Chemical evolution of the Sacramento urban plume: Transport and oxidation

M. B. Dillon[1]

Department of Chemistry, University of California, Berkeley, California, USA

M. S. Lamanna, G. W. Schade, and A. H. Goldstein[1]

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

R. C. Cohen[1,2]

Department of Chemistry, University of California, Berkeley, California, USA

[1] Measurements of anthropogenic hydrocarbons, ozone, and meteorological variables were obtained during the summer of 1997 near the University of California Blodgett Forest Research Station on the western slope of the Sierra Nevada Mountains. These measurements and related observations obtained upwind in Sacramento and Folsom, California, by the California Air Resources Board and the National Weather Service demonstrate that the transport of the Sacramento plume is controlled by extremely consistent, terrain-driven winds that draw polluted air into the Sierra Nevada by day and flush the mountains at night with clean, continental background air. In effect the plume serves as a mesoscale (100 km) daytime flow reactor where the daily evolution of the Sacramento urban plume can be characterized as a Lagrangian air parcel transported from the urban core into the sparsely populated Sierra Nevada mountains. Using observations of slowly reacting anthropogenic hydrocarbons, we demonstrate that at the peak impact of the Sacramento plume the air at Blodgett Forest can be characterized as a mixture of 32% air from the urban core and 68% from the relatively clean background. From measurements of more reactive hydrocarbons we infer an average daytime OH concentration of 1.1×10^7 molecules cm^{-3} during the transit of the urban plume.   INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 3322 Meteorology and Atmospheric Dynamics: Land/atmosphere interactions; KEYWORDS: Sacramento, California; urban plume; OH; VOC

1. Introduction

[2] The midelevations of the western Sierra Nevada Mountains lie at the interface between California's Central Valley and the heavily forested high Sierra. The cities in the Central Valley (Sacramento, Stockton, Fresno, and Bakersfield) and the suburbs and towns in the foothills of the Sierra Nevada are experiencing rapid population growth with the associated potential for rapid changes in emissions of precursors to ozone and fine particles as farmland is converted into residential neighborhoods. The region is frequently in violation of proposed federal ozone ($[O_3] \geq 80$ ppb, 8-hour average) and state particulate ($[PM_{10}] \geq 30$ µg m^{-3}, 24-hour average) standards. The Mountain Counties Air Basin (encompassing the northwestern Sierra Nevada and foothills, a region often referred to as "Gold Country") exceeded the proposed federal ozone standard 59, 28, 42, and 65 times and state particulate standards a minimum of 18, 66, 24, and 36 times in 1996–1999, respectively. The Sacramento Valley Air Basin, which

is immediately to the west and upwind, exceeded the federal ozone standard 44, 15, 60, and 43 times and state particulate standards 42, 24, 60, and 66 times in 1996–1999, respectively [*California Air Resources Board* (*CARB*), 2001a].

[3] There have been few previous studies of the factors controlling ozone abundances in the Gold Country. *Van Ooy and Carroll* [1995] measured ozone and local meteorological variables (temperature, wind speed, wind direction, relative humidity, and solar radiation) at six sites along a 400-km north-south transect of the Sierra Nevada foothills (1100–1200 m elevation) during the summer of 1992. They demonstrated that the anthropogenic influence on ozone abundance in the foothills is highly variable. At the three sites where east-west wind patterns are predominant (advecting air from the cities of the California Central Valley in the east during the day and from the sparsely populated high Sierra in the west at night), there was a strong correlation between wind direction and ozone concentrations. At these sites, there was a regular diurnal pattern with ozone concentrations peaking at 1500–1700 LT (LT, Pacific Standard Time) and reaching a minimum at 0700 LT. At the other three sites where north-south winds were predominant the diurnal variation in ozone was small. The sites with east-west wind patterns had higher peak ozone abundances and violated the 1-hour state ozone standard of 90 ppb up to 40% more often than the sites with predominantly north-south winds. While these correlations between wind direction and ozone suggest that plumes originating in the Central Valley have a strong

impact on Sierra Nevada air quality, a reliable quantitative description of the interactions between ozone and its controlling factors (meteorology and precursor compounds) remains elusive.

[4] The regular wind patterns observed by *Van Ooy and Carroll* [1995] suggest that observations from sites along the prevailing winds within the Sacramento Valley and Sierra Nevada might be effectively analyzed assuming Lagrangian transport to quantify the different factors controlling ozone concentrations within the Sacramento urban plume. Lagrangian analyses from aircraft and from pairs of ground stations located along the prevailing winds have been used to study photochemistry in Freiburg, Germany; Nashville, Tennessee; and the northwest Atlantic Ocean [*Daum et al.*, 2000; *Fehsenfeld et al.*, 1996; *Ryerson et al.*, 1998; *Volz-Thomas et al.*, 2000]. *Volz-Thomas et al.* [2000] used observations at two sites spaced by 10 km to constrain a Lagrangian analysis of the oxidation and dilution that occurs during transport of the Freiburg, Germany, urban plume. On a larger scale ($\approx$100 km), aircraft observations in the Nashville, Tennessee, urban plume were used to demonstrate that the factors limiting ozone production chemistry change from the hydrocarbon-limited regime in the urban core to nitrogen oxide limited regime as the plume evolves [*Daum et al.*, 2000]. Aircraft observations in a series of power plant plumes in the Nashville area constrain the chemical evolution and deposition from the plumes [*Ryerson et al.*, 1998, 2001]. Analysis by *Ryerson et al.* [1998, 2001] shows that ozone production on the first day following emission from power plants was not linear in NO_x emissions, with the ozone production per unit NO_x decreasing with increasing emission rates. On a yet larger spatial scale the North Atlantic Regional Experiment (NARE) followed the evolution of the aggregate plume originating in the cities of the eastern United States up to 1000 km into the northwest Atlantic Ocean [*Fehsenfeld et al.*, 1996, and references therein].

[5] In this paper, we develop a Lagrangian framework to interpret observations within the Sacramento urban plume. Taking advantage of the regular mesoscale meteorology, we describe the connection between observations within and just downwind of the Sacramento urban core and late afternoon observations at the University of California Blodgett Forest Research Station (UC-BFRS), a rural site in the Mountain Counties Air Basin, 75 km downwind (Figure 1). Using these observations and estimates of anthropogenic hydrocarbon emissions developed by CARB, we characterize the dilution and chemical oxidation of the Sacramento urban plume and compare these characteristics with observations in other urban plumes.

2. Experimental

2.1. University of California Blodgett Forest Research Station

[6] Observations were obtained from a 10-m walk-up tower installed near the UC-BFRS during the summer of 1997. The research site, an even-aged ponderosa pine plantation owned by Sierra Pacific Industries, lies $\sim$75 km NE of Sacramento (38.89525°N and 120.6328°W; 1315 m above sea level (asl)). Wind speed, wind direction, humidity, temperature, CO_2 concentration, ozone concentration, net and photosynthetically active radiation, and pressure were measured and recorded as half-hour averages [*Goldstein et al.*, 2000]. The ozone measurements were obtained using a Dasibi 1008-RS ozone analyzer. A three-dimensional sonic anemometer (ATI Electronics Inc.) was used for the wind direction and speed measurements.

[7] C_2–C_{10} hydrocarbons were measured during July 1997 by cryoconcentration of air samples followed by in situ gas chromatographic analysis (HP-6890) [*Lamanna and Goldstein*, 1999]. The sample inlet was $\sim$6 m above the forest canopy. Air was pulled at 8 L min^{-1} through 2 μm PTFE particulate filters and 10 m of tubing and was subsampled at 20 mL min^{-1} onto a graphitized carbon black and carbon molecular sieve preconcentration system packed in series and mounted in a cold block

(-80°C). After preconcentrating samples for 20 min it was rapidly heated to 250°C, flushing samples into PLOT Rt-Alumina and DB-WAX columns for separation and quantification by dual-flame ionization detectors. The experimental detection limit, precision, and accuracy for the compounds discussed in this paper are estimated to be 6–8 parts per trillion (ppt), 6%, and $\leq$7%, respectively [*Lamanna and Goldstein*, 1999].

[8] The site is powered by a diesel generator located $\sim$130 m to the northwest. During the day, westerlies of 3.5 m s^{-1} are strong enough that plumes from the generator were rarely observed. At night the winds were weaker, 1.2 m s^{-1}, and occasionally, short-duration plumes were observed. These data points were identified by the large concentrations of anthropogenic alkenes observed and were removed from the analysis.

2.2. Sacramento and Folsom, California

[9] The California Air Resources Board maintains several long-term monitoring sites within and surrounding the Sacramento urban core (Figure 1). These sites are primarily situated along Highways 50 and 80. As of 1998, there were 14 ozone monitors, seven NO and NO_y ($NO_y \equiv$ NO + NO_2 + HNO_3+ RO_2NO_2 + $RONO_2$ + $\ldots$) monitors, and five nonmethane hydrocarbons (NMHC, total hydrocarbons excluding CO and methane) monitors. Eight of the ozone and four of the NO_y monitors have been operating for more than 10 years. Ozone was measured by UV photometry. NO was measured by chemiluminescence, and NO_y was converted via molybdenum oxide converter to NO which was subsequently detected by chemiluminescence. Total NMHC were first separated from CO and methane via gas chromatography and then quantified using a flame ionization detector. These quantities are reported as 1-hour averages [*CARB*, 1999a]. The general instrument design and quality control protocols for these measurements were established by the U.S. Environmental Protection Agency and were recently summarized by *Demerjian* [2000].

[10] Speciated hydrocarbon samples were collected at the Natoma Street, Folsom (38.68389°N and 121.16361°W, 110 m elevation), and Del Paso Manor (DPM), California (38.614167°N and 121.366944°W, 5 m elevation), monitoring stations near Sacramento, California. Both sites are Photochemical Assessment Monitoring Stations (PAMS). The hydrocarbon samples were periodically collected and stored in polished stainless steel containers, analyzed using a gas chromatograph with flame ionization detector, and reported as 3-hour averages. The standard operating procedure for these measurements is described by *CARB* [1999b]. The detection limit, precision, and accuracy of these measurements are 1 ppb C, <15%, and ±10%, respectively (S. Roy, personal communication, 2001). PAMS measure the surface meteorology, ozone, nitrogen oxides, and speciated hydrocarbons. The PAMS 1997 speciated hydrocarbon and ozone measurements were obtained directly from *CARB* [1998a]. Photographs and more detailed description of these sites are available from *CARB* [2001b].

3. Regional Climate and Meteorology

3.1. Climate

[11] The Sacramento Valley has a Mediterranean climate. National Weather Service observations from 1980 to 1999 in Sacramento, California (Weather-Bureau-Army-Navy (WBAN) 23232), show that on average, only 4.4 cm (10% of the yearly total) of precipitation falls each dry season (May through September). The Sacramento Valley is rarely cloudy during the dry season. On average it experiences 95% of total possible sunlight and has 30% minimum (afternoon) relative humidity and 30.8°C daily maximum temperature [*National Climate Data Center* (*NCDC*), 2000b].

