

Surface ozone in Yosemite National Park

Joel D. Burley^{a,*}, John D. Ray^b

^a*Department of Chemistry, Saint Mary's College of California, Moraga, CA 94575-4527, USA*

^b*National Park Service, Air Resources Division, P.O. Box 25287, Denver, CO 80225-0287, USA*

Received 28 October 2006; received in revised form 10 February 2007; accepted 9 March 2007

Abstract

During the summers of 2003 and 2005, surface ozone concentrations were measured with portable ozone monitors at multiple locations in and around Yosemite National Park. The goal of these measurements was to obtain a comprehensive survey of ozone within Yosemite, which will help modelers predict and interpolate ozone concentrations in remote locations and complex terrain. The data from the portable monitors were combined with concurrent and historical data from two long-term monitoring stations located within the park (Turtleback Dome and Merced River) and previous investigations with passive samplers. The results indicate that most sites in Yosemite experience roughly similar ozone concentrations during well-mixed daytime periods, but dissimilar concentrations at night. Locations that are well exposed to the free troposphere during evening hours tend to experience higher (and more variable) nocturnal ozone concentrations, resulting in smaller diurnal variations and higher overall ozone exposures. Locations that are poorly exposed to the free troposphere during nocturnal periods tend to experience very low evening ozone, yielding larger diurnal variations and smaller overall exposures. Ozone concentrations are typically highest for the western and southern portions of the park and lower for the eastern and northern regions, with substantial spatial and temporal variability. Back-trajectory analyses suggest that air with high ozone concentrations at Yosemite often originates in the San Francisco Bay Area and progresses through the Central California Valley before entering the park.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Ozone; Yosemite; Portable ozone monitor; HYSPLIT model

1. Introduction

First established as a national park in 1890, Yosemite is one of the most spectacular—and popular—destinations within the national park system. Since 1987 the Air Resources Division of the National Park Service (NPS) has monitored

surface ozone and other pollutants at a variety of sampling locations within Yosemite in order to better understand how air pollution impacts park resources ([Air Quality in the National Parks, 2002](#)). The deleterious effects of elevated ozone on Sierra Nevada forests have been thoroughly investigated; readers seeking a comprehensive review of this topic are directed to the excellent monograph edited by [Bytnerowicz et al. \(2003\)](#). Most of the studies that have been conducted so far have focused upon the western slope of the Sierra Nevada; relatively few measurements of ozone have been made along the

*Corresponding author. Tel.: +1 925 631 4839;
fax: +1 925 376 4027.

E-mail addresses: jburley@stmarys-ca.edu (J.D. Burley),
John_D_Ray@nps.gov (J.D. Ray).

eastern slope, which lies along the eastern border of Yosemite. This lack of data has made it difficult for modelers to predict/interpolate ozone concentrations for these locations (Fraczek et al., 2003). The general problem of mapping/estimating ozone distributions has also been complicated by the complex transport and mixing phenomena and variable topography that are present throughout this region. Lee (2003) has specifically noted that more intensive sampling is needed in locations (e.g. Yosemite, Lassen Volcanic NP) where these conditions are prevalent.

Limited studies with low time resolution have attempted to determine ozone concentrations within Yosemite based on simultaneous measurements at multiple sites throughout the park (Bytnerowicz et al., 2003; Ray, 2001). In the study by Ray (2001), passive ozone samplers were deployed at 11 locations spread across the park over 18-week summer-time periods to augment the concurrent measurements from the long-term monitoring station at Turtleback Dome. The results indicated that mean ozone concentrations within the park increased with increasing elevation at western sampling sites (approximate elevations of 1200–2000 m above sea level), but became variable at higher elevation sites between 2000 and 3000 m in the eastern part of the park.

The present report describes a series of surface ozone measurements that were made in and around Yosemite National Park during the summers of 2003 and 2005. These measurements were combined with concurrent data from the Turtleback Dome and Merced River monitoring stations and previous results from passive samplers to yield a more complete picture of surface ozone within the park.

2. Experimental methods and procedures

2.1. Portable ozone monitor, measurement protocols

Ambient ozone concentrations were measured using small, lightweight 2B Technologies Model 202 ozone monitors. Two separate monitors were utilized during the 2003 measurements, and a single monitor was used in 2005. In all cases, the sampling inlet consisted of a downward-facing 47 mm diameter Teflon filter holder equipped with a 1–2 μm Teflon filter membrane. The filter holder was connected directly to the ozone monitor by a 2 m length of 6.35 mm (0.25 in.) o.d. Teflon tubing. For

deployments at remote locations, the ozone monitor was enclosed within a weatherproof plastic case and the sampling inlet was covered by a plastic rain shield. Power for these remote deployments was provided by a rechargeable 12-V lead–acid battery with a capacity of 21 A h. This battery was connected to a 20-W solar panel attached to the top of the plastic case. Ozone concentrations were measured at 10-s intervals, and the data were recorded into internal monitor memory as 1-min averages. These 1-min values were later converted into hourly averages after being downloaded from the ozone monitor. The hourly data were then further averaged to obtain the average diurnal cycle for each deployment location.

2.2. Sampling locations

Measurements were conducted at a total of 12 different locations in 2003, and five different locations in 2005. These sampling locations are summarized in Table 1 and depicted in Fig. 1. For sampling sites located near automobile traffic, the monitor was positioned at least 100 m away from the closest road or parking lot in order to minimize perturbations from vehicular exhaust. In all cases, the monitor was placed in an open clearing (i.e. away from nearby trees or bushes), with the sampling inlet positioned roughly 1.3 m above ground level.

2.3. Fixed-location monitoring stations

In addition to the data collected by the portable ozone monitors, hourly ozone values were available from two long-term monitoring stations located within the park. The Turtleback Dome station was fully operational in both 2003 and 2005, and the Merced River station provided partial coverage in 2003 and full coverage in 2005. Both stations followed Environmental Protection Agency (EPA) guidelines for sampling and analysis and utilized the Thermo Environmental Instruments Model 49C photometric ozone analyzer to measure O_3 . The Turtleback Dome station also served as a test site where the performance of the portable ozone monitors was verified under realistic sampling conditions. One of the co-located comparisons conducted at the Turtleback Dome station in June 2003 is discussed in detail below.

