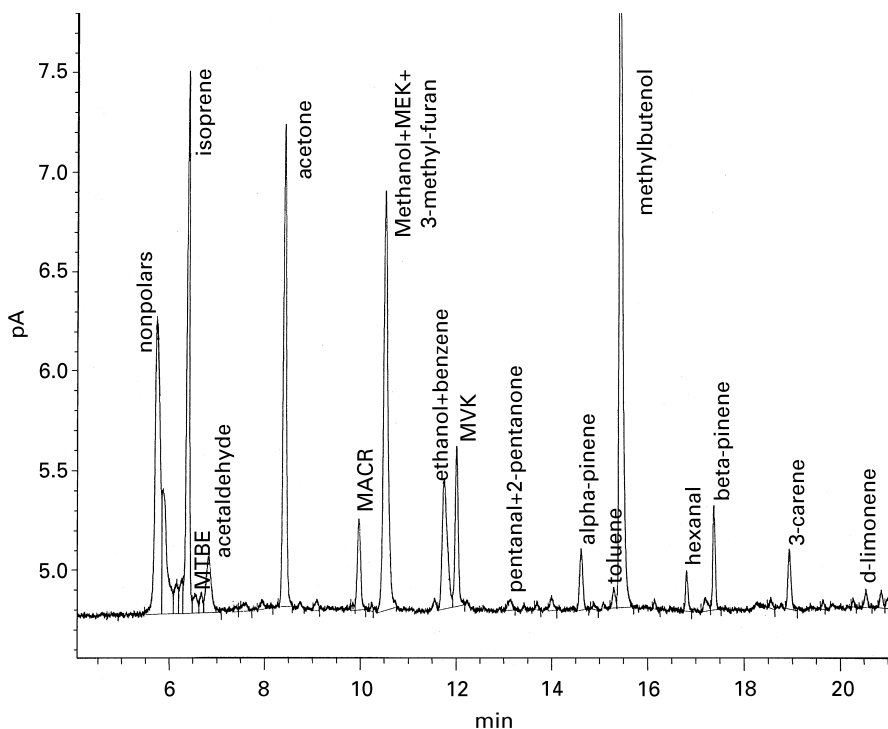


Fig. 1. Sample chromatogram from the Rtx-WAX column (July 1999).

(General Valve/Parker, Fairfield, NJ) inside the laboratory container. The residence time in the tubing was 2.3 ± 0.2 s (3 S.D., $n = 7$), determined by popping balloons near the anemometer and measuring the lag time between the sonic spike and the CO_2 response in an infrared analyzer (LICOR 6262). Updrafts and downdrafts were separated with the segregator valve when the vertical wind speed (w) exceeded a deadband of $0.6 \sigma_w$ (Oncley et al., 1993), using a 5 min running average of w and its standard deviation (σ_w), similar to Guenther et al. (1996). The segregator valves switched between sampling ambient air or zero air (from a zero air generator, AADCO, Clearwater, FL). Samples were collected on the Silcosteel microtraps at -10°C with a flow rate of 15 ml min^{-1} . Sample size was determined by summing times a segregator valve was “open” during the half-hour period, and was typically of order 150 ml. Flux (F) was calculated using the relationship:

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

where β was determined from measurements of sensible heat flux and air temperature (Bowling et al., 1998), and C_u and C_d were the VOC mixing ratios in the updrafts and downdrafts, respectively. The REA system will be described in more detail elsewhere (Schade and Goldstein, 2000).

Instrument calibration was achieved by periodically diluting ppm level gas standards (Scott-Marrin Inc., Riverside, CA) into the main sample stream to achieve low ppb and sub ppb standard additions. In 1997, standard additions were performed every few days, while in 1998 and 1999 standard additions were automatically performed every 15 or 30 h, respectively. The instrument response factors were nearly the same in all three years and their RSDs were generally better than 10% for acetylene, methylbutenol, and the monoterpenes in all years, and for acetone in 1997 and 1999. However, acetone measurements in 1998 had a larger uncertainty including possible contamination that precluded determination of its flux from the measured gradients. The accuracy of measurements for the reported compounds is mainly limited by the stated accuracy of the high mixing ratio standards, and the quality of the chromatography, which was poorer in 1998 leading to higher uncertainties for acetone and methylbutenol.