[12] The dry season climate is extremely consistent from year to year. Figures 2a–2d show the median and 1σ variance for monthly averaged climatic variable for data from 1980 to 1999.
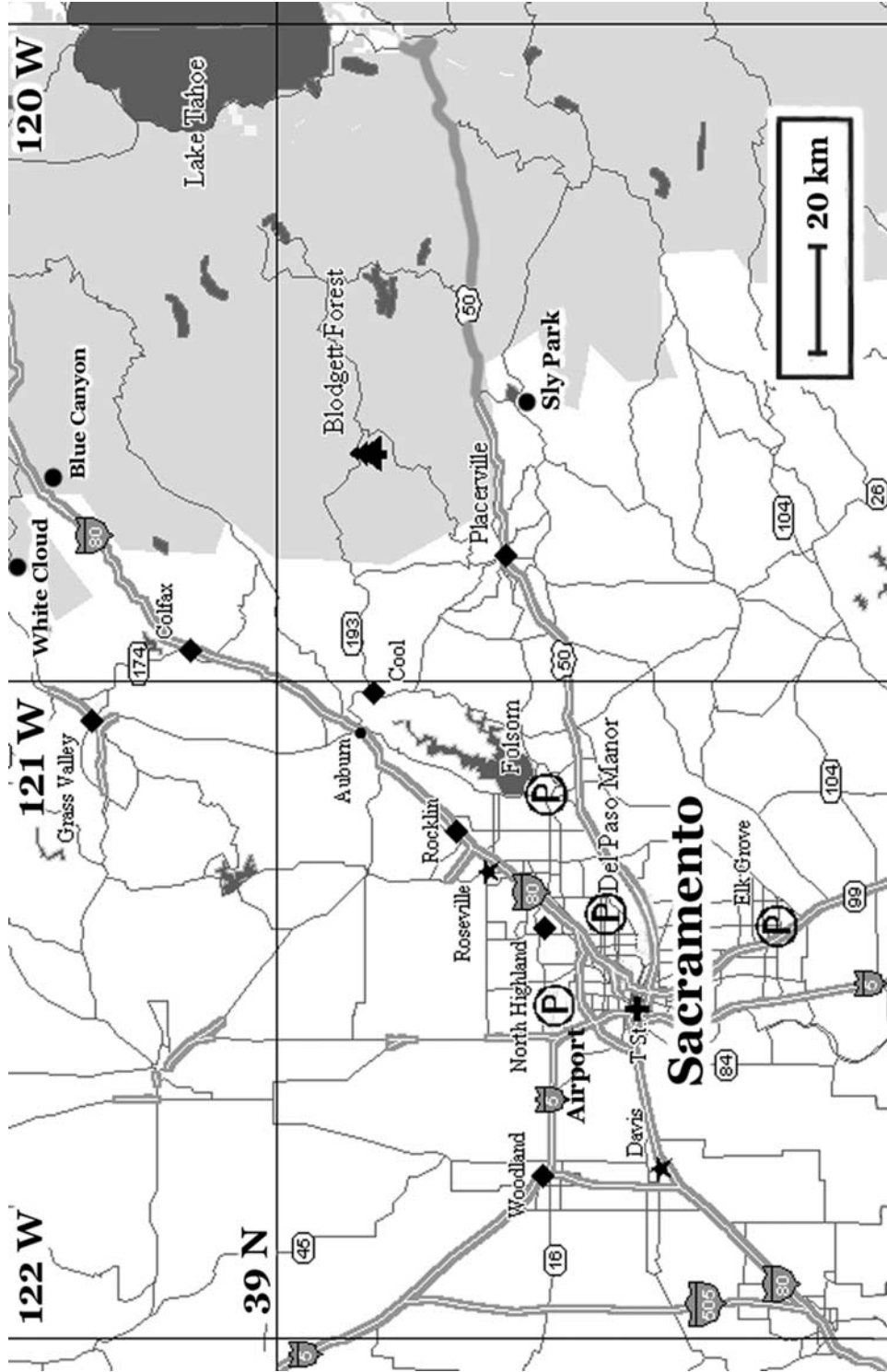
Figure 1. Major roads and 1998 California Air Resources Board (CARB) atmospheric sampling sites upwind of the Blodgett Forest Research Station. Circled P, Photochemical Assessment Monitoring Stations (PAMS); plus, colocated ozone, nitrogen oxide, and nonmethane hydrocarbon monitors; star, colocated ozone and nitrogen oxide monitors; diamonds, ozone monitors. Most observations used in this study were taken from the Blodgett Forest Research Station and the Folsom sampling site.
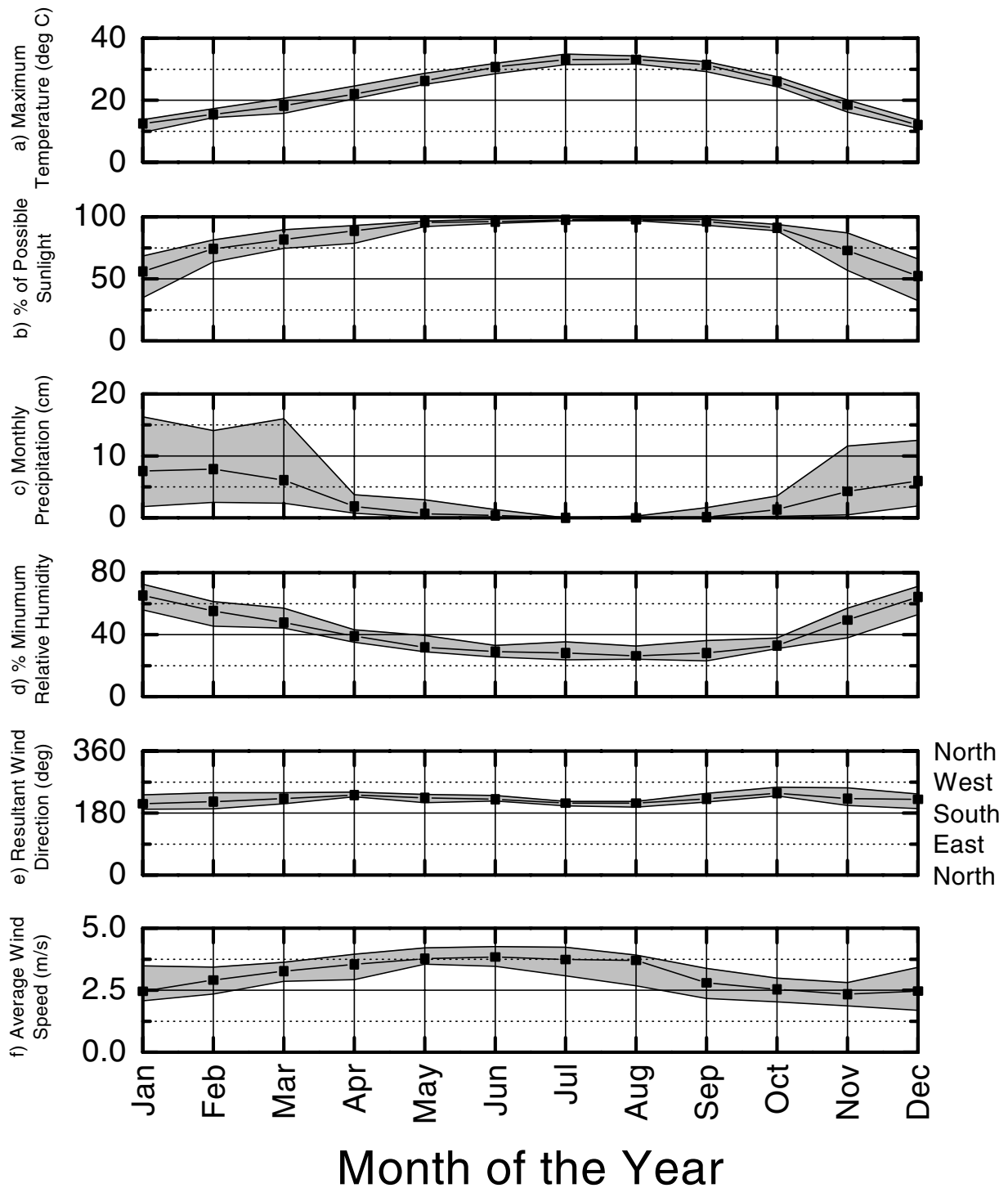
Figure 2. Monthly averaged observations at the Sacramento Executive Airport (WBAN 23232) demonstrate the interannual and intra-annual variance of climatological variables in the region from 1980 through 1999. The line with solid squares is the median of monthly means, while the gray swath denotes the 1σ variance. (a) Maximum daily temperature. (b) Percent of total possible hours of direct sunlight (no observations were available in 1998 and 1999). (c) Sum of monthly rainfall. (d) The lowest relative humidity recorded each day (typically a late afternoon observation). (e) Daily origin direction of 24-hour average of recorded winds (also called resultant wind direction). (f) The 24-hour average of recorded wind speeds.

[13] July 1997, the month when the measurements used in this paper were obtained, was climatically typical. The average maximum temperature during this period was 34.6°C [*U.S. Department of Commerce*, 1997], and the mean minimum relative humidity was 27%. At Blodgett Forest the average maximum daily temperature, 25°C, was cooler than Sacramento and was consistent with Blodgett Forest's higher elevation (5 m versus 1315 m). Photosynthetically active radiation measurements at Blodgett Forest
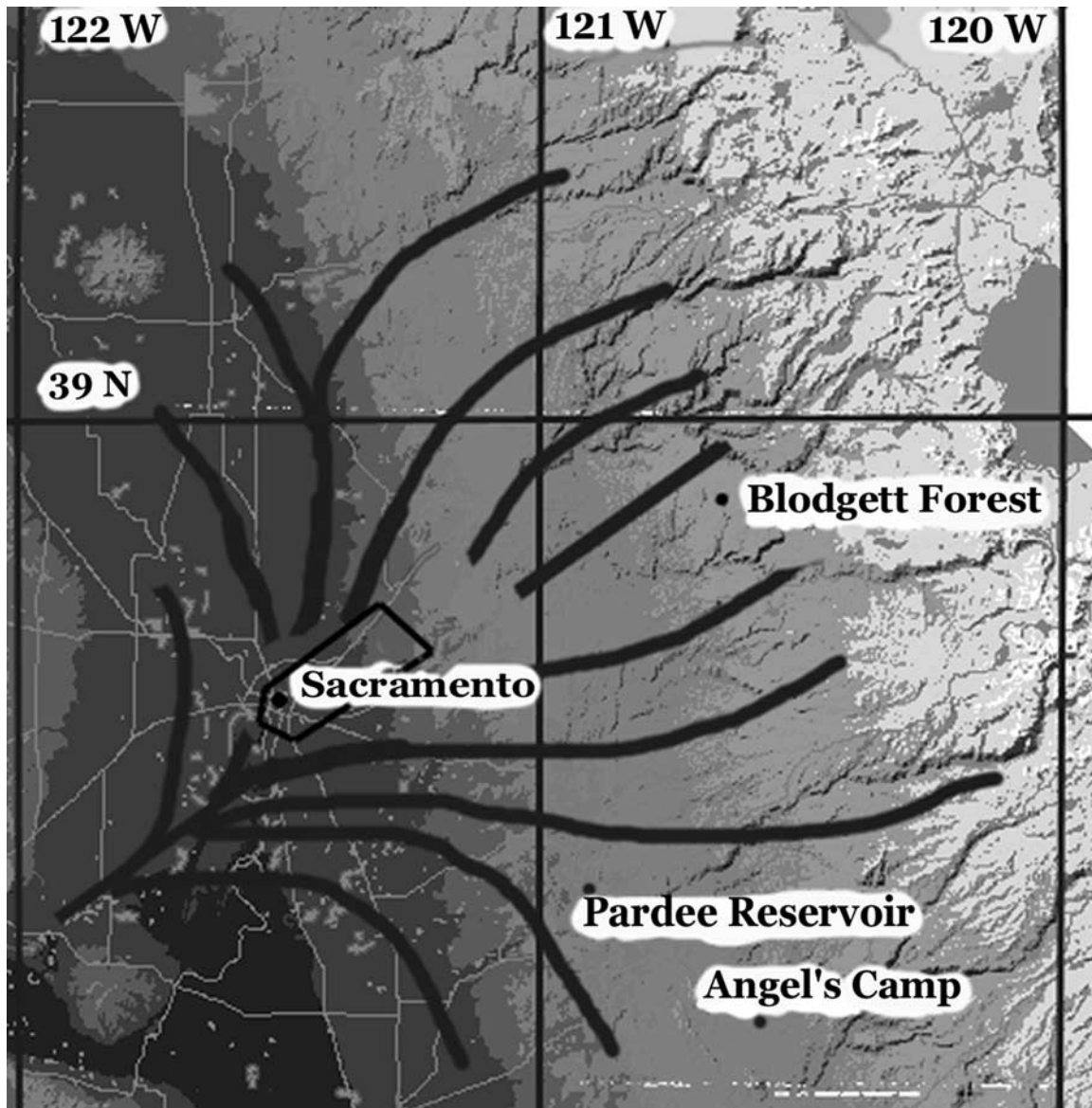
Figure 3. Elevation relief [*Sierra Nevada Ecosystem Project*, 2000] and overlaid dominant daytime summer winds in the California Sacramento Valley after *Hayes et al.* [1984]. The outline encircles the Sacramento urban core.