Table 1
Sampling locations

	Code	Elevation (m)	Latitude	Longitude	Start	End	Passive sampler data periods
<i>2003 sites sampled by portable monitors</i>							
Turtleback Dome	TD	1604	37.7133	−119.7060	18 June	25 June	2000–2003
Lee Vining Canyon	LVC	2212	37.9371	−119.1382	27 June	2 July	2001
Tioga Pass #1	TP1	3037	37.9108	−119.2587	2 July	8 July	1998–2001
Crane Flat Lookout	CFL	2022	37.7595	−119.8206	8 July	14 July	1999–2003
El Portal	EP	603	37.6749	−119.8056	10 July	11 August	
Tioga Road (T14)	T14	2396	37.8397	−119.5904	14 July	21 July	1998–2001
Tuolumne Meadows #1	TM1	2623	37.8765	−119.3479	21 July	26 July	1998–2001
Siesta Lake	SL	2446	37.8519	−119.6592	26 July	31 July	2000–2001
Merced River	MR	1213	37.7431	−119.5940	1 August	5 August	
Mirror Lake	ML	1341	37.7518	−119.5522	7 August	11 August	2001
Tioga Pass #2	TP2	3021	37.9120	−119.2573	11 August	20 August	
Tuolumne Meadows #2	TM2	2612	37.8757	−119.3763	11 August	20 August	
<i>2005 sites sampled by portable monitors</i>							
Turtleback Dome	TD	1604	37.7133	−119.7060	17 July	20 July	2000–2003
Tuolumne Meadows #1	TM1	2623	37.8765	−119.3479	20 July	30 July	1998–2001
Dana Meadows	DM	2869	37.8776	−119.2829	30 July	11 August	
Lee Vining Canyon	LVC	2212	37.9371	−119.1382	11 August	19 August	2001
Mono Lake	MO	1957	37.9558	−119.0549	19 August	26 August	
<i>Sites sampled only by passive samplers</i>							
Camp Mather	CM	1432	37.8886	−119.8411	1998	2003	
Wawona Valley	WV	1231	37.5402	−119.6524	1998	2003	
Pohono (Valley A)	PV	1210	37.7186	−119.6623	2000	2001	
Taft Toe (Valley B)	TT	1267	37.7208	−119.6235	2000	2001	
Village (Valley C)	YV	1224	37.7490	−119.5874	2000	2001	
El Capitan Meadow	ECM	1241	37.7259	−119.6383	2002	2003	
Wood Yard	WY	1272	37.7262	−119.6465	2002	2003	

2.4. Sampling timelines

All of the portable ozone monitor data presented in this report were collected between 18 June and 20 August 2003 (day of year = 169–232), or between 17 July and 26 August 2005 (day of year = 198–238). For most of the 2003 sampling period, it was possible to obtain simultaneous ozone values at three separate locations (Turtleback Dome station plus one 2B monitor deployed to a remote site and a second 2B monitor deployed to a site where AC power was available). During those periods when the Merced River station was operational, the number of simultaneous ozone measurements increased to four. For the 2005 sampling period, simultaneous ozone values were available at three locations: Turtleback Dome station, Merced River station, and one 2B monitor deployed to a remote site. In most cases, the sampling periods for the portable monitor deployments to remote locations do not overlap and are of different lengths.

2.5. Meteorological measurements at Tuolumne Meadows and Tioga Pass

In order to better understand the transport mechanisms that can influence ozone concentrations in alpine environments, the measurements performed in August 2003 at Tuolumne Meadows and Tioga Pass were co-located with extensive meteorological instrumentation (Clements *et al.*, 2004; Clements, 2007). At Tuolumne Meadows (TM2), the ozone monitor was positioned near a Doppler sonic detection and ranging (SODAR) instrument and a portable meteorological tower. Concurrent measurements at Tioga Pass (TP2) employed an ozone monitor and a meteorological tower, but no SODAR. In both cases, the logistical requirements of the meteorological measurements required that the sampling locations be moved from their previous sites, so that while these new measurements correspond to the same approximate areas that had been sampled previously (TM1 and

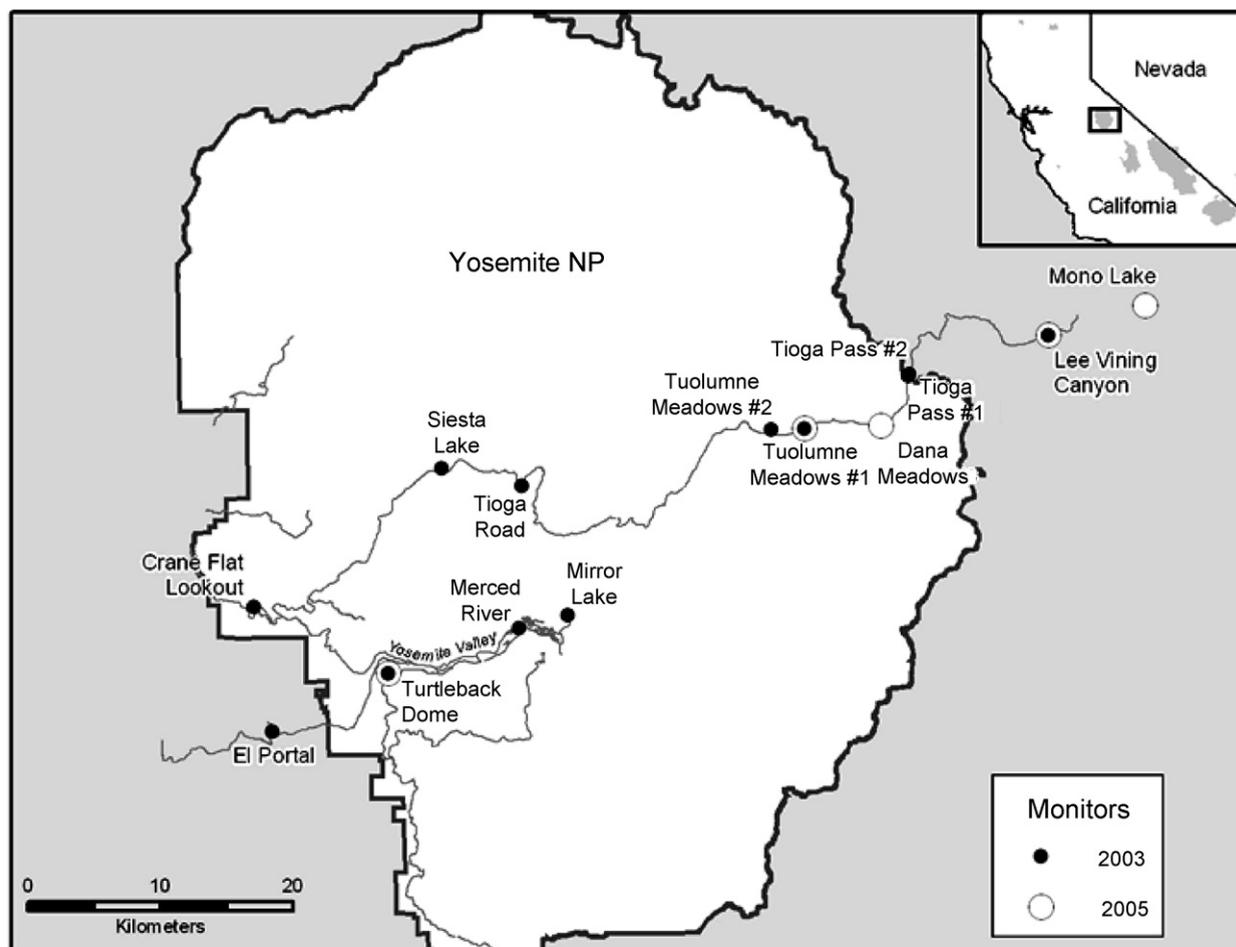


Fig. 1. Locations sampled by the portable ozone monitors. Sites sampled in 2003 are denoted by solid dots, while those sampled in 2005 are designated by larger open circles.

TP1), they do not correspond to the exact same positions.

2.6. 2005 measurements at eastern sites

In the summer of 2005, measurements were conducted along the easternmost portion of Tioga Pass Road in order to obtain better coverage of high-elevation sites extending eastward from Yosemite into Inyo National Forest. Sampling sites included two locations sampled in 2003 (Tuolumne Meadows and Lee Vining Canyon) and two new locations not previously sampled (Dana Meadows and Mono Lake). The Dana Meadows site was selected because of its location midway between Tuolumne Meadows and Tioga Pass, and the Mono Lake site was selected in order to determine if ozone trends observed in the western portions of Yosemite

were being propagated eastward over Tioga Pass and down into the Mono Lake basin.