Note that the accuracy of the analysis presented here regarding percentage of acetone derived from biogenic versus anthropogenic and primary versus secondary sources should not be significantly affected by the accuracy of the mixing ratio and flux measurements. Because the conclusions drawn in this paper are based mainly on internally consistent data sets, only the precision of the mixing ratio measurements

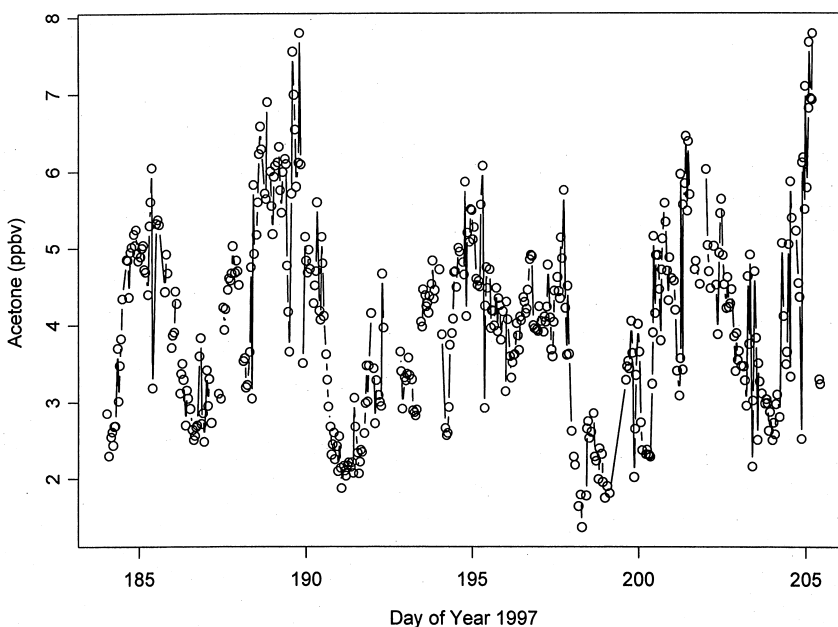


Fig. 2. Acetone mixing ratios measured during July 1997.

affects the accuracy of our quantification of the local acetone sources.

3. Results and discussion

Observed acetone mixing ratios at Blodgett Forest ranged from 1.4 to 7.8 ppb in 1997 (Fig. 2), 1.1 to 7.8 ppb in July 1998, and 1.0 to 8.0 ppb in July 1999. Acetone was one of the most abundant VOCs (after methane and methanol) measured over the ponderosa pine plantation. The range of acetone mixing ratios observed were similar to those reported from other rural regions, including 1.7–8 ppb during June and July 1995 at the YOUTH site in rural Tennessee (Riemer et al., 1998), 1.4–5.1 ppb during August 1998 at the PROPHET site in rural Michigan (D. Riemer, personal communication), ~ 1 to ~ 9 ppb during June and July 1990 at the ROSE site in rural Alabama (Goldan et al., 1995), and 1–3.5 ppb during August and September 1993 at Idaho Hill in the mountains of Colorado (Goldan et al., 1997), suggesting that high mixing ratios of acetone during summer in rural environments are common. Measurements in more remote and higher altitude regions of the northern mid-latitudes had a lower range of mixing ratios, 0.4–2.3 ppb during ABLE3B, July–August 1990, 0–6 km, 35–65°N (Singh et al., 1994), suggesting that the rural measurements were significantly closer to large acetone sources.

Temporal changes in acetone mixing ratios did not show an obvious pattern that was typical of exclusively

biogenically or anthropogenically emitted compounds. Biogenic compounds that are emitted as a function of light and temperature (e.g. methylbutenol) have a diurnal cycle where mixing ratios increase with light in the morning, reach a maximum during the day, and decrease at night. Anthropogenic compounds (e.g. acetylene or toluene) have a diurnal cycle at this site where mixing ratios increase around midday as air masses are transported up to the site from the polluted Central Valley below, and decrease throughout the night and morning as air travels downslope back toward the valley. Careful comparison between observed patterns for acetone, anthropogenic compounds (acetylene, toluene), and biogenic compounds (methylbutenol) over a few days suggests that temporal changes in acetone can be attributed to a combination of anthropogenic and biogenic sources (Figs. 3(a)–(d)). The data from 1997 show days where both (a) anthropogenic (acetylene) and (b) biogenic (methylbutenol) compounds were correlated with changes in acetone mixing ratios. On day 194, acetone mixing ratios rose in the morning following sunrise along with methylbutenol, then rose again just before noon along with acetylene. In addition, there were strong short-term increases in both acetone and methylbutenol in the evening of day 194 and the morning of day 195 – both of these increases occurred when vertical dilution was slow and local biogenic emissions increased the mixing ratios dramatically near the forest canopy. The data from 1998 show a day where there was little influence from (c) anthropogenic (toluene) emissions, and thus