indicate that the site received 95% of the total possible sunlight. There was no precipitation recorded anywhere along the path between Sacramento and UC-BFRS.

3.2. Winds

[14] The dry season mesoscale winds in the foothills and midelevations of the western Sierra Nevada are dominated by east/west, upslope/downslope flow patterns. Figure 3 is an elevation relief map overlaid with the dominant daytime mesoscale summer wind pattern. Regular daytime winds result from the heating along the mountain slopes where warmed air, instead of rising directly upward, is channeled along the surface of the mountainside, drawing air out of the Sacramento Valley. At night the flow is reversed as cooling air descends back down the mountains. The dominant synoptic wind patterns reinforce the upslope mountain winds. A persistent east Pacific ridge off the west coast of North America and daily heating in California's Central Valley creates a pressure differential that drives marine air through the San Francisco Golden Gate and into the California Central Valley [*Seaman et al.*, 1995]. On approximately two thirds of summer

days, air masses of marine origin penetrate hundreds of kilometers into the Sacramento Valley and push northeast past Sacramento until finally flowing out of the Sacramento Valley basin and over the Sierra Nevada Mountains [*Hayes et al.*, 1984; *Zaremba and Carroll*, 1999].

[15] *Zaremba and Carroll* [1999] describe wind patterns in the Sacramento Valley observed during the summer of 1991. They note that regardless of the Sacramento Valley wind pattern the airflow at the Sly Park and White Cloud, California, observation stations east of Sacramento (Figure 1) was dominated by the mountain/valley wind patterns. In a similar study by the California Air Resource Board from 1974 to 1979, observations at the Blue Canyon Airport, 1609 m (Figure 1), located near the White Cloud observational site, demonstrated the regularity of the daytime upslope and nighttime downslope flow [*Hayes et al.*, 1984]. The Blue Canyon data suggest that at some sites the upslope/downslope winds persist year-round, although the daytime wind speeds slow by 50% during the wet season (November through March). The local winds observed at the Blodgett Forest Research Station during our July 1997 intensive were consistent with the dry season

upslope/downslope mesoscale flow [*Lamanna and Goldstein*, 1999]. The winds observed in Sacramento, California, during July 1997 were typical of the 20-year average.

3.3. Mixed Layer Height

[16] The mixed layer height throughout the Central Valley and Sierra Nevada mountains is low. In the summer throughout the Central Valley a stable layer (without inversion) often develops. This layer caps the mixing height in and around the Central Valley at ∼800 m despite surface temperatures exceeding 40°C. This is in contrast to typical continental mixed layer heights of 2−4 km for these conditions [*Seaman et al.*, 1995]. *Seaman et al.* [1995] conclude that the spatial variability of the mixed layer height is ∼400−800 m in the foothills and midelevation Sierra Nevada mountains on the basis of calculations using the nonhydrostatic MM5 mesoscale model constrained by observations on 6 August 1990. The observations were collected during the San Joaquin Valley Air Quality Study and Atmospheric Utility Signatures, Predictions, and Experiments Regional Modeling Adaptation Project (SARMAP) study of the California Central Valley meteorology and ozone. SARMAP included sites at Angel's Camp and Pardee Reservoir, where radiosondes characterized the vertical structure of the mixed layer height over the Sierra Nevada. Both sites are south of Sacramento (Figure 3) and are ∼500 m asl.

[17] The spatial variability of the mixed layer height reported by *Seaman et al.* [1995] is based on an analysis of a single day, and consequently, it might not capture the temporal variability of boundary layer height in the region. We estimate an upper bound on the temporal variability of the mixed layer height using the variability of 1-hour averaged NO_y concentrations at a single location within the Sacramento urban core. In Sacramento the urban core NO_y concentrations are primarily determined by the flux of NO (primarily from vehicle emissions) into the mixed layer within that hour since the surface winds, 4.2 m s^{-1} [*U.S. Department of Commerce*, 1997], are nearly always sufficiently rapid to prevent stagnation within the urban core, and the NO_y concentrations outside the urban core are small (3 ppb) compared with those observed within the urban core (20 ppb). Statistics of variability were constructed using July 1997 one-hour average observations of NO_y at the CARB T Street, Sacramento, sampling site. For example, the July 1997 observations of NO_y from 1000 to 1100 LT have a median, mean, and 1σ variance of 18, 20, and 9 ppb, respectively. The daily variance in the NO_y concentration (i.e., 50% at 1000 LT) is equal to the daily variation in the boundary layer height if the source distribution at this hour of the day is nearly constant. Because the NO_y source is primarily vehicular traffic, we expect that it is nearly constant each day. However, to the extent that the observed NO_y variance is due to changes in emission patterns, such as might be associated with weekday/weekend differences in motor vehicle traffic (and assuming these changes have no covariance with the boundary layer height), then the actual temporal variability in the boundary layer height is likely <50%.

4. Anthropogenic Emissions in the Sacramento Region

[18] The dominant source of photoreactive anthropogenic emissions in the Sacramento region is vehicular traffic. The California Air Resources Board estimates that 93% of the 127 Mg of NO_2 d^{-1} of nitrogen oxides released and 61% of the 147 Mg d^{-1} of reactive hydrocarbons released into the Sacramento region (Placer, El Dorado, and Sacramento counties) in 1996 were from mobile sources [*CARB*, 1998b]. There are no major industrial point sources (sources >0.25 Mg d^{-1}) of ozone precursors in a corridor bounded by Highways 50 and 80 to the north and south, by Sacramento to the west, and by the UC-BFRS to the east. CARB has catalogued seven small point sources of reactive hydrocarbons and one of nitrogen oxides within 100 km of the UC-BFRS. These stationary point sources contribute 5% of the nitrogen oxides and 26% of the reactive anthropogenic hydrocarbons emitted in the Sacramento region. Dispersed area-wide sources, e.g., solvent evaporation and residential fuel combustion, contribute the remaining 2% and 13% of the anthropogenic NO_x and hydrocarbon emissions, respectively.

[19] In the midelevation Sierra Nevada (above ∼500 m and east of the town of Folsom), anthropogenic emissions are small compared with those of Sacramento. Total nitrogen oxide and reactive hydrocarbon emissions in portions of the Placer and El Dorado counties (the counties downwind of Sacramento) located in the Mountain Counties Air Basin are 17 and 25 Mg d^{-1}, respectively (15% of the total Sacramento area emissions) [*CARB*, 1998b]. As in the urban core, the dominant source (98% for nitrogen oxides and 60% for hydrocarbons) of these downwind emissions is motor vehicle traffic (i.e., Highways 50 and 80). We note that these highways diverge away from a line connecting the Sacramento urban core and the UC-BFRS. Liquid propane gas (LPG) (90% propane, 5% butanes, and 5% other compounds) is used for residential heating and cooking in this region. CARB has estimated the hydrocarbon emissions associated with LPG use for heating during the winter months to be 0.01 Mg d^{-1} [*CARB*, 1997]. Since heating is the dominant use of LPG, the emissions during the summer months are expected to be smaller than this estimate. This is <0.1% of the CARB estimates of hydrocarbon emissions from all sources in the region between Folsom and UC-BFRS.

[20] Observations of nitrogen oxides and nonmethane hydrocarbons in the region are consistent with the assumption that anthropogenic ozone precursor concentrations are strongly concentrated in Sacramento's urban core. Daytime NO_y concentrations are highest in downtown Sacramento. Simultaneous measurements of NO_y at other sampling sites surrounding downtown (Elk Grove, Davis, and Folsom) are 50−75% lower. One-hour averaged NO_y and total NMHC measurements at the T Street sampling site in downtown Sacramento were strongly correlated ($r^2 = 0.74$) during the 1997 and 1998 dry seasons, consistent with a colocated or common source for emissions of both species.

[21] The spatial distribution of anthropogenic emissions is also consistent with the distribution of population in the region. The 40-km-long urban core of Sacramento, California (population 1,531,963 in 1998) [*U.S. Census Bureau*, 1998] begins at the intersection of Highways 50 and 80 (Figure 1), accounts for 75% of the region's population, and has a relatively uniform population distribution [*U.S. Census Bureau*, 1995]. The outline in Figure 3 encircles this area. Outside the urban core the population density is typically <100 people km^{-2} and always <700 people km^{-2}. For comparison, peak urban core densities approach 5000 people km^{-2}, and the population density of the average census tract within the urban boundary shown in Figure 3 is 1900 people km^{-2}.