2.7. Calibrations and comparisons involving the portable ozone monitors

A variety of calibrations and comparisons were performed in order to verify the accuracy of the portable ozone monitors. Prior to field deployment, all of the 2B monitors used in this study were calibrated in the laboratory against a transfer-standard Thermo Environmental Instruments Model 49C photometric ozone analyzer. These initial tests typically spanned a concentration range of 0–470 ppb and indicated that the portable monitors had an overall precision of ± 4 ppb and an accuracy of $\pm 6\%$. Analogous post-deployment measurements after the completion of the summer sampling

period indicated that the portable monitors had retained a precision of ± 5 ppb and an accuracy of $\pm 6\%$.

In addition to the laboratory calibrations, field tests were conducted at Turtleback Dome station. These tests demonstrated the reliability of the solar panel/rechargeable battery power source used for remote deployments and allowed for direct comparisons between the portable monitors and the station. Representative results from these tests are shown in Fig. 2a. The hourly O_3 values measured by the station

are, on average, 3.4 ppb higher than those measured by the portable monitor, and daytime deviations are typically in the order of 0–3 ppb. Significant deviations are observed in the predawn hours for days 172–175, with the portable monitor yielding values that are consistently low compared to the station. The probable cause for these predawn deviations is the different inlet locations employed by the two measurements. As noted above, the sampling inlet used by the portable monitors was located approximately 1.3 m above ground level. In contrast, the inlet for the station was

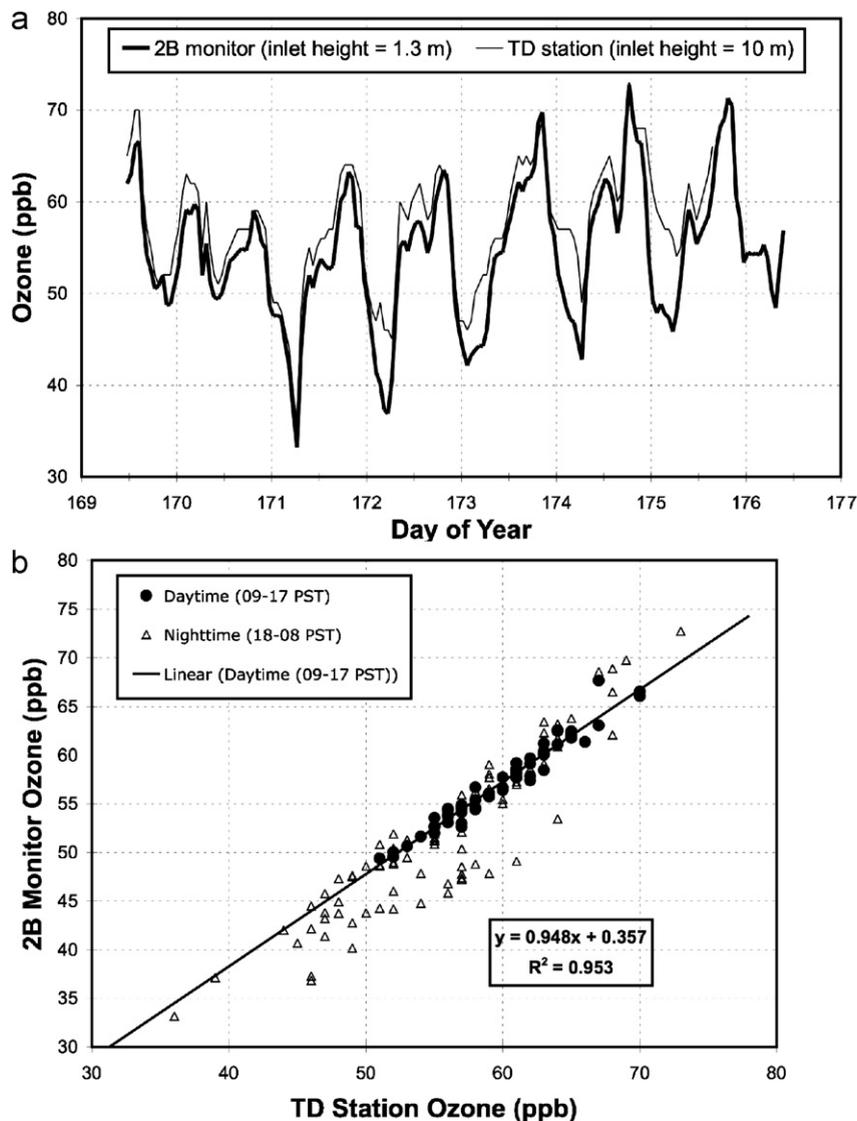


Fig. 2. (a) 2003 field test at Turtleback Dome station: time series comparison. The thick line specifies the hourly ozone concentrations measured by the portable ozone monitor and the thin line denotes the hourly concentrations recorded by the Turtleback Dome monitoring station. (b) 2003 field test at Turtleback Dome station: scatter-plot analysis. Daytime data (9:00–17:00 PST) are indicated by solid circles and nighttime data (18:00–8:00 PST) are designated by open triangles. The linear regression shown on the graph corresponds to the daytime data; if the nighttime data are included in the linear regression the R^2 value decreases to 0.879.

mounted on a tower at a height of 10 m. Localized variations in O_3 concentration resulting from poor mixing can typically become more pronounced during evening hours (as opposed to the well-mixed daylight hours), so that the two different inlets can sample different packets of air. A scatter-plot analysis of the time series data from Fig. 2a, presented in Fig. 2b, is consistent with this hypothesis. The scatter-plot indicates good agreement ($R^2 = 0.953$, slope = 0.948, y -intercept = 0.357 ppb) between the 2B monitor and the station monitor for the well-mixed daylight hours of 9:00–17:00 Pacific Standard Time (PST). If the data for the evening and early morning hours (18:00–8:00 PST) are added to the analysis so that the linear regression now includes all available data, a poorer correlation ($R^2 = 0.879$, slope = 1.060, y -intercept = -6.88 ppb) is obtained. Observations of inlet height-dependent sampling variations in predawn ozone values have also occurred during field-based comparisons of the recently developed portable ozone monitoring systems (POMS) to tower-based NPS monitoring stations (Ray, 2006).

3. Results

3.1. 2003 measurements along Tioga Pass Road

The average diurnal cycles for the 2003 sampling locations along Tioga Pass Road are shown in Fig. 3, along with representative uncertainties (± 1 S.D. of the

mean) for Crane Flat Lookout and Tuolumne Meadows #1. These data indicate that all of the Tioga Pass Road sites experience similar ozone concentrations during the well-mixed daytime hours of 9:00–16:00 PST, with significant deviations during the late evening and early morning hours. As one moves from east to west, a number of general trends emerge. The cycles for Lee Vining Canyon and Tioga Pass #1 are roughly similar, except for diverging during the evening period of 18:00–midnight PST. Both of these sites experience elevated ozone concentrations (≥ 40 ppb) throughout the evening or early morning hours, yielding relatively small overall diurnal variations. The results for Tuolumne Meadows #1, in contrast, display a much larger diurnal variation. As one moves westward from Tuolumne Meadows, the diurnal variation in O_3 is initially reduced (T14, Siesta Lake), and then inverted at Crane Flat Lookout. This westward progression is marked by a significant increase in nighttime and early morning levels of ozone. Crane Flat Lookout, which had the highest average ozone exposure of all of the sites that were sampled, achieved this distinction because of its consistently high nocturnal ozone concentrations.