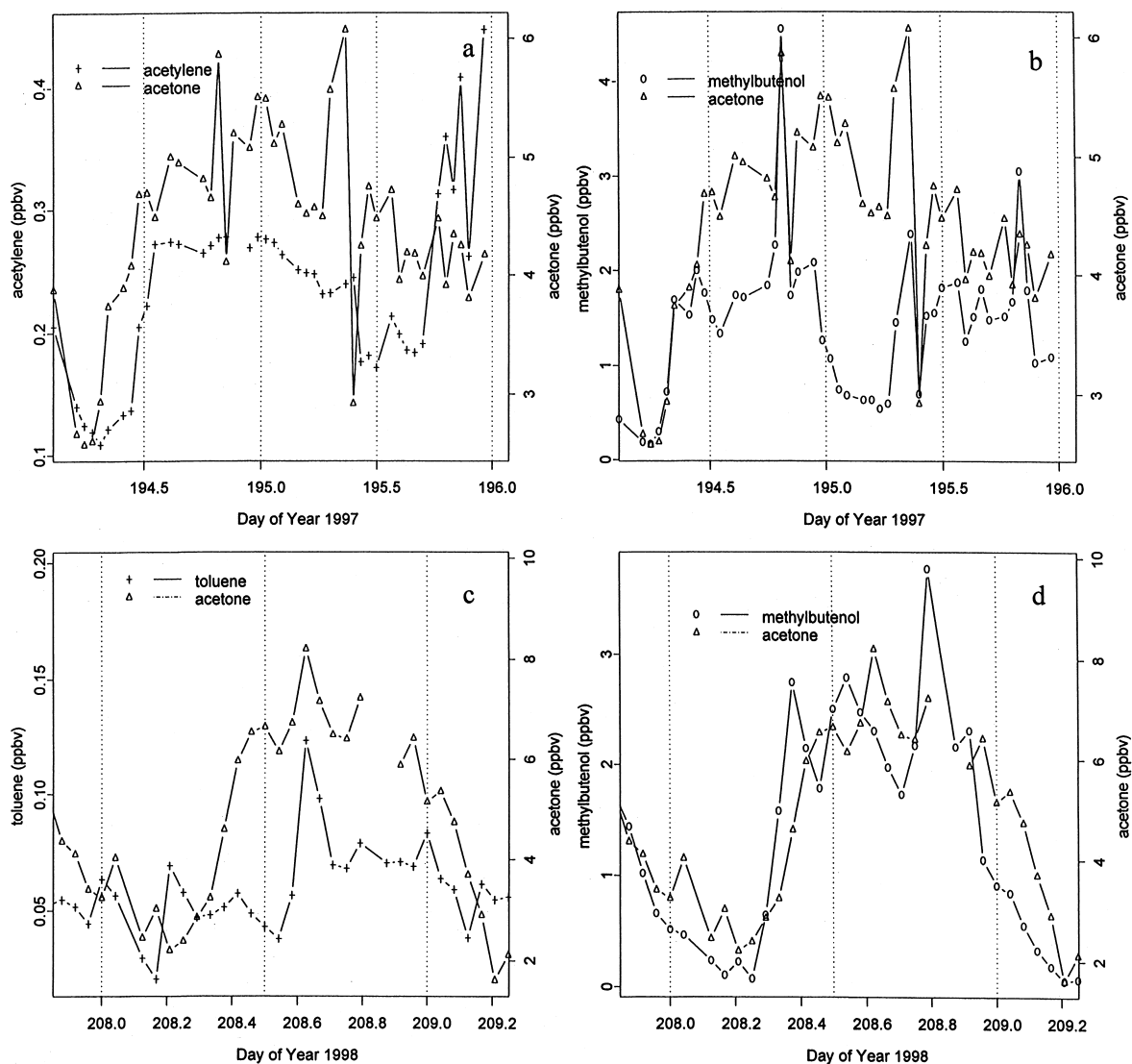


Fig. 3. A few days of mixing ratio data for acetone, acetylene, toluene, and MBO indicate how temporal changes in these trace gases are related. Data from 1997 show a day where (a) anthropogenic (acetylene) and (b) biogenic (MBO) emissions both strongly impacted acetone. Data from 1998 show a day where there was little influence from (c) anthropogenic (toluene) emissions, and thus (d) the biogenic compound (MBO) and acetone had a very similar pattern. Acetone lagged slightly behind MBO suggesting that it was mostly derived from MBO oxidation.

(d) the biogenic compound (methylbutenol) and acetone have a very similar pattern. The toluene data show only a slight increase in the early afternoon of day 208, with a concurrent small increase in acetone. During this time period (with little influence from anthropogenic sources) the acetone diurnal cycle lags slightly behind methylbutenol suggesting that acetone is at least partially derived from methylbutenol oxidation.

Acetone mixing ratios were correlated with compounds of biogenic and anthropogenic origin (Figs.

4(a)–(d)). During sunny periods ($\text{PAR} > 1300 \mu\text{mol cm}^{-2} \text{s}^{-1}$) (a) acetone was correlated with methylbutenol (biogenic emission from ponderosa pine, $r^2 = 0.48$). Under the same conditions, (b) acetone was also correlated with acetylene (anthropogenic emission, $r^2 = 0.52$). (c) A best fit linear combination of $1.34 \times \text{methylbutenol} + 9.64 \times \text{acetylene} + 0.43$ was even more highly correlated with acetone ($r^2 = 0.80$, standard error of slopes was 0.13 and 0.90, respectively, standard error of intercept was 0.21), suggesting that the quantity of