5. Observational Constraints on Transport, Oxidation, and Emissions in the Sacramento Urban Plume

[22] The description of the site, meteorology, and regional emissions given in sections 2 through 4 provide context for interpretation of anthropogenic hydrocarbons measurements in Sacramento, Folsom, and the UC-BFRS. We describe the evolution of the Sacramento urban plume within and downwind of the urban core using observations of anthropogenic hydrocarbon concentrations and assuming a constant dilution, oxidation, and emission rate as the urban plume mixes with a uniform background. The Lagrangian model we develop builds on work by *Calvert* [1976] and *McKeen and Liu* [1993]. Recent analyses using this approach to quantify the average abundance of OH on large spatial scales include the experiments of *Satsumabayashi et al.* [1992] in Tokyo, Japan, and the Schauinsland Ozone Precursor Experiment (SLOPE96) by *Volz-Thomas et al.* [2000].
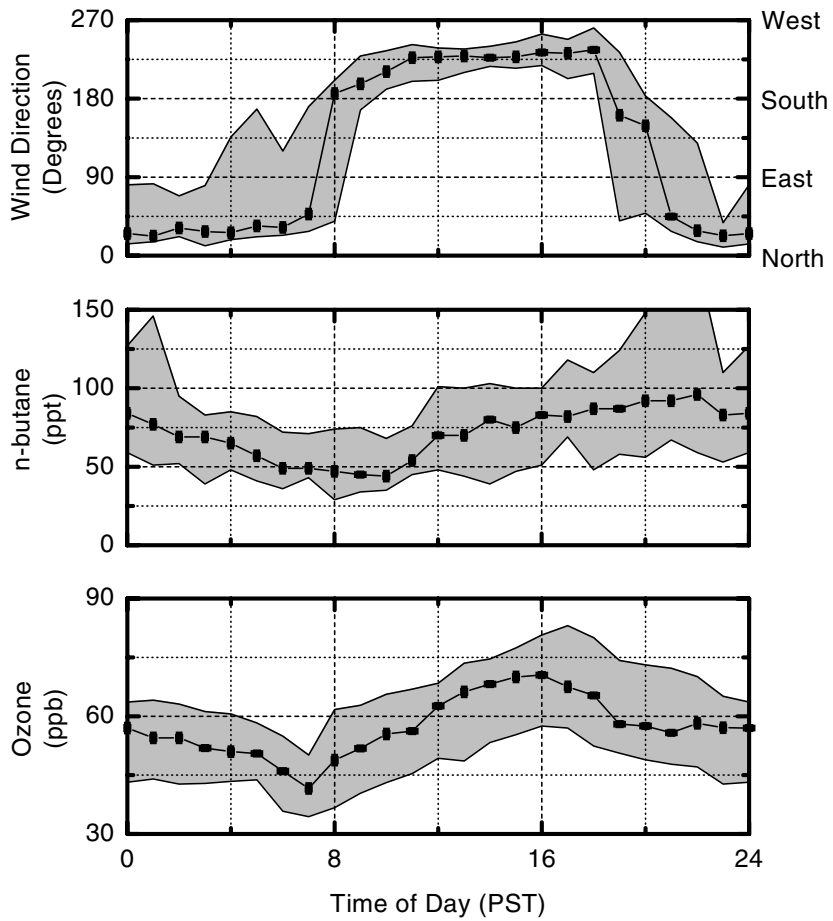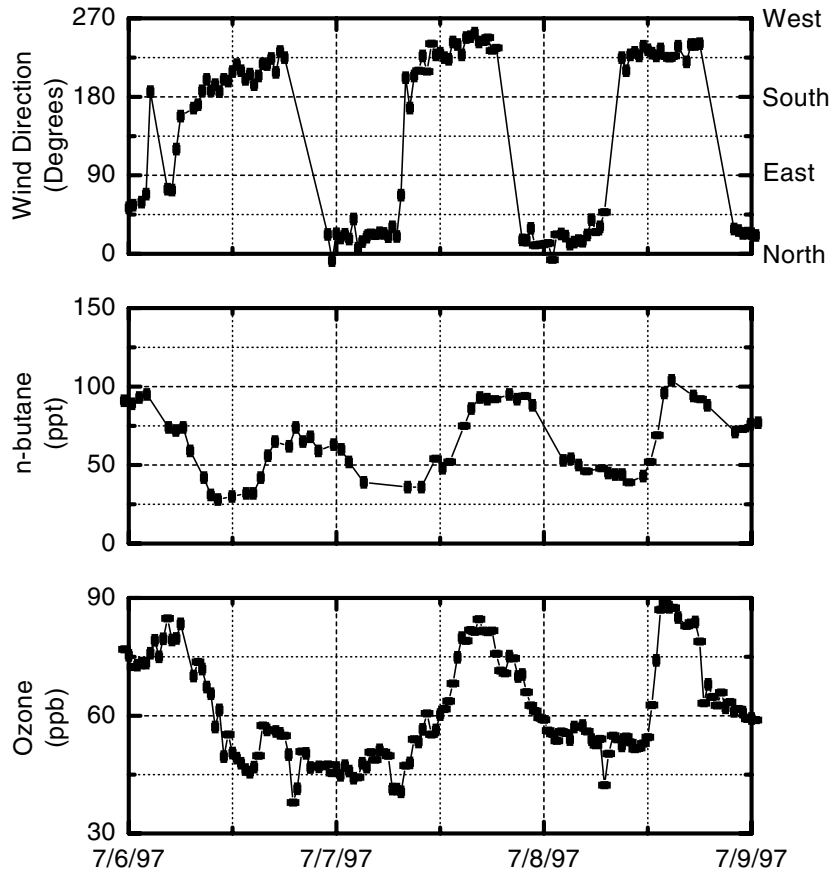
[23] Following an air parcel released from Sacramento in a Lagrangian sense, the temporal evolution of a compound X can be described by

$$d[X]/dt = \text{photochemical production} - \text{photochemical loss}$$
$$- \text{deposition} + \text{emissions} - \text{entrainment of background air.} \quad (1)$$

For the hydrocarbons used in this analysis (propane, acetylene, n-butane, n-pentane, isopentane, and toluene), photochemical production and deposition are negligible. We assume that the dominant photochemical loss mechanism for these species is oxidation by the hydroxy radical with rate constants, $k_{OH + X}$, from *Atkinson* [1994, 1997]. With these assumptions, (1) simplifies to

$$d[X]/dt = -\text{entrainment of background air}$$
$$- \text{photochemical loss} + \text{emissions}$$
$$= -K([X] - [X]_b) - k_{OH+X}[OH][X] + E_x, \quad (2)$$

where $[X]$ is the instantaneous hydrocarbon concentration in the Sacramento plume, $[X]_b$ is the regional background concentration of the hydrocarbon, K is the rate of entrainment of background air into the plume, $k_{OH + X}$ is the rate constant for the reaction of compound x with OH, and E_x is the rate of emission of hydrocarbon x into the plume.

[24] Integrating (2) numerically, we solve for the concentration, $[X]$, as a function of time during the transport of the Sacramento plume into the foothills. Constraints on the solution are derived from observations during July 1997. The quantities we derive are K and [OH]. The values for these parameters are determined by nonlinear least squares fit of the model to measurements of six different hydrocarbons in Folsom and UC-BFRS as described below. We also investigate the sensitivity of our results to hydrocarbon emission rates downwind of the Sacramento urban core and find that they are likely <5% of the urban emissions.

5.1. Hydrocarbon Concentrations ($[X]$, $[X]_b$) at the UC-BFRS

[25] The strong diurnal cycle of wind direction dominates the diurnal cycle of anthropogenic hydrocarbon concentrations at Blodgett Forest. Figure 4a shows observations of wind direction, n-butane, and ozone from 6 to 9 July 1997. Figure 4b shows the median and 1σ variance of the data for the month of July 1997 versus time of day. The variance in hydrocarbon mixing ratio at the end of the downslope flow period (0800–1000 LT) is about half the variance of the afternoon data. The median observation and the lowest observation at this time are nearly identical. These facts support the notion that the downslope flow brings air to Blodgett Forest, and by extension throughout the midelevations of the Sierra, that is representative of a regionally uniform background. After the morning flow reversal the upslope flow brings the plume from the Sacramento Valley into the foothills. There is initially little change in the abundance of anthropogenic compounds at the UC-BFRS as the clean air that traveled farther down the mountain washes back up. Starting around noon, concentrations rise through the afternoon and evening. The wind flow reverses between 1800 and 2000 LT, and concentrations reach a maximum at 2200 LT. We focus on characterizing the peak impact of the urban plume at the UC-BFRS by examining data just before the wind reversal, 1600–1800 LT (Table 1 shows observations for each day in July 1997). On 5 out of 20 days for which we have data both in the morning and late afternoon, we did not observe the urban plume at the UC-BFRS. On these days the late afternoon acetylene concentra-

tions and those of other long-lived hydrocarbons did not rise above the morning background concentrations. We omit these 5 days from our analysis. The hydrocarbon concentrations, $[X]$, used as input to our model are the median of the remaining observations and are summarized in Table 2. The values presented here and throughout this paper are nonparametric statistics, e.g., medians and their 1σ confidence limits [*Neave and Worthington*, 1988], and include the effects of instrument precision as well as the variability of the atmospheric concentrations due to fluctuations in transport, OH concentrations, and emissions. We use the total uncertainty of these observations (instrumental precision, instrumental accuracy, and atmospheric variability) to weight observations used in the least squares regression.

[26] In the morning at the end of the downslope flow, observations of anthropogenic hydrocarbons at Blodgett Forest are comparable to the lowest values observed in clean continental air masses (Table 3 shows observations for each day in July 1997; Table 4 provides an average over the month). For convenience of statistical comparison to data sets with less regular meteorology the value marking the upper bound of the lowest 16th percentile (data below the 1σ variance) of the entire July 1997 record of hydrocarbon measurements at Blodgett is also indicated in Table 4 for six anthropogenic hydrocarbons. With the exception of ethane the 16th percentile and median concentrations are indistinguishable. Additionally, one third of the lowest 16% of the observed data are measurements within ±1 hour of 0900 LT. One half of these observations are within ±2 hours. For ethane the 200-ppt difference between the morning and 16th percentile concentrations is due to the seasonal cycle in the ethane concentration, and most of the 16th percentile data was observed during the last week of July.

[27] Table 4 also includes the hydrocarbon measurements at other sites classified as background. Hydrocarbon concentrations at the end of the period of downslope flow at Blodgett Forest are comparable to the measurements made nearby in the free troposphere over San Jose, California, in 1991 during the Pacific Exploratory Mission West A [*Blake et al.*, 1996]. They are also comparable to the lowest 10th–20th percentiles of observations at Harvard Forest, Massachusetts [*Goldstein et al.*, 1995], which *Moody et al.* [1998] suggest are representative of a large-scale regional background originating at high altitudes over rural Canada. The three midlatitude sites, San Jose, Blodgett Forest, and Harvard Forest, have substantially higher concentrations of anthropogenic hydrocarbons than do sites that are at latitudes remote from populated source regions. With the exception of ethane, concentrations of hydrocarbons in the remote Northern Forests near Fraserdale, Canada [*Jobson et al.*, 1994], are typically a factor of 3 lower than Blodgett Forest at its cleanest in the summer. Concentrations observed at Mauna Loa, Hawaii [*Greenberg et al.*, 1996], during free tropospheric flow are nearly 2 orders of magnitude lower than observed at Blodgett Forest, as might be expected on the basis of its distance from continental sources.