3.2. 2003 measurements at El Portal and Yosemite Valley

Average diurnal cycles for 2003 data from El Portal, Merced River, Mirror Lake, and Turtleback

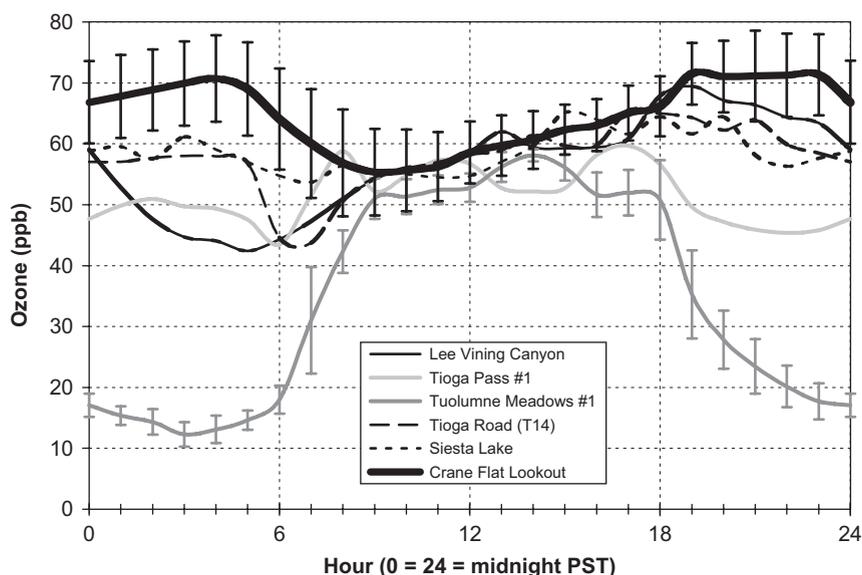


Fig. 3. Average diurnal cycles for sites along Tioga Pass Road in 2003. Uncertainties (± 1 S.D. of the mean) are indicated for Crane Flat Lookout and Tuolumne Meadows; the other sampling locations have uncertainties similar to those measured at Tuolumne Meadows.

Dome station are presented in Fig. 4, along with the corresponding uncertainties. In contrast to Fig. 3, these sites show pronounced differences in the magnitudes of their afternoon maxima. El Portal, Merced River, Mirror Lake all display large diurnal variations of >40 ppb, while at Turtleback Dome the diurnal variation is <30 ppb.

3.3. Additional 2003 measurements at Tuolumne Meadows and Tioga Pass

The diurnal patterns resulting from the August 2003 measurements with the co-located meteorological instrumentation (TM2 and TP2) are shown in Fig. 5, along with the earlier data for TM1 and TP1. (The uncertainties for the TM2 and TP2 data—which are slightly smaller than those observed for TM1 and TM2—have been omitted for purposes of legibility.) The reproducibility that is observed suggests that the diurnal cycles presented here are not significantly perturbed by small changes in the sampling locations.

A preliminary analysis of the meteorological data (Clements et al., 2004) suggests that middle-of-the-night spikes in observed ozone concentrations result from nocturnal mixing events in which air from aloft (with elevated concentrations of O₃) is mixed downwards at higher elevations. This air is then entrained into the surface layer, where it can be transported to lower elevations via nocturnal down-

valley flows. A detailed analysis of the results is being prepared by Clements (2007).

3.4. 2005 measurements at eastern sites

The diurnal patterns for the 2005 measurements are shown in Fig. 6. All of the eastern Tioga Pass Road sites display roughly similar behavior, with a pronounced minimum near 6:00 followed by a broad maximum of approximately 45–50 ppb extending between 10:00 and 16:00 PST. Comparison of the data of Fig. 6 to analogous results from 2003 indicates excellent reproducibility for Turtleback Dome station (Figs. 4 and 6) and good reproducibility for Tuolumne Meadows (Figs. 5 and 6). The 2005 measurements at Lee Vining Canyon, however, are dissimilar to those recorded in 2003 (Fig. 3). The 2005 values are roughly 10–12 ppb lower during daylight hours and up to 30 ppb lower at night, primarily because the nighttime spikes frequently observed at Lee Vining Canyon in the 2003 hourly data are largely absent in 2005.

4. Analysis and discussion

4.1. Potential wildfire impacts

During the summers of 2003 and 2005, Yosemite experienced a number of wildfires ([| Hour | El Portal \(ppb\) | Merced River \(ppb\) | Mirror Lake \(ppb\) | Turtleback Dome Station \(ppb\) |
|------|-----------------|--------------------|-------------------|-------------------------------|
| 0 | 35 | 30 | 28 | 55 |
| 3 | 30 | 28 | 26 | 52 |
| 6 | 25 | 24 | 22 | 45 |
| 9 | 55 | 50 | 48 | 65 |
| 12 | 70 | 65 | 60 | 68 |
| 15 | 75 | 70 | 65 | 72 |
| 18 | 65 | 60 | 55 | 70 |
| 21 | 40 | 35 | 30 | 55 |
| 24 | 35 | 30 | 28 | 55 |](http://</p>
</div>
<div data-bbox=)

Fig. 4. Average diurnal cycles for El Portal and Yosemite Valley sites in 2003. The plotted uncertainties correspond to ± 1 S.D. of the mean.

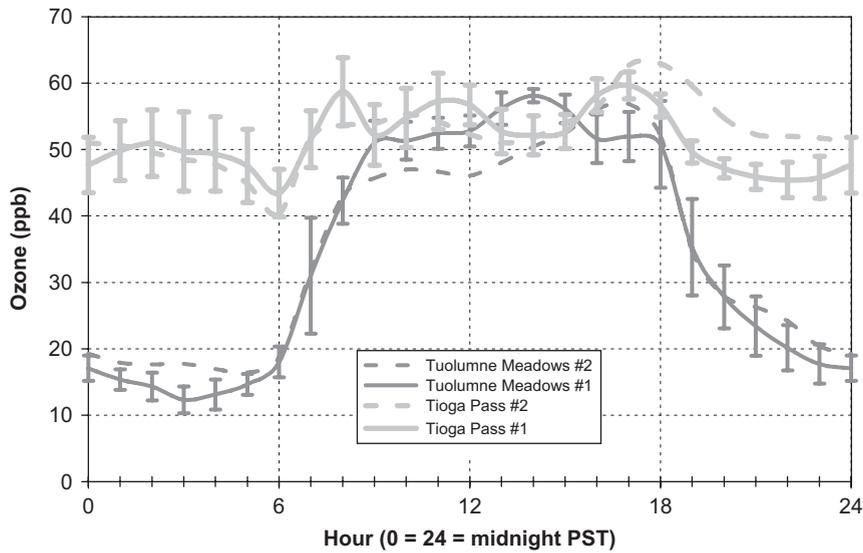


Fig. 5. Average diurnal cycles for deployments at Tuolumne Meadows and Tioga Pass in 2003. The TM1 and TP1 data are the same as those presented in Fig. 3, and their plotted uncertainties correspond to ± 1 S.D. of the mean. The uncertainties for TM2 and TP2 (which are not shown) are slightly smaller than those for TM1 and TP1.