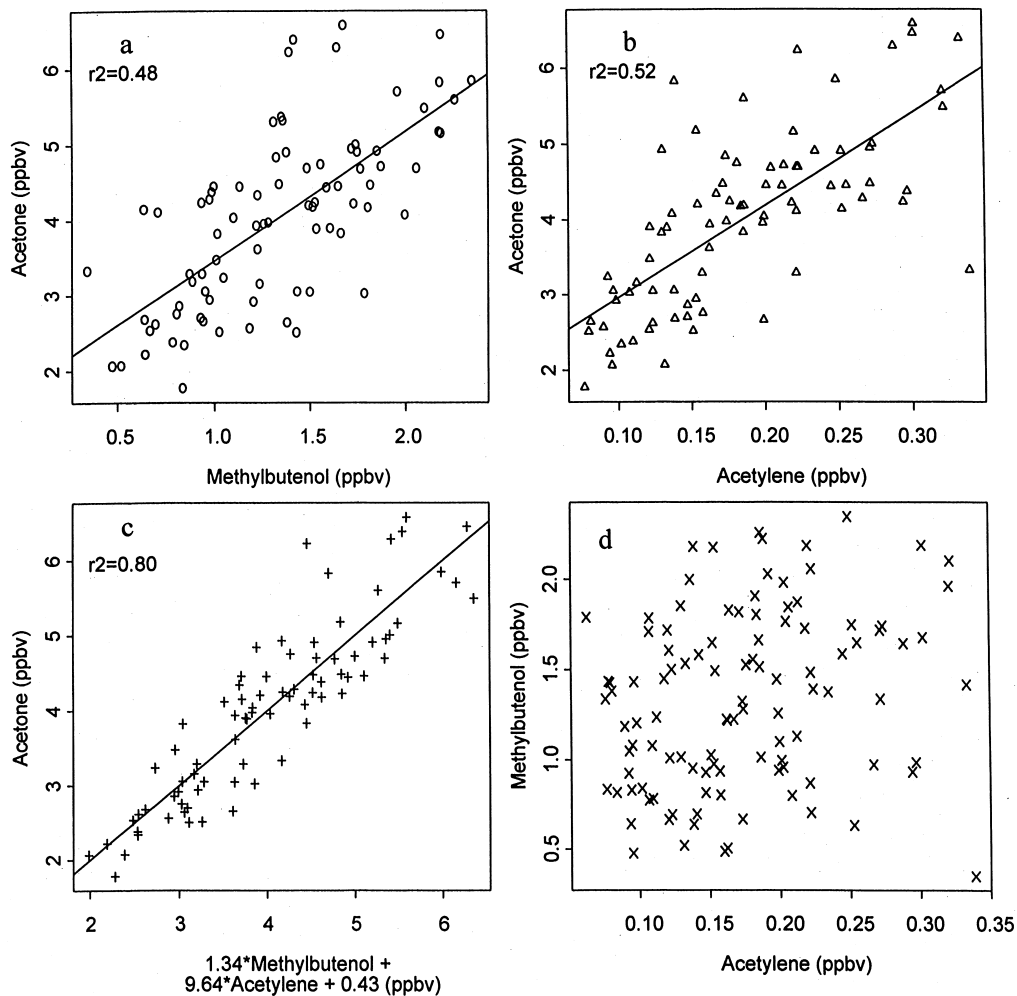


Fig. 4. Correlation of acetone with compounds of biogenic and anthropogenic origin during sunny periods ($\text{PAR} > 1300 \mu\text{mol cm}^{-2} \text{s}^{-1}$) in July 1997: (a) methylbutenol (biogenic emission from ponderosa pine, $r^2 = 0.48$), (b) acetylene (anthropogenic emission, $r^2 = 0.52$), and (c) a linear combination of methylbutenol and acetylene ($r^2 = 0.80$). (d) Acetylene and methylbutenol were not correlated with each other ($r^2 = 0.06$).

biogenic and anthropogenic contributions to the observed acetone mixing ratios can be described using this correlation. (d) Note that acetylene and methylbutenol were not correlated with each other ($r^2 = 0.06$), suggesting that their sources were completely unrelated.

3.1. Anthropogenic or biogenic?

Based on the slopes given in Fig. 4c, and measurements of acetone and methylbutenol in 1997, we estimate that $45 \pm 12\%$ of the observed acetone was due to biogenic emissions, $14 \pm 14\%$ was due to anthropogenic emissions, and $41 \pm 14\%$ could be attributed to the regional background level during the daytime (Table 1). Percent-

age contributions were calculated for each measurement time, and reported as the mean of all times ± 1 standard deviation. Background for acetone was defined based on the intercept of the fit between methylbutenol + acetylene versus acetone (0.43 ppb acetone, Fig. 4(c)), plus an offset due to the northern midlatitude background for acetylene in July of approximately 0.1 ppb (Goldstein et al., 1995) times 9.64 acetone/acetylene, resulting in a background estimate of 1.4 ppb acetone. This background estimate is consistent with the lowest levels of acetone observed during the measurement period at Blodgett Forest, and at the rural sites in Tennessee, Michigan, Colorado, and Alabama (Riemer et al., 1998; D. Riemer, personal communication; Goldan et al., 1997,

Table 1