[28] The background concentrations of ethane and acetylene varied over the month-long experiment. The trend in background hydrocarbon mixing ratios at the UC-BFRS were quantitatively similar to the seasonal trends observed at Harvard Forest, Massachusetts, where *Goldstein et al.* [1995] showed that the variations were largely driven by the seasonal cycle in OH abundance and the compound's lifetime with respect to OH. We observed decreases from 1 July to 1 August of 38% for ethane and 8% for acetylene. No seasonal trend for propane was observed. Concentrations of the short-lived hydrocarbons (e.g., n-butane, n-pentane, isopentane, and isobutane) did not change significantly during this period. *Goldstein et al.* [1995] showed that at Harvard Forest these

Figure 4. (opposite) Observations of wind direction, n-butane, and ozone at Blodgett Forest. (a) Time series of half-hour averages from 6 to 9 July 1997. (b) Median ±1σ observations during July 1997. PST, Pacific Standard Time.

Table 1. Median of the Late Afternoon (1600–1800 LT) Anthropogenic Hydrocarbon Mixing Ratios at the UC-BFRS[a]

Day	Propane	Acetylene	n-Butane	n-Pentane	Isopentane	Toluene
4 July	389.5	210.5	101.0	74.0	135.0	66.0
5 July	-	-	-	-	-	-
6 July	264.0	103.0	56.0	38.0	60.0	28.0
7 July	352.5	234.5	89.5	67.5	135.0	61.0
8 July	-	-	-	-	-	-
9 July	392.0	236.5	82.0	67.0	-	64.0
10 July	281.5	160.0	53.0	40.0	-	37.5
11 July	196.0	121.0	45.0	29.0	-	20.0
12 July	-	-	-	-	-	-
13 July	331.0	257.0	90.0	59.0	150.0	56.0
14 July	412.0	265.0	118.0	67.0	170.0	43.0
15 July	243.5	187.5	63.5	34.0	85.0	25.0
16 July	331.5	205.5	90.0	44.5	120.0	32.0
17 July	692.0	321.0	140.0	84.0	200.0	68.0
18 July	310.0	145.0	72.0	40.0	45.0	28.0
19 July	407.5	220.5	89.0	60.0	145.0	42.5
20 July	419.0	261.0	95.0	57.0	160.0	44.0
21 July	373.0	263.0	100.0	57.0	150.0	34.0
22 July	263.5	173.5	57.5	32.0	80.0	33.0
23 July	321.0	143.0	83.0	40.0	120.0	31.0
24 July	-	-	-	-	-	-
25 July	-	-	-	-	-	-
26 July	300.0	170.5	53.5	33.5	85.0	29.0
27 July	-	-	-	-	-	-
28 July	135.5	88.0	29.0	20.5	60.0	15.0
29 July	739.0	160.0	214.0	54.0	170.0	23.0
30 July	271.5	202.0	66.5	35.0	95.0	31.0
31 July	248.0	177.0	47.0	26.0	65.0	-
1 Aug.	211.0	114.0	69.5	29.0	65.0	16.0
2 Aug.	-	-	-	-	-	-

[a] Mixing ratios are given in parts per trillion.

compounds were already in a photostationary state with the higher summertime OH by the beginning of July. We use the median of the 0800–1000 LT measurements as the background concentrations, $[X]_b$, in our analysis.

5.2. Hydrocarbon Concentrations at Folsom, California

[29] The Natoma Street, Folsom, sampling site is located on the eastern, downwind edge of the urban core (30 km from downtown Sacramento). We use observations at this site to define the initial conditions for solution of (2). During the day, when the winds are from the west, the site should effectively integrate the influence of emissions from the urban core. Figure 5a shows the observations of n-butane at Folsom from 16 to 20 July 1997, and Figure 5b shows the ensemble of data for July 1997 as a function of time of day.

There is a small day/night difference in the Folsom hydrocarbon concentrations, with nighttime concentrations 20% higher than daytime. The median daytime local wind speed at the UC-BFRS suggests that air arriving at 1600–1800 LT passed Folsom ~5 hours earlier. Ideally, we would restrict our analysis to data collected in this time window; however, in Folsom, there were only eight observations between 1100 and 1300 LT during July 1997. This is too small a sample to be considered representative of the July 1997 average. As an approximation, we use the median of all daytime (0800–1900 LT) observations in July 1997 to characterize the air in Folsom that arrives at the UC-BFRS 5 hours later. The dominant source of uncertainty in characterizing the hydrocarbon concentration at Folsom is the instrument precision: ~200–500 ppt or 30–90% of the median daytime concentration

Table 2. Median of the July 1997 Del Paso Manor, Folsom, and UC-BFRS Hydrocarbon Observations and RMS of the 1σ Observational Uncertainty and the Instrumental Accuracy Used in This Analysis[a]

Compound	Del Paso Manor, 0800–1900 LT		Folsom, 0800–1900 LT		UC-BFRS, 1600–1800 LT		UC-BFRS Least Squares Fit Concentration[b]
	Median Concentration	σ	Median Concentration	σ	Median Concentration	σ	
Ethane	1100	167	1050	129	1000	130	940
Propane	500	97	600	102	353	48	278
Acetylene	550	207	600	96	211	41	251
n-butane	300	48	275	37	90	9	80
Isobutane	<DL[c]	-	<DL	-	50	10	-
n-pentane	280	41	220	30	57	10	47
Isopentane	1020	252	800	128	135	18	154
Toluene	471	79	329	39	40	13	45

[a] Hydrocarbon observations given in parts per trillion. Observational uncertainty includes both instrument precision and atmospheric variability.
[b] Late afternoon UC-BFRS hydrocarbon mixing ratios calculated by the nonlinear least squares fit.
[c] The term <DL indicates that the concentration was below the instrumental detection limit of 250 ppt.

Table 3. Median of Morning (0800–1000 LT) Anthropogenic Hydrocarbon Mixing Ratios at the UC-BFRS ($[X]_b$)[a]

Day	Propane	Acetylene	n-Butane	n-Pentane	Isopentane	Toluene
4 July	157.0	121.0	38.0	35.0	30.0	30.0
5 July	-	-	-	-	-	34.0
6 July	166.0	129.5	36.5	32.0	45.0	31.0
7 July	164.0	122.5	36.0	33.0	50.0	35.5
8 July	184.0	139.0	44.0	35.0	60.0	45.0
9 July	209.0	171.0	46.5	39.0	75.0	50.5
10 July	193.5	149.0	38.0	30.5	-	30.5
11 July	202.0	131.0	39.0	26.0	-	26.0
12 July	-	-	-	-	-	-
13 July	142.0	141.0	36.0	24.0	60.0	36.0
14 July	190.0	135.0	49.0	28.0	50.0	29.0
15 July	280.5	210.5	65.0	35.0	85.0	24.5
16 July	355.0	174.0	74.0	25.0	50.0	13.5
17 July	439.0	207.0	83.0	39.0	90.0	30.0
18 July	137.5	80.0	24.0	70.0	40.0	17.0
19 July	-	-	-	-	-	-
20 July	110.5	101.0	27.5	22.0	30.0	21.0
21 July	219.0	172.0	53.0	37.0	80.0	31.0
22 July	440.0	201.0	88.5	40.5	95.0	22.0
23 July	212.0	134.0	52.0	23.0	50.0	14.0
24 July	1132.0	418.0	290.0	170.0	350.0	125.5
25 July	286.0	121.0	49.0	28.0	50.0	20.5
26 July	-	-	-	-	-	-
27 July	223.5	152.5	45.0	27.0	60.0	7.0
28 July	115.0	76.0	24.0	17.0	20.0	9.0
29 July	190.0	117.0	34.5	26.0	55.0	19.0
30 July	-	-	-	-	-	-
31 July	356.0	168.0	59.0	29.0	70.0	22.0
1 Aug.	282.5	176.0	47.0	23.0	55.0	14.0
2 Aug.	190.0	101.5	30.0	17.0	30.0	10.0

[a] Mixing ratios are given in parts per trillion.

for each sample. The median and variance is summarized in Table 2.

### 5.3. Hydrocarbon Emission Rates Downwind of Folsom (E_x)

[30] The majority of the anthropogenic hydrocarbons emitted downwind of Folsom as the urban plume is advected toward UC-BFRS are associated with vehicular traffic. Consequently, the six compounds used in this analysis are expected to be emitted in fixed ratios characteristic of California's vehicular traffic. In our analysis we constrain the relative emission rates using observations from the Sacramento, Del Paso Manor, sampling site. This constraint reduces the number of unknown emission rates in (2) from 6 to 1. The DPM site is located within the urban core and lies 14 km downwind of downtown Sacramento. We use the median of all daytime (0800–1900 LT) July

1997 observations. The median and variance are summarized in Table 2. We assume that these concentrations are controlled solely by a combination of emissions and mixing with a regional background. We fix the emission ratios to an estimate of the concentrations that would be observed if the background were zero by subtracting the regional background from the measured concentrations. Relative to acetylene, the emission rates are 0.71, 0.61, 0.6, 2.3, and 1.1 for propane, n-butane, n-pentane, isopentane, and toluene, respectively. With the exception of the very high concentrations of propane observed in the Sacramento region, these ratios are similar to 1997 observations of light-duty vehicle mass emission rates in the San Francisco Bay Area (relative to acetylene, 0.03, 0.44, 0.42, 1.7, and 1.2 for propane, n-butane, n-pentane, isopentane, and toluene, respectively) [Kirchstetter et al., 1999].

Table 4. Median of the July Observations in the Morning (0800–1000 LT) at the UC-BFRS and Background Mixing Ratios of Trace Gases for Several Sites[a]

Compound	Blodgett Forest, July 1997, 0800–1000 LT	Blodgett Forest, July 1997, 16th Percentile	San Jose, July 1993, 10th Percentile	Harvard Forest, July 1993, 10th Percentile	Fraserdale, Summer 1990–1994 Mean	Mauna Loa, Summer 1992 Median of the Downslope Flow
Ethane	932	773	844	858	820	429
Propane	202	212	224	208	78	17
Acetylene	139	133	153	127	75	29
n-butane	45	45	45	75	15	1
Isobutane	20	21	46	34	7	0.3
n-pentane	29	30	40	41	13	0.5
Isopentane	55	50	16	-	8	-
Toluene	25	27	<5	-	-	-