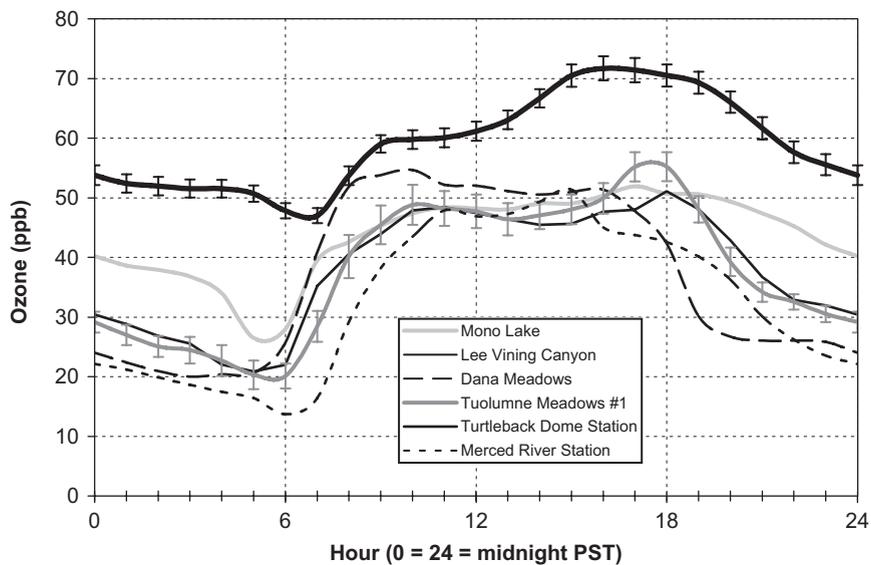


Fig. 6. Average diurnal cycles for 2005 measurements. Representative uncertainties (± 1 S.D. of the mean) are indicated for Turtleback Dome station and Tuolumne Meadows; the other sampling locations have uncertainties similar to those measured at Tuolumne Meadows.

map.ngdc.noaa.gov/website/firedetects/viewer.htm). The largest burn area was along the northwest boundary of the park and the burn areas along Tioga Road occurred in late August and September after the portable ozone measurements were completed. While these wildfires could potentially have perturbed the ozone results presented here (Honrath, 2004; McMeeking et al., 2005; APCD, 2003), a

preliminary analysis—based on fire records and particulate matter data (PM 2.5 samplers and IMPROVE (Interagency Monitoring of Protected Visual Environments) monitors) collected in Yosemite—does not suggest a strong influence. The fine particle data that would relate to wildfires were not high during the ozone sampling periods. Likewise, the ozone record at Turtleback Dome was

consistent with values obtained over the last 10 years. The agreement between the 2003 and 2005 ozone data at three out of the four locations sampled in both years (Turtleback Dome, Merced River, Tuolumne Meadows) also supports the general conclusion that the 2003 fires did not significantly perturb local ozone.

4.2. Diurnal patterns: general trends

The general features of the diurnal patterns presented in Figs. 3–6 most likely reflect the surrounding topography and mixing dynamics, rather than local photochemical production of O_3 . According to this hypothesis, pronounced diurnal variations with very low predawn ozone (such as is observed at Tuolumne Meadows and Merced River) tend to be associated with flat topography that permits the recurring formation of a stable nocturnal boundary layer near the surface. This boundary layer typically prevents the downward mixing of ozone-rich air from the free troposphere during evening hours, and allows for ozone near the surface to be removed by deposition and/or titration with NO_x from nearby combustion sources. (Meteorological and NO_x data from the Merced River station suggest that dry deposition, rather than titration with nitric oxide, is responsible for most of the ozone loss that is observed at the Merced River site, but analogous data are not available for Tuolumne Meadows.) Small diurnal variations are typically observed when a sampling location lacks either (i) the flat topography and/or (ii) the local meteorological conditions needed to produce a stable nocturnal boundary layer. Instead, these latter sites typically experience turbulent mixing throughout the evening hours, and are well exposed to the free troposphere.

4.3. Dual-peaked maxima in the diurnal plots

A number of sites sampled in 2003 and/or 2005 display double-peaked maxima in their diurnal plots, with the observation of two distinct “humps”—one in the mid-morning and the other in the early evening. Although most readily observed in the hourly data—which had to be omitted from the present report because of space constraints—this phenomenon is clearly present in Fig. 4 (Mirror Lake), Fig. 5 (Tuolumne Meadows #2 and Tioga Pass #2), and Fig. 6 (Tuolumne Meadows #1). Similar behavior has been previously

studied in alpine environments by Loffler-Mang et al. (1997), who attributed the first peak to the morning break-up of the nocturnal stable boundary layer, with ozone-rich air mixing downwards from above. The second peak that arises a few hours later corresponds to the horizontal transport of air via up-valley winds.

The results from the two sites measured in Yosemite Valley indicate that formation of double-peaked maxima may be highly dependent upon the specific location of the sampling site. In this instance, the Mirror Lake data exhibit a pronounced double-humped appearance while the nearby Merced River data are consistently single-humped. The localized mixing dynamics at these two valley sites may be very different (up-valley, base of cliffs for Mirror Lake versus down-valley, middle of meadow for Merced River), despite their relatively close proximity. The Mirror Lake site may be seeing a wind rotator perpendicular to the up-valley flow that sets up as the sunlight warms the nearby canyon walls.

4.4. Small variation versus large variation sites

In general, the locations sampled in this report tend to fall into two separate categories based upon the magnitude of their diurnal variation. Small variation (or small delta) sites typically have predawn ozone minima of ~ 40 ppb or higher, with relatively small diurnal variations of ~ 25 ppb or less. These sites can experience frequent middle-of-the-night spikes in O_3 , which suggests that they are well exposed to the free troposphere during evening hours. Because these sites experience high levels of nocturnal ozone, their average ozone exposures over a 24-h period are typically 50 ppb or higher. The small variation sites include Turtleback Dome station, Tioga Pass, Crane Flat Lookout, T14, and Siesta Lake. Large variation (or large delta) sites typically display predawn ozone minima of ~ 25 ppb or lower, with diurnal variations of ~ 40 ppb or more. These sites usually experience diurnal patterns with relatively few nocturnal ozone spikes, and they are not well exposed to the free troposphere during the evening. Because these locations experience very low levels of nocturnal ozone, their average ozone exposures over a 24-h period are typically below 50 ppb. The large variation sites include El Portal, Tuolumne Meadows, Dana Meadows, Merced River station, Mirror Lake, and Mono Lake.

The Lee Vining Canyon site—which was measured by the portable monitor in both 2003 and 2005—may be unlike the other locations in that it does not consistently demonstrate “small-delta” or “large-delta” behavior. The lack of reproducibility in the 2003 versus 2005 results might indicate that this site is topographically “flat” enough to experience stable nocturnal boundary layers when allowed by local meteorological conditions (2005 data) while at the same time exposed enough to experience recurring downward mixing events during periods of greater nocturnal turbulence (2003 data).

Similar variations in the magnitude of the diurnal variability have been observed in previous studies of Sierra Nevada ozone. Van Ooy and Carroll (1994) observed significant differences in the strength of the diurnal pattern at six remote sites along the western slope of the Sierra Nevada. They hypothesized that local topographical characteristics and their effect on the local transport of polluted air were the predominant factors in determining the strength of the diurnal variation, rather than the linear distance of the site from urban sources. The present results support this hypothesis and suggest that it can be extended to sites at higher elevations than those measured by Van Ooy and Carroll (1994).