Contributions to the observed daytime acetone mixing ratio (± 1 S.D.)

Background (%)		Anthropogenic (%)		Biogenic (%)	
41 \pm 14		14 \pm 14		45 \pm 12	
Anthropogenic	Biogenic	Primary	Secondary	Primary	Secondary
34 ^a	66 ^a	1	99	35	65 ^b

^aNumbers according to Singh et al. (2000).

^b63% from methylbutenol, and 2% from monoterpene oxidation.

1995). This background estimate is also consistent with the mean mixing ratio reported by Singh et al. (1994) for 0–6 km at 35°–65°N from July to August 1990 (1.1 \pm 0.4 ppb). Our estimate of the anthropogenic contribution assumes that the correlation between acetylene and acetone is completely driven by anthropogenic sources, and that biogenic acetone added to the air mass during transport from the pollution sources has not significantly influenced the observed slope. Our estimate of the anthropogenic contribution to acetone should therefore be viewed as an upper limit.

3.2. Anthropogenic emissions: primary or secondary?

Anthropogenic contributions to the observed acetone mixing ratios can be separated into direct emissions and secondary production from oxidation of anthropogenically emitted VOCs. Measurements of car exhaust in the Caldecott tunnel in 1997 gave a direct fuel combustion emission ratio of 0.03 moles acetone per mole acetylene (Kirchstetter et al., 1999). Neither acetone nor acetylene is a component of evaporative emissions from gasoline headspace (Kirchstetter et al., 1999), thus we presume primary anthropogenic emissions are due almost exclusively to fuel combustion and the tunnel measurements provide a reasonable estimate of the regional anthropogenic emission ratio. Measurements by Grosjean et al. (1997), showing a molar ratio of ~ 0.07 for acetone to acetylene in the ambient air of downtown Porto Alegre, Brazil, where vehicle exhaust emissions account for approximately 99% of total VOC emissions, strongly support that view.