[a] Observations given in parts per trillion. The mixing ratios listed from sites other than the UC-BFRS are those identified by the authors as background. Blodgett Forest from *Lamanna and Goldstein* [1999]; San Jose, California, from *Blake et al.* [1996]; Harvard Forest, Massachusetts, from *Goldstein et al.* [1995]; Fraserdale, Canada, from *Jobson et al.* [1994]; and Mauna Loa, Hawaii, from *Greenberg et al.* [1996].
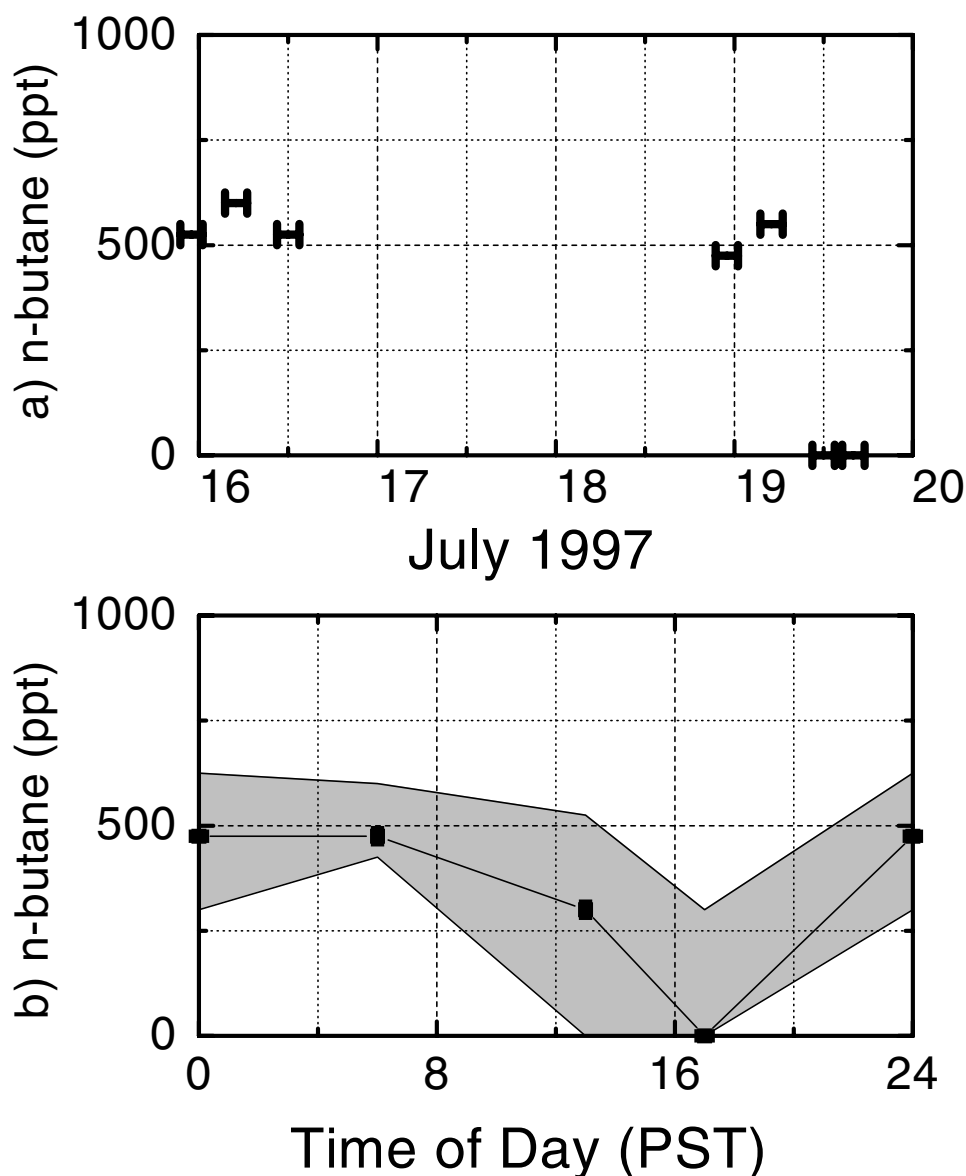
Figure 5. Observations of *n*-butane (values given in parts per trillion) in Folsom, California (just downwind of the urban core). (a) Time series of 3-hour averages of *n*-butane from 16 to 20 July 1997. (b) Median ±1σ observations during July 1997.

[31] The CARB emissions inventory suggests total emissions downwind of Folsom could be as high as 15% of emissions in the urban source region of the Sacramento plume. This is likely an upper bound to the influence of emissions downwind of Folsom on concentrations observed at UC-BFRS since the majority of these emissions (i.e., Highways 50 and 80) are not located along a straight line transect between Folsom and the UC-BFRS. In the model we estimate E_x at 7.5% of the urban emissions. For acetylene the emissions in Sacramento are estimated to be 410 ppt h^{-1} and those downwind of Folsom to be 31 ppt h^{-1} (7.5% of 410 ppt h^{-1}). We estimate the uncertainty in the emissions downwind of Folsom to be ±100%.

6. Results and Discussion

[32] An estimate of the dilution and oxidation rates along the path from Folsom to the UC-BFRS can be obtained using propane and toluene observations. To first order, propane concentrations are insensitive to the presence of OH since the propane lifetime is long (10 days) compared to the transit time of a few hours from Folsom to UC-BFRS. The effective decay constant for propane is approximately equal to the constant describing dilution: $K \approx -(1/5)$ $\ln(([X] - [X]_b)/([X]_o - [X]_b))$ h^{-1}. Solving for K using the propane data, $[X] = 353$, $[X]_b = 202$, and $[X]_0 = 600$ ppt, from Table 2 gives $K = 0.2$ h^{-1}. The toluene lifetime to reaction with OH is ∼1.9 days. The observed background adjusted decay rate for toluene, $-(1/5)$ $\ln(([X] - [X]_b)/([X]_o - [X]_b))$ h^{-1} is 0.6 h^{-1}. The difference between the two decay rates can be used to infer ∼1.3 × 10^7 molecules cm^{-3} of OH.

[33] A more precise estimate can be arrived at using all of the data as input to a nonlinear least squares optimization of the parameters K and [OH] in the model described by (2). The constraints derived above, $[X_{t=0}]$, $[X]_b$, E_x, $[X]$, and a transit time of 5 hours were used as input to the model, which was numerically integrated to calculate the concentration $[X]$ of each compound at 1700 LT at UC-BFRS (Table 2). The measured concentration of each of the six compounds at the UC-BFRS, $[X]$, was weighted by the inverse square of the

parametric addition of the uncertainty from atmospheric variance and the instrumental accuracy (Table 2). The nonlinear least squares minimization routine described by *Bevington* [1969] was used to optimize the parameters K and [OH]. The optimized values are $K = 0.23$ (± 0.07) h^{-1} and [OH] $= 1.1$ (± 0.4) $\times 10^7$ molecules cm^{-3} for $E_{acetylene} = 0$ ppt h^{-1} (reduced $\chi^2 = 1.6$). We varied $E_{acetylene}$ from 0 to 20 ppt h^{-1}. At $E_{acetylene} = 20$ ppt h^{-1} the reduced χ^2 is increased by 50% from its optimum value at $E = 0$. We take this condition to be an upper limit on the amount of emissions that could be contributed from sources downwind of Folsom. While this number is smaller than the 31 ppt h^{-1} estimated by the CARB, it is reasonable since the bulk of the anthropogenic emissions occurs along Highways 50 and 80, which are to the south and north, respectively, of the straight line transect between Folsom and the UC-BFRS. At $E_{acetylene} = 20$ ppt h^{-1}, $K = 0.28$ (± 0.09) h^{-1}, and [OH] $= 2$ (± 0.6) $\times 10^7$ molecules cm^{-3}.

[34] The late afternoon mixing ratios produced by the fitting procedure using $E_{acetylene} = 0$ are shown in Table 2. Given the uncertainties in the input data and the simplifications of a 1-day model, the fit does a reasonable job of reproducing the late afternoon UC-BFRS measurements. The fitted parameters are strongly anticorrelated ($r^2 = 0.87$) with an increase in the dilution rate offset by a compensating decrease in estimated [OH] and vice versa. Uncertainties in the initial conditions at Folsom, in the ratio of emissions, and in the background concentrations were investigated parametrically. Combining all of these uncertainties by RMS increases the uncertainty in K and [OH] by 20%. The uncertainty in the transit time of 5 hours is estimated to be ± 1 hour. The dilution rate and average OH concentration scale inversely with the transit time.

6.1. Dilution

[35] The best estimate dilution rate we derive for the Sacramento urban plume, 0.23 (± 0.09) h^{-1}, is similar to those observed in other plumes of comparable spatial scale. While the dilution of individual plumes is determined by local topographical and meteorological considerations, comparison of the Sacramento urban plume with others provides context for our results. For example, over a 130-km transport we estimate that the Toronto urban plume was diluted at an average rate of 0.1 h^{-1} on the basis of acetylene and wind speed data presented by *Lin et al.* [1996]. The Nashville, Tennessee, urban plume diffused into the background at a rate of 0.20–0.22 h^{-1} on 18 July 1995 on the basis of aircraft carbon monoxide measurements that sampled as far as 80 km downwind [*Nunnermacker et al.*, 1998]. *Lin et al.* [1996] suggest that ~50% of the Toronto plume dilution is due to horizontal mixing. The estimate that dilution is affected approximately equally by vertical and horizontal components is consistent with the observed Nashville power plant plume vertical venting rate of 0.10 (± 0.02) h^{-1} [*Ryerson et al.*, 1998; *Sillman*, 2000]. As the majority of the Folsom hydrocarbon observations were made after the morning breakup of the nocturnal boundary layer, we expect that the 0.23 h^{-1} dilution rate we infer includes both vertical venting and horizontal diffusion but not the mixing associated with morning increase in the boundary layer height. On a smaller scale (8 km and 90-min transit), *Kalthoff et al.* [2000] estimate the Freiburg, Germany, plume dilution rate to be an order of magnitude higher (1.5 h^{-1}) during morning hours of the SLOPE96 experiments using SF_6 as an inert tracer released 2–4 km upwind of the Grosses Tal valley inlet. *Fiedler et al.* [2000] and *Kalthoff et al.* [2000] note that the tracer was not homogeneously distributed at the valley inlet and attribute the unusually strong dilution rate to a combination of the morning evolution of the mixed layer height (0.44 h^{-1}), flow splitting between multiple valleys (0.34 h^{-1}), mountain venting, and homogenization of the tracer throughout the valley. We obtained another perspective on the dilution of the Sacramento urban plume during July 1997 using the Hysplit trajectory/dispersion model developed by the National Oceanic and Atmos-

pheric Administration (NOAA) and the Australian Bureau of Meteorology [*NOAA Air Resources Laboratory*, 1997]. We used this model with the 80-km resolution ETA data assimilation system data sets of wind, temperature, and humidity [*NCDC*, 2000a] as input to calculate the time evolution of an inert tracer released continuously from 1000 to 1100 LT at the Del Paso Manor sampling site. Calculations were performed for each day in July 1997. Figure 6 represents a typical plume location 7 hours after release from Sacramento, which is ~2 hours west of Folsom for typical wind speeds. On this day the urban plume traveled 100 km to the east, spread symmetrically, and diluted to 10–20% of urban core concentrations. The Hysplit model predicts that the point release rapidly diffuses in 1–2 hours to encompass an area approximately the size of the urban core. Subsequently, this small area plume is further diluted ($K = 0.3$ to 0.5 h^{-1}) during the transport into the Sierra Nevada that occurs over the next 4–7 hours. Owing to inability of the Hysplit model to accurately resolve spatial structures significantly smaller than the urban core, we believe the second timescale should be compared to our results. After 7 hours the modeled tracer concentrations were approximately equal above and below 800 m at the UC-BFRS (the typical regional mixed layer height). Given the coarse spatial resolution of the input wind fields, the Hysplit model is consistent with the results of our anthropogenic hydrocarbon analysis.