4.5. Comparisons of scaled results to passive sampler data

In order to quantitatively compare ozone trends across different sampling locations and remove temporal variability, the raw hourly data were multiplied by scaling factors that are specific to the day on which the data were collected

Daily scaling factor

$$= \frac{[\text{TD station average for 1 June to 31 August}]}{[\text{TD station average for that day}]} \quad (1)$$

These scaling factors assume that Turtleback Dome station can serve as a reliable frame of reference for the entire park and that regional trends in ozone concentration will be seen more or less uniformly throughout the park. No adjustments are made for potential year-to-year variations between the 2003 and the 2005 data, and the scaling factors applied to the 2003 results are therefore completely independent of those applied to the 2005 data. (The

2003 ozone concentrations are somewhat higher than those collected in 2005, so that the numerator of Eq. (1) decreases from 60.6 ppb in 2003 to 56.7 ppb in 2005.)

On days when regional ozone concentrations are high, the daily scaling factor is <1 , while on days when regional ozone values are low the scaling factor is >1 . As a result, sites that were sampled during periods of high regional ozone have their ozone values scaled downwards while those sampled during cleaner periods have their ozone values adjusted upwards. After the scaling factors are applied to the hourly data for a given site, the scaled hourly data are averaged to yield a single ozone value for that location. To prevent the results from being skewed by inconsistent sampling periods, only complete, contiguous 24-h blocks of data are included in the calculation of the overall average. This scaling and averaging process makes it possible to estimate a single average value for a 3-month seasonal period (June–July–August) from a limited-duration time series of hourly data. It also facilitates direct comparisons to passive sampler data from previous years, which have been archived as weekly values and can therefore be converted directly into 3-month seasonal averages.

4.6. Spatial trends

The ozone concentrations resulting from the scaling and averaging process outlined above are presented in Figs. 7–9, along with June–July–August seasonal average values for passive sampler data from 1998 through 2003. Most locations have results from both the portable monitor measurements and the passive samplers, but seven sites have only passive sampler data (Table 1).

A number of general trends are apparent in the data of Figs. 7–9. The portable ozone monitors and the passive ozone samplers (Ray, 2001) yield similar results, as indicated by the small range of ozone values at each site. Larger scatter is observed for measurements within Yosemite Valley and at Lee Vining Canyon. When the data for the small variation and large variation sites are examined independently, two distinct bands emerge, as suggested by the trend lines plotted in Fig. 7. These linear regressions are based only on the 2003 and 2005 data from the continuous samplers and exclude the results from the Yosemite Valley (too much site-to-site variability within the valley) and Lee Vining Canyon (inconsistent behavior between

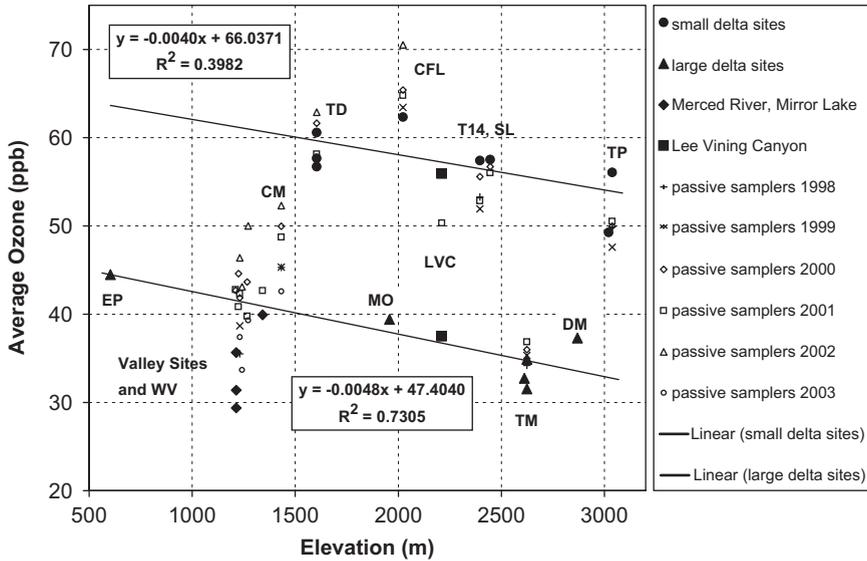


Fig. 7. Elevation dependence of scaled average ozone values. Trend lines for the small variation and large variation sites are based upon continuous measurements from 2003 and 2005 (excluding Yosemite Valley and Lee Vining Canyon) and do not include any passive sampler data.

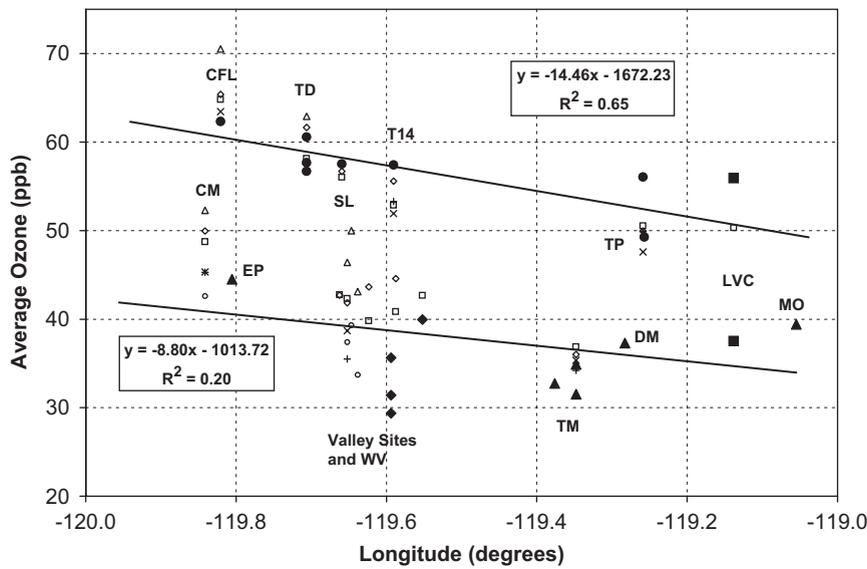


Fig. 8. Longitudinal dependence of scaled average ozone values. Trend lines for the small variation and large variation sites are based upon continuous measurements from 2003 and 2005 (excluding Yosemite Valley and Lee Vining Canyon) and do not include any passive sampler data. The data symbols are the same as those used in Fig. 7.

2003 and 2005). Both the small variation and the large variation sites experience average ozone exposures that decrease with increasing elevation, and the observed slopes are roughly similar for the two different types of locations. (It should be noted, however, that the small-delta and large-delta slopes are not co-linear—the regressions shown in Figs. 7–9 have low R^2 values.) A longitudinal

analysis (Fig. 8) also separates into distinct bands for the small variation and large variation sites, with average ozone decreasing as one moves from west to east. A latitudinal analysis (Fig. 9) shows a similar pattern, with ozone concentrations decreasing as one moves from south to north. The overall picture that emerges is that average ozone exposures within the park generally decrease as one moves from low