The observed slope of acetone to acetylene at Blodgett Forest was 9.64, suggesting less than 1% of the anthropogenic acetone came from primary emissions, and more than 99% must have been produced as the polluted air was photochemically aged during transport from the upwind urban areas (~ 75 km from Sacramento). A similar slope of acetone to acetylene was reported by Singh et al. (1994) for the northern mid-latitude-free troposphere, implying that most of the photochemical production of acetone in urban/industrial plumes occurs rapidly during transport to the free troposphere.

In Sacramento, the major upwind urban area, the summertime mean acetylene mixing ratio was 1.3 ppb (range from below detection limit up to 6.5 ppb) (California Air Resources Board (CARB) Air Quality Data, 1997) while at Blodgett Forest it was 0.2 ppb (range 0.1–0.5 ppb). Assuming an acetylene background of 0.1 ppb during July (Goldstein et al., 1995), acetylene was diluted by at least a factor of 10 between Sacramento and Blodgett Forest (photochemical loss of acetylene during transport from Sacramento should be small, lifetime ~ 1 week, transport time $\sim \frac{1}{2}$ day). The mean acetone mixing ratio was 1.8 ppb (range 0.4–4.7 ppb) in Sacramento (CARB Air Quality Data, 1997). Since dilution between Sacramento and Blodgett Forest would be similar to acetylene, the contribution of acetone due to primary anthropogenic emissions should be at most a few tenths of a ppb. This estimate is roughly consistent with our fuel combustion estimates, showing that primary anthropogenic emissions cannot account for much of the acetone observed at Blodgett Forest.

The secondary anthropogenic acetone must be accounted for by photochemical production from anthropogenically emitted hydrocarbons. These hydrocarbons must have a significantly shorter lifetime than acetylene or else the secondary production of acetone would not be correlated to acetylene. Oxidation of propane is not a likely source because the lifetime of propane is too long and too similar to acetylene. The most likely source is oxidation of reactive alkenes such as isobutene or isopentene. Since the lifetime of these precursors is much shorter than acetylene, the ratio of acetone to acetylene should be a function of time and therefore might provide some indication of the age of the air mass under ideal conditions, that is without the contribution of non-anthropogenic sources.

3.3. Biogenic emissions: primary or secondary?

Oxidation of biogenically emitted compounds by OH or ozone provide a secondary source of acetone, including monoterpenes (8–15% yield of acetone (Aschmann et al., 1998; Reissell et al., 1999)) and methylbutenol (50% yield of acetone (Ferronato et al., 1998; Alvarado et al., 1999)). Simultaneous emissions from the ponderosa pine