[36] As we described above, acetylene concentrations indicate the urban plume arrived at the UC-BFRS on 15 of the 20 days during July 1997 for which we have observations. We computed plume trajectories for all 31 days of July 1997. On 19 days the model shows the leading edge of the plume arrives at the UC-BFRS between 6 and 9 hours after release in downtown Sacramento after passing over the Folsom observation site 2–3 hours after release. On 9 days the model indicates that the plume traveled east into the Sierra Nevada mountains but passed either north or south of UC-BFRS by ~20 km. On 3 days the modeled plume remained in the Central Valley and did not enter the Sierra Nevada Mountains. The 3 days where Hysplit suggests that the urban plume was not transported into the foothills did not coincide with the 5 days when the observed acetylene concentration did not rise above the regional background at the UC-BFRS. The statistics of plume observations, 15 out of 20, are higher than predicted by Hysplit, 19 out of 31. This suggests that the Hysplit model predictions of its travel to the north or south of UC-BFRS cannot be easily tested. This is likely because both the initial release is a more extended source than is represented by the model, and the terrain driven mountain/valley wind patterns contain important spatial variations below the 800-km resolution of the ETA data assimilation system meteorological data.

6.2. OH Oxidation

[37] The best estimate OH concentration, 1.1 (± 0.5) $\times 10^7$ molecules cm^{-3}, in the Sacramento urban plume is similar to measured OH concentrations in air masses with comparable NO_x ($\equiv NO + NO_2$) concentrations [*Hofzumahaus et al.*, 1996; *Mount et al.*, 1997; *Tanner et al.*, 1997; *Volz-Thomas et al.*, 2000]. Model predictions suggest that OH concentrations will increase linearly with NO_x due to the reaction $HO_2 + NO \rightarrow OH + NO_2$ until the OH loss to nitric acid, $OH + NO_2 \rightarrow HNO_3$, becomes competitive with $HO_2 + NO \rightarrow OH + NO_2$. Factors that affect the primary HO_x production rate (e.g., the intensity of the radiation field, temperature, ozone concentrations, and humidity) or the partitioning of HO_x between RO_2, HO_2, and OH (e.g., CO and hydrocarbon abundance) are as important as NO_x in controlling the absolute abundance of OH. *Sillman et al.* [1990] suggest that these factors often compete with each other and predict that a range of chemical environs will experience peak OH when NO_x is in the range 2–4 ppb. Daytime NO_x concentrations in the Sacramento plume peak at ~13 ppb in the urban core are ~5–6 ppb in Folsom and decrease to ~1 ppb at the UC-BFRS. If OH concentrations responded to

Tracer Remaining
■ 1.6 % ■ 0.2 %
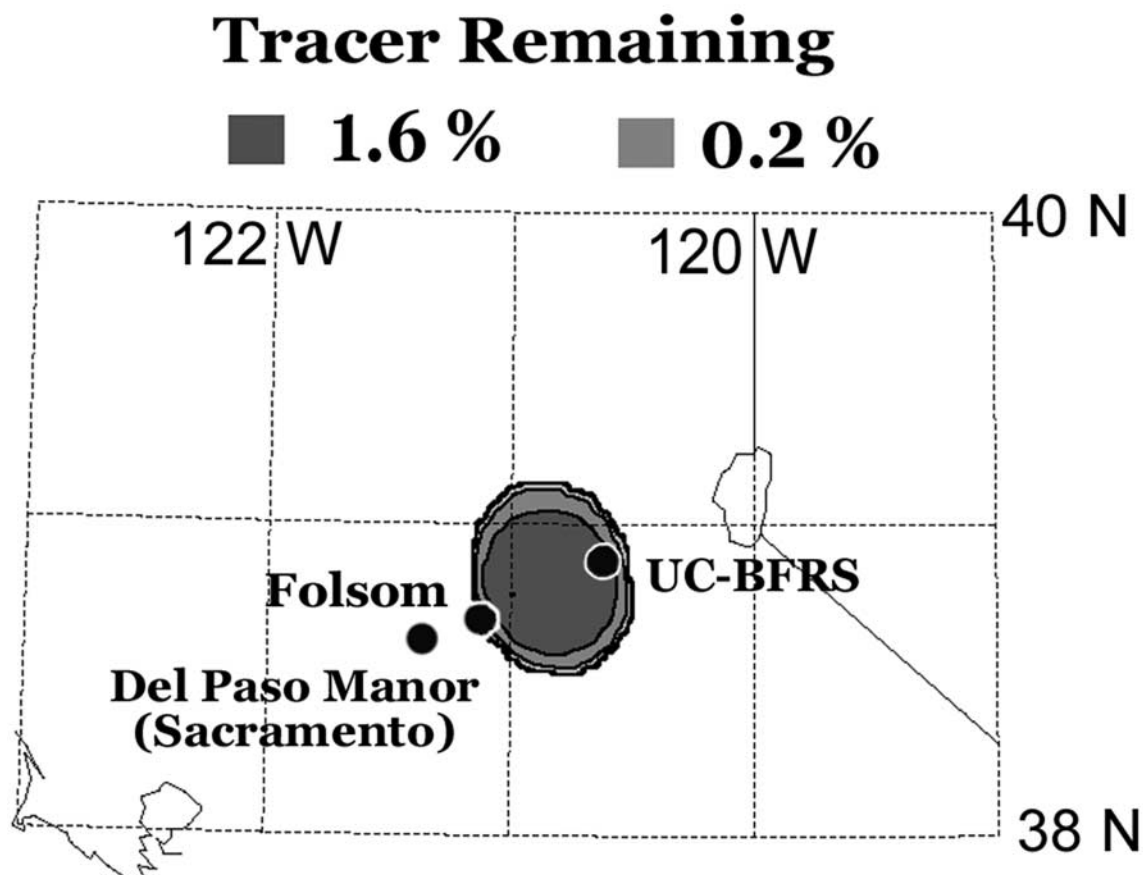
Figure 6. The distribution of an inert tracer 7 hours after release at 1000 LT on 16 July from the Del Paso Manor sampling site in Sacramento as computed using the Hysplit 4 model [*NOAA Air Resources Laboratory*, 1997]. The leading edge of the plume has reached the Blodgett Forest Research Station. The area over which the plume extends is ~700 km^2.

NO_x as expected on the basis of the above analysis, OH concentrations in the Sacramento urban core were probably lower than the mean along the plume and OH concentrations from Folsom to UC-BFRS should be close to the peak values consistent with the primary HO_x production rates. For comparison, low OH concentrations between 2 and 6×10^6 molecules cm^{-3} were observed on 24–26 September 1993 at high $NO_x \approx 35$ ppb in Claremont, California (downwind of Los Angeles) [*George et al.*, 1999]. In the urban plume of Freiburg, Germany, where [NO_x] is similar to [NO_x] in Folsom, ~6 ppb, *Volz-Thomas et al.* [2000] inferred OH concentrations in the range of $7-10 \times 10^6$ molecules cm^{-3} in the morning hours (0950–1150 LT) on 5 June 1996. Presumably, they would have observed higher values in the afternoon when solar intensity is higher and ozone concentrations are higher. *Mount et al.* [1997] and *Tanner et al.* [1997] measured peak OH concentrations of 1.2×10^7 molecules cm^{-3} outside of Boulder, Colorado ($NO_x \approx 3$ ppb [*Williams et al.*, 1997]). Both of these OH concentrations are consistent with our estimates for OH at similar NO_x abundances. *Hofzumahaus et al.* [1996] measured a daytime average (1200–1400 LT) OH concentration of 6×10^6 molecules cm^{-3} with a peak of 1.4×10^7 molecules cm^{-3} in northeastern Germany on 16 August 1994 ($NO_x \approx 1$ ppb [*Rohrer et al.*, 1998]). This is a NO_x value similar to what we observe at UC-BFRS, and again, the [OH] measured is similar to what we infer. At still lower NO_x ($NO_x < 0.5$ ppb), significantly lower OH concentrations were observed outside of Boulder, Colorado. Noontime OH concentrations in clean air were observed to be in the range $2-4 \times 10^6$

molecules cm^{-3} [*Mount et al.*, 1997]. We expect [OH] at UC-BFRS to be similar in the absence of the influence of the urban plume.

7. Conclusions

[38] Sacramento is an island city. The nearest city, Davis (population 46,209), is 40 km upwind, and the surrounding land is sparsely populated farmland. Emission estimates by the California Air Resources Board suggest that ~85% of the regional anthropogenic emissions originate from within the Sacramento urban core. Motor vehicle traffic dominates the anthropogenic emissions (93% of nitrogen oxides and 61% of reactive hydrocarbons), and there are only a few point sources within the region but no major power plants. From the view point of UC-BFRS, Sacramento is effectively a point or small area source.

[39] The daily evolution of the Sacramento urban plume during the summer is remarkably consistent. During the day, terrain-driven winds blow steadily from Sacramento into the Sierra Nevada foothills, drawing polluted air into the sparsely populated mountains. During the night the wind reverses and clears out the mountains, replacing the urban plume with a clean, regional background. This diurnal wind cycle is evident in observations of anthropogenic hydrocarbon concentrations at the UC-BFRS, which peak in the late afternoon/evening and decrease steadily with the downslope flow during the night. The major climate variables controlling plume transport (temperature, sunlight, pre-

cipitation, relative humidity, and wind) as measured in Sacramento have been nearly constant for 20 years (1980–1999).

[40] Using observations of six anthropogenic hydrocarbons with long and short lifetimes to oxidation by OH, propane, acetylene, *n*-butane, *n*-pentane, isopentane, and toluene obtained at Folsom, Del Paso Manor, and UC-BFRS, we derive effective dilution and oxidation rates within the Sacramento plume. Using the CARB estimates of anthropogenic emissions within the region, we conclude that after 60 km and 5 hours of transport the Sacramento urban plume was diluted to 32% of the initial concentration at Folsom and oxidized by $\sim 1.1 \times 10^7$ molecules cm^{-3} of OH. The dilution and oxidation rates derived here delimit two of the important factors controlling ozone abundance in the Sierra Nevada. Comparison to observations in other urban plumes suggests some generalizations about dilution rates and [OH] may be developed as we expand the number of plumes for which we have analyses of these factors.

References

Atkinson, R., Gas-phase tropospheric chemistry of organic compounds, *J. Phys. Chem. Ref. Data. Monogr.*, 3, 1–216, 1994.

Atkinson, R., Gas-phase tropospheric chemistry of volatile organic compounds, 1, Alkanes and alkenes, *J. Phys. Chem. Ref. Data*, 26, 215–290, 1997.

Bevington, P. R., *Data Reduction and Error Analysis for the Physical Sciences*, 336 pp., McGraw-Hill, New York, 1969.

Blake, D. R., T. Chen, T. W. Smith Jr., C. J. Wang, O. W. Wingenter, N. J. Blake, and F. S. Rowland, Three-dimensional distributions of nonmethane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Missions (PEM-West A), *J. Geophys. Res.*, 101, 1763–1778, 1996.

California Air Resources Board, Residential fuel combustion, in *Emission Inventory Procedural Manual, vol. 3, Methods for Assessing Area Source Emissions*, pp. 7.3-1–7.3-7, Sacramento, Calif., 1997.