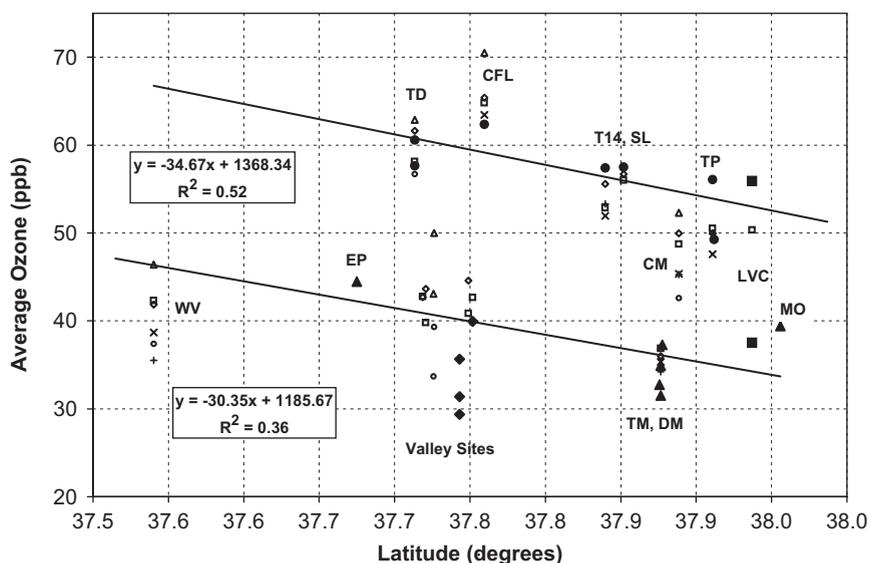


Fig. 9. Latitudinal dependence of scaled average ozone values. Trend lines for the small variation and large variation sites are based upon continuous measurements from 2003 and 2005 (excluding Yosemite Valley and Lee Vining Canyon) and do not include any passive sampler data. The data symbols are the same as those used in Fig. 7.

elevations in the south and west to higher elevations in the north and east, but with substantial spatial and temporal variability.

4.7. Back-trajectory calculations

In order to understand the transport dynamics that bring polluted air into Yosemite, the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model from the Air Resources Laboratory of the National Oceanic and Atmospheric Administration was used to perform a series of back-trajectory calculations (Draxler and Rolph, 2003; Rolph, 2003). Calculations were conducted for days between 1 June and 31 August 2003, when the maximum 1-h ozone concentration measured at Turtleback Dome station exceeded 80 ppb. In all cases, the back-trajectories were configured with an initial elevation of 100 m above ground level, an arrival time at Turtleback Dome of 14:00 PST, and an overall length of 48 h. The Eta Data Assimilation System (EDAS) 80 km data set was used to provide the archived meteorological data required for model input (Draxler and Rolph, 2003).

The results from the back-trajectory calculations indicate that most of the air that was transported into Yosemite originated in the San Francisco Bay Area before passing through the Central Valley and then into the park. In a typical trajectory, such as the one shown in Fig. 10, an onshore flow occurs in

Marin County and then proceeds eastward through the Carquinez Strait and up into the Delta before turning to the south and entering the Central Valley. (In some cases, the onshore flow can originate south of San Francisco and travel inland over the Altamont Pass before turning southward.) After traveling down the Central Valley, the air parcel then turns to the east to ascend through the Sierra Nevada foothills and make a final approach into Yosemite. Typical transit times from the Bay Area to Yosemite are on the order of 24–36 h. The general pattern displayed in Fig. 10 is fully consistent with previous investigations of surface-level meteorology (California Air Resources Board, 2001).

While the back-trajectory pictured in Fig. 10 represents the most common scenario for pollutant transport into Yosemite, approaches from other directions are also frequently observed. It is therefore useful to calculate the relative probabilities for all possible approaches into the park. Fig. 11 presents the weighted source contribution plot (Ashbaugh et al., 1985; Gebhart et al., 2006) for the summer 2003 high ozone back-trajectories at Turtleback Dome station. In this representation, the shade of a given grid element indicates the relative source contribution from back-trajectories that passed through that particular region before arriving at Turtleback Dome station. In addition to a heavy source contribution from the San Francisco

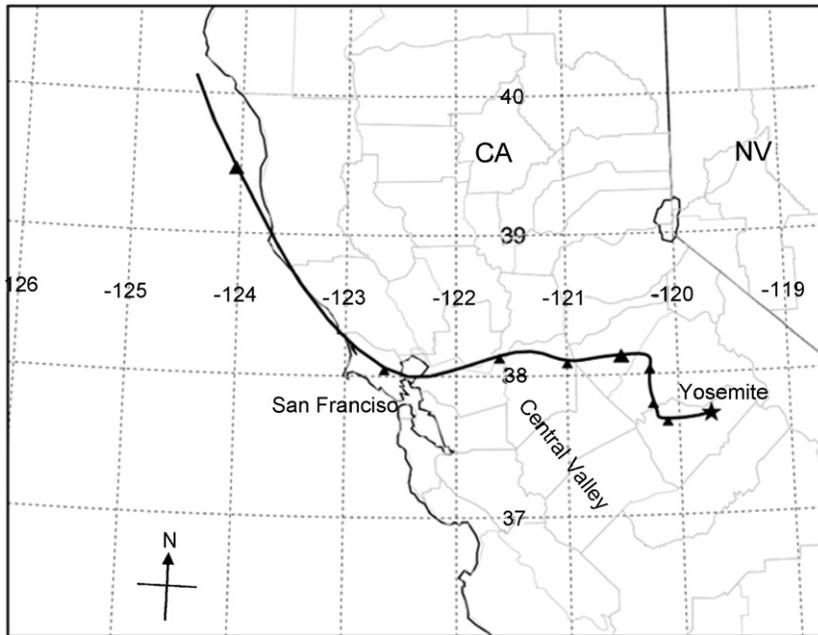


Fig. 10. Air mass back-trajectory (100 m AGL) for 14 August 2003. Arrival time at Turtleback Dome station (latitude = 37.713°; longitude = -119.706°) is 14:00 PST (22:00 UTC). Trajectory duration = 48 h.

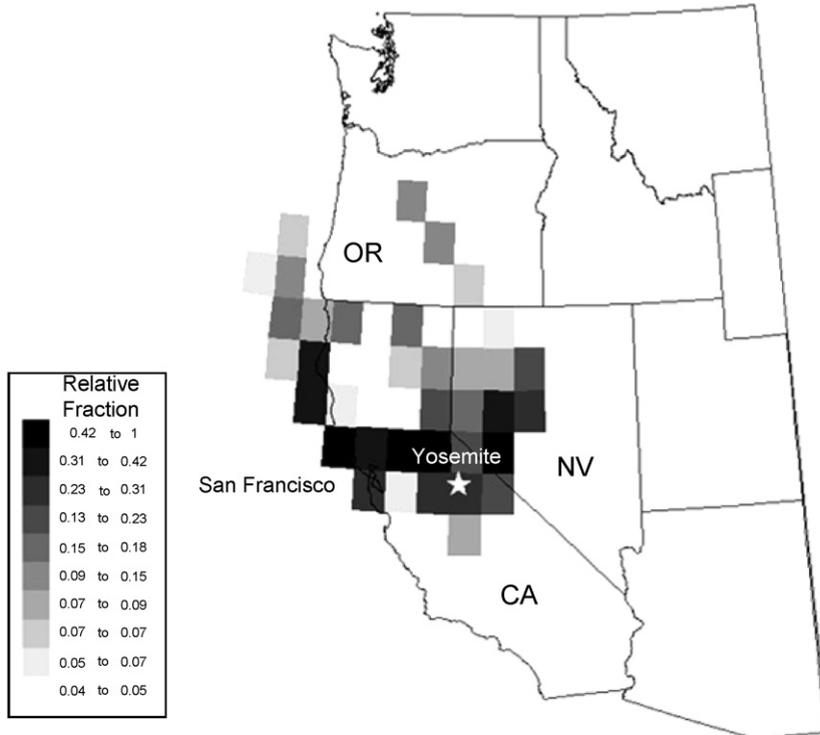


Fig. 11. Source contribution plot based on daily back-trajectory calculations for June–August 2003. Back-trajectories are restricted to days with ozone of 80 ppb or greater. The arrival time at Turtleback Dome station is 14:00 PST (22:00 UTC), the trajectory height is 100 m AGL, and the trajectory duration is 48 h. Darker grid rectangles have a higher fraction of trajectories that traverse that area.