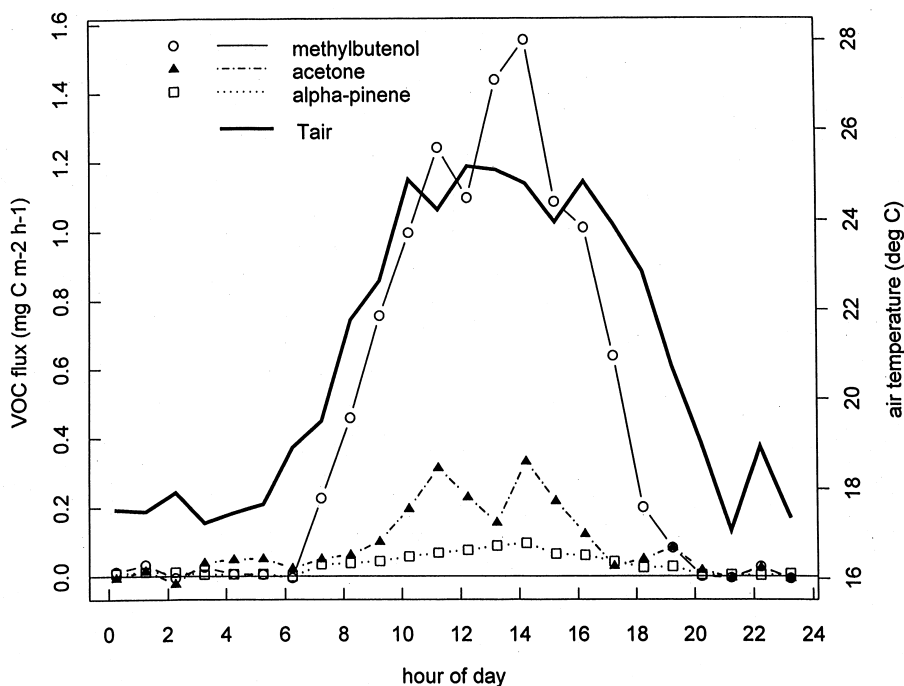


Fig. 5. Mean diurnal cycle of methylbutenol, acetone, and α -pinene fluxes and air temperature from 10 July through 20, 1999 (144 flux measurements for each compound).

plantation for α -pinene, methylbutenol, and acetone measured by the REA method in 1999 (Fig. 5) allow calculation of their relative contributions to the local acetone mixing ratio. For the ten day period shown, the mean daytime direct biogenic acetone emission rate was $0.22 \text{ mg C m}^{-2} \text{ h}^{-1}$. We scaled the α -pinene emissions to account for all observed monoterpenes (total monoterpene emission was 3.6 times α -pinene emission, following Schade et al. (1999)). The molar ratio of mean daytime direct emissions for methylbutenol to acetone and total monoterpenes to acetone was 3.6 and 0.49, respectively. Assuming a 10% yield of acetone from monoterpene oxidation, and a 50% yield of acetone from methylbutenol oxidation, we estimate that 35% of the biogenic acetone was due to direct biogenic emissions, 63% was due to oxidation of methylbutenol, and 2% was due to oxidation of monoterpenes.

3.4. Primary biogenic acetone sources

Sources of primary biogenic acetone emissions could include the ponderosa pine trees, shrubs, organic debris, or the bare soils at Blodgett Forest. Leaf cuvette measurements of emissions from live ponderosa pine needles were not able to detect any acetone, suggesting that live pine needles provided a negligible or small acetone source (D. Gray, personal communication).

Ground chamber measurements of acetone emissions from bare soil and soil covered with litter showed a strong increase with topsoil temperature, and the measured rates could account for roughly half of the observed ecosystem scale emissions (Schade and Goldstein, 2000). All shrubs were removed from the measurement site in the spring and early summer of 1999, so shrubs did not contribute substantially to the observed ecosystem scale acetone emissions. We conclude that the large amounts of organic debris left over from logging operations (~ 10 years ago) along with the accumulated leaf litter probably dominated acetone emissions from this ponderosa pine plantation. Future work should include more detailed measurements of acetone emissions from the various components of the ecosystem.

4. Conclusions

Acetone is one of the dominant VOC compounds present in rural forested regions with mixing ratios that often exceed those observed in urban areas. We quantified the local acetone budget for a rural forested site in the Sierra Nevada Mountains, $\sim 75 \text{ km}$ downwind of a major urban center (Sacramento, CA). Acetone could be attributed 14% to anthropogenic emissions (1% primary, 99% secondary) and 45% to biogenic emissions

(35% primary, 63% secondary from methylbutenol oxidation, and 2% secondary from monoterpene oxidation, with the anthropogenic contribution being viewed as an upper limit. The remaining 41% were attributed to the northern mid-latitude background. We conclude that substantial amounts of acetone are being emitted to the global atmosphere from pine forest ecosystems, including significant emissions from accumulated plant debris on the ground. The most recent global budget estimates for acetone suggest its origin is 66% biogenic and 34% anthropogenic (Singh et al., 2000), and our results suggest that the fraction of acetone from biogenic sources is even higher in a forested region just 75 km downwind of a major urban area. This is the first paper reporting ecosystem scale acetone flux measurements. Measurements of ecosystem scale methylbutenol emissions, a significant acetone precursor, have so far only been reported for the same site (Blodgett Forest) in the Sierra Nevada Mountains (Baker et al., 1999; Schade et al., 2000). To better quantify the global acetone budget, acetone and methylbutenol emission measurements are needed from a much wider variety of ecosystems.

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