California Air Resources Board, Air Quality Data, California Air Resources Board 1997 and 1998 PAMS hydrocarbon, ozone, and NO$_y$ data from the Del Paso Manor sampling site, Sacramento, Calif., 1998a.

California Air Resources Board, 1996 emissions inventory, Sacramento, Calif., 1998b. (Available at http://www.arb.ca.gov/emisinv/96inven/96inv.htm.)

California Air Resources Board, California ambient air quality data: 1980–1998, *Rep. PTSD-99–012-CD*, Sacramento, Calif., 1999a.

California Air Resources Board, Standard operating procedure for the determination of non-methane organic compounds in ambient air by gaschromatography using dual capillary columns and flame ionization detection, *Rep. SOP MLD 032 v3.1*, Sacramento, Calif., 1999b. (Available at http://arbis.arb.ca.gov/aaqm/sop/SOP032.pdf.)

California Air Resources Board, The 2001 California almanac of emissions and air quality, Sacramento, Calif., 2001a.

California Air Resources Board, Site description and quality assurance information, Sacramento, Calif., 2001b. (Available at http://www.arb.ca.gov/aqdas/sitex.php3?table=county&code=067.)

Calvert, J. G., Hydrocarbon involvement in photochemical smog formation in Los Angeles atmosphere, *Environ. Sci. Technol.*, 10, 256–262, 1976.

Daum, P. H., et al., Analysis of O$_3$ formation during a stagnation episode in central Tennessee in summer 1995, *J. Geophys. Res.*, 105, 9107–9119, 2000.

Demerjian, K. L., A review of national monitoring networks in North America, *Atmos. Environ.*, 34, 1861–1884, 2000.

Fehsenfeld, F. C., M. Trainer, D. D. Parrish, A. Volz-Thomas, and S. Penkett, North Atlantic Regional Experiment 1993 summer intensive, *J. Geophys. Res.*, 101, 28,869–28,875, 1996.

Fiedler, F., I. Bischoff-Gauss, N. Kalthoff, and G. Adrian, Modeling of the transport and diffusion of a tracer in the Freiburg-Schauinsland area, *J. Geophys. Res.*, 105, 1599–1610, 2000.

George, L. A., T. M. Hard, and R. J. O'Brien, Measurements of free radicals OH and HO$_2$ in Los Angeles smog, *J. Geophys. Res.*, 104, 11,643–11,655, 1999.

Goldstein, A. H., S. C. Wofsy, and C. M. Spivakovsky, Seasonal variations of nonmethane hydrocarbons in rural New England: Constraints on OH concentrations in northern mid-latitudes, *J. Geophys. Res.*, 100, 21,023–21,033, 1995.

Goldstein, A. H., N. E. Hultman, J. M. Fracheboud, M. R. Bauer, J. A. Panek, M. Xu, A. B. Guenther, and W. Baugh, Effects of climate variability on the carbon dioxide, water, and sensible heat fluxes above a ponderosa pine plantation in the Sierra Nevada (CA), *Agric. For. Meteorol.*, 101, 113–129, 2000.

Greenberg, J. P., D. Helmig, and P. R. Zimmerman, Seasonal measurements of nonmethane hydrocarbons and carbon monoxide at the Mauna Loa Observatory during the Mauna Loa Observatory Photochemistry Experiment 2, *J. Geophys. Res.*, 101, 14,581–14,598, 1996.

Hayes, T. P., J. J. Kinney, and N. J. Wheeler, California surface wind climatology, Calif. Environ. Prot. Agency, Sacramento, Calif., 1984.

Hofzumahaus, A., U. Aschmutat, M. Hebling, F. Holland, and D. H. Ehhalt, The measurement of tropospheric OH radicals by laser-induced fluorescence spectroscopy during the POPCORN field campaign, *Geophys. Res. Lett.*, 23, 2542–2544, 1996.

Jobson, B. T., Z. Wu, and H. Niki, Seasonal trends of isoprene, C$_2$-C$_5$ alkanes, and acetylene at a remote boreal site in Canada, *J. Geophys. Res.*, 99, 1589–1599, 1994.

Kalthoff, N., V. Horlacher, U. Corsmeier, A. Volz-Thomas, B. Kolahgar, H. Geiss, M. Mollmann-Coers, and A. Knaps, Influence of valley winds on transport and dispersion of airborne pollutants in the Freiburg-Schauinsland area, *J. Geophys. Res.*, 105, 1585–1597, 2000.

Kirchstetter, T. W., B. C. Singer, R. A. Harley, G. R. Kendall, and M. Traverse, Impact of California reformulated gasoline on motor vehicle emissions, 1, Mass emission rates, *Environ. Sci. Technol.*, 33, 318–328, 1999.

Lamanna, M. S., and A. H. Goldstein, In-situ measurements of C$_2$-C$_{10}$ VOCs above a Sierra-Nevada ponderosa pine plantation, *J. Geophys. Res.*, 104, 21,247–21,262, 1999.

Lin, X., P. B. Roussel, S. Laszlo, R. Taylor, O. T. Melo, P. B. Shepson, D. R. Hastie, and H. Niki, Impact of Toronto urban emissions on ozone levels downwind, *Atmos. Environ.*, 30, 2177–2193, 1996.

McKeen, S. A., and S. C. Liu, Hydrocarbon ratios and photochemical history of air masses, *Geophys. Res. Lett.*, 20, 2363–2366, 1993.

Moody, J. L., J. W. Munger, A. H. Goldstein, D. J. Jacobs, and S. C. Wofsy, Harvard Forest regional-scale air mass composition by Patterns in Atmospheric Transport History (PATH), *J. Geophys. Res.*, 103, 13,181–13,194, 1998.

Mount, G. H., F. L. Eisele, D. J. Tanner, J. W. Brault, P. V. Johnston, J. W. Harder, E. J. Williams, A. F. Fried, and R. Shetter, An intercomparison of spectroscopic laser long-path and ion-assisted in situ measurements of hydroxyl concentrations during the Tropospheric OH Photochemistry Experiment, fall 1993, *J. Geophys. Res.*, 102, 6437–6455, 1997.

National Oceanic and Atmospheric Administration Air Resources Laboratory (NOAA), HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) model, Silver Spring, Md., 1997. (Available at http://www.arl.noaa.gov/ready/hysplit4.html.)

National Climate Data Center, Eta data assimilation system, July and August 1997 data, Asheville, N. C., 2000a. (Available at http://www.arl.noaa.gov/ss/transport/archives.html.)

National Climate Data Center, 1980–1999 maximum temperature, total possible sunlight, average afternoon humidity, average wind speed, and precipitation at the Sacramento Executive Airport, Asheville, N. C., 2000b. (Available at http://www.ncdc.noaa.gov/ol/climate/stationlocator. html)

Neave, H. R., and P. L. Worthington, *Distribution-Free Tests*, Chapman and Hall, New York, 1988.

Nunnermacker, L. J., et al., Characterization of the Nashville urban plume on July 3 and July 18, 1995, *J. Geophys. Res.*, 103, 21,148–28,129, 1998.

Rohrer, F., D. Brüning, E. S. Grobler, M. Weber, D. H. Ehhalt, R. Neubert, W. Schüßler, and I. Levin, Mixing ratios and photostationary state of NO and NO$_2$ observed during the POPCORN field campaign at a rural site in Germany, *J. Atmos. Chem.*, 31, 119–137, 1998.

Ryerson, T. B., et al., Emissions lifetimes and ozone formation in power plant plumes, *J. Geophys. Res.*, 103, 22,569–22,583, 1998.

Ryerson, T. B., et al., Observations of ozone formation in power plant plumes and implications for ozone control strategies, *Science*, 292, 719–723, 2001.

Satsumabayashi, H., H. Kurita, Y. Chang, G. R. Carmichael, and H. Ueda, Diurnal variation of OH radicals and hydrocarbons in a polluted air mass during long-range transport in central Japan, *Atmos. Environ. Part A*, 26, 2835–2844, 1992.

Seaman, N. L., D. R. Stauffer, and A. M. Lario-Gibbs, A multiscale four-dimensional data assimilation system applied in the San Joaquin Valley during SARMAP, I, modeling design and basic performance characteristics, *J. Appl. Meteorol.*, *34*, 1739–1761, 1995.

Sierra Nevada Ecosystem Project, Shaped relief map of California, Univ. of Calif. Cent. for Water and Wildland Resour., Davis, Calif., 2000. (Available at http://www.ice.ucdavis.edu/snep/.)

Sillman, S., Ozone production efficiency and loss of NO_x in power plant plumes: Photochemical model and interpretation of measurements in Tennessee, *J. Geophys. Res.*, *105*, 9189–9202, 2000.

Sillman, S., J. A. Logan, and S. C. Wofsy, The sensitivity of ozone to nitrogen oxides and hydrocarbons in regional ozone episodes, *J. Geophys. Res.*, *95*, 1837–1851, 1990.

Tanner, D. J., A. Jefferson, and F. L. Eisele, Selected ion chemical ionization mass spectrometric measurements of OH, *J. Geophys. Res.*, *102*, 6415–6426, 1997.

U.S. Census Bureau, Topologically integrated geographic encoding and referencing system (TIGER) 1995 data, Washington, D. C., 1995. (Available at http://www.esri.com/data/online/tiger/index.html.)

U.S. Census Bureau, Metropolitan area population estimates for July 1, 1998 for Sacramento, CA, Washington, D. C., 1998. (Available at http://www.census.gov/population/estimates/metro-city/ma98-01.txt.)

U.S. Department of Commerce, 1997 local climatological data: Annual summary with comparative data, Sacramento, California (SAC), Natl. Clim. Data. Cent., Ashville, N. C., 1997. (Available at http://ols.ncdc.noaa.gov/onlinestore.html.)

Van Ooy, D. J., and J. J. Carroll, The spatial variation of ozone climatology on the western slope of the Sierra Nevada, *Atmos. Environ.*, *29*, 1319–1330, 1995.

Volz-Thomas, A., H. Geib, and N. Kalthoff, Schauinsland Ozone Precursor Experiment (SLOPE96): Scientific background and main results, *J. Geophys. Res.*, *105*, 1553–1561, 2000.

Williams, E. J., J. M. Roberts, K. Baumann, S. B. Bertman, S. Buhr, R. B. Norton, and F. C. Fehsenfeld, Variations in NO_y composition at Idaho Hill, Colorado, *J. Geophys. Res.*, *102*, 6297–6314, 1997.

Zaremba, L. L., and J. J. Carroll, Summer wind flow regimes over the Sacramento Valley, *J. Appl. Meteorol.*, *38*, 1463–1473, 1999.

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R. C. Cohen and M. B. Dillon, Department of Chemistry, University of California, Berkeley, Latimer Hall, Berkeley, CA 94720-1640, USA. (cohen@cchem.berkeley.edu; dillon@uclink4.berkeley.edu)

A. H. Goldstein, M. S. Lamanna, and G. W. Schade, ESPM Ecosystems Sciences Division, University of California, Berkeley, 151 Hilgard Hall, Berkeley, CA 94720-3110, USA. (ahg@nature.berkeley.edu; Ozone925@aol.com; gws@nature.berkeley.edu)