Bay Area, Fig. 11 indicates a secondary contribution from eastern Nevada. A longer period was also investigated for hourly ozone maxima >80 ppb at Turtleback Dome during summers between 1999 and 2004. The eastern Nevada/Reno region was indicated as a source area even more strongly in this analysis.

4.8. Emission sources

Although the HYSPLIT back-trajectory calculations indicate that air transported into Yosemite on high ozone days usually originates in the Bay Area, most of the pollution entering the park is believed to result from emissions that occur downwind from the Bay Area, as the trajectories pass through the Central Valley and Sierra Nevada foothills. Dreyfus et al. (2002) and Dillon et al. (2002) examined the transport and chemical evolution of pollutants emitted in the Sacramento urban plume. Their results indicated that high ozone at the Blodgett Forest Research Station (located northwest of Sacramento along the western slope of the Sierra Nevada) is caused by anthropogenic emissions in the Central Valley and/or biogenic emissions in the Sierra Nevada foothills, and that the latter can play a significant role (Dreyfus et al., 2002). Jacobsen (2001) used a global-through urban-scale nested air pollution/weather forecast model to estimate the sources of surface ozone measured at numerous locations throughout northern and central California, including Yosemite. His calculations indicated that for typical summertime maxima, roughly 54% of the ozone in Yosemite was from anthropogenic sources, 4% was biogenic-hydrocarbon in origin, and the rest was background. The present results do not address the relative magnitudes of the different upwind emission sources that are expected to be important for Yosemite, but they do support the general hypothesis that regional-scale transport of pollutants into the park greatly exceeds local, park-based emissions.

5. Conclusion

Most sites in and around Yosemite experience roughly similar ozone concentrations during well-mixed daytime periods, but dissimilar concentrations at night. Locations that are well exposed to the free troposphere during evening hours tend to experience higher (and more variable) nocturnal ozone concentrations, resulting in smaller diurnal

variations and higher overall ozone exposures. Locations that are poorly exposed to the free troposphere during nocturnal periods tend to experience very low evening ozone, yielding larger diurnal variations and smaller overall exposures. The present data suggest that modelers need to explicitly include the local topography and transport dynamics when attempting interpolations/assessments for remote locations and complex terrain.

Acknowledgments

Financial support for this project was provided by the Faculty Alumni Fellowship Fund and the Faculty Development Fund at Saint Mary's College (SMC), and by the Air Resources Division of the National Park Service. SMC students Christina Estill and Jason McLean assisted with data collection and analysis in 2003. Essential logistical support at Yosemite National Park was provided by Katy Warner, Kyle Kline, and Lee Tarnay, while Larry Ford provided support for measurements in Inyo National Forest. Debbie Miller and Drew Bingham at the NPS Air Resources Division assisted in the map and back-trajectory graphics. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model used in this publication. Thanks are also due to Craig Clements for sharing his SODAR and meteorological data.

References

- Air Pollution Control Division (APCD), 2003. Colorado Department of Public Health and Environment, Denver, CO <<http://apcd.state.co.us/psi/smkozone.html>>.
- Air Quality in the National Parks, 2002. Air Resources Division Report, National Park Service, Denver, CO <<http://www2.nature.nps.gov/air/pubs/aqnps.htm>>.
- Ashbaugh, L.L., Malm, W.C., Sadeh, W.Z., 1985. A residence time probability analysis of sulfur concentrations at Grand Canyon National Park. *Atmospheric Environment* 19, 1263–1270.
- Bytnerowicz, A., Arbaugh, M.J., Alonso, R. (Eds.), 2003. *Ozone Air Pollution in the Sierra Nevada: Distribution and Effects on Forests*. Elsevier, Amsterdam.
- California Air Resources Board, 2001. *Ozone Transport: 2001 Review*. California Environmental Protection Agency, Sacramento, CA.
- Clements, C.B., 2007, in preparation.
- Clements, C.B., Zhong, S., Kim, S.B., Kim, S., Burley, J.D., 2004. High-altitude ozone concentrations in Yosemite

- National Park, Sierra Nevada. In: Proceedings of the 16th Conference on Air Pollution Meteorology, American Meteorological Society. Vancouver, BC, 22–27 August 2004.
- Dillon, M.B., Lamanna, M.S., Schade, G.W., Goldstein, A.H., Cohen, R.C., 2002. Chemical evolution of the Sacramento urban plume: transport and oxidation. *Journal of Geophysical Research* 107 (D5), 4045–4059.
- Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website <<http://www.arl.noaa.gov/ready/hysplit4.html>>. NOAA Air Resources Laboratory, Silver Spring, MD.
- Dreyfus, G.B., Schade, G.W., Goldstein, A.H., 2002. Observational constraints on the contribution of isoprene oxidation to ozone production on the western slope of the Sierra Nevada, California. *Journal of Geophysical Research* 107 (D19), 4365–4381.
- Fraczek, W., Bytnerowicz, A., Arbaugh, M.J., 2003. Use of geostatistics to estimate surface ozone patterns. In: Bytnerowicz, A., Arbaugh, M.J., Alonso, R. (Eds.), *Ozone Air Pollution in the Sierra Nevada: Distribution and Effects on Forests*. Elsevier, Amsterdam, pp. 215–247.
- Gebhart, K.A., Schichtel, B.A., Barna, M.G., Malm, W.C., 2006. Quantitative back-trajectory apportionment of sources of particulate sulfate at Big Bend National Park, TX. *Atmospheric Environment* 40, 2823–2834.
- Honrath, R.E., 2004. Regional and hemispheric impacts of anthropogenic and biomass burning emissions on summertime CO and O₃ in the North Atlantic lower free troposphere. *Journal of Geophysical Research* 109 (D24).
- Jacobsen, M.Z., 2001. GATOR-GCMM 2. A study of daytime and nighttime ozone layers aloft, ozone in national parks, and weather during the SARMAP field campaign. *Journal of Geophysical Research* 106 (D6), 5403–5420.
- Lee, E.H., 2003. Use of auxiliary data for spatial interpolation of surface ozone patterns. In: Bytnerowicz, A., Arbaugh, M.J., Alonso, R. (Eds.), *Ozone Air Pollution in the Sierra Nevada: Distribution and Effects on Forests*. Elsevier, Amsterdam, pp. 165–194.
- Löffler-Mang, M., Kossmann, M., Vogtlin, R., Fiedler, F., 1997. Valley wind systems and their influence on nocturnal ozone concentrations. *Contributions to Atmospheric Physics* 70, 1–14.
- McMeeking, G.R., Kreidenweis, S.M., Carrico, C.M., Lee, T., Collet Jr., J.L., Malm, W.C., 2005. Observations of smoke influenced aerosol during the Yosemite Aerosol Characterization Study: size distributions and chemical composition. *Journal of Geophysical Research* 110 (D18).
- Ray, J.D., 2001. Spatial distribution of tropospheric ozone in National Parks of California: interpretation of passive-sampler data. *The Scientific World* 1, 483–497.
- Ray, J.D., 2006. Portable Ozone Systems (POMS). Air Resources Division, National Park Service <<http://www2.nature.nps.gov/air/studies/portO3.cfm>>.
- Rolph, G.D., 2003. Real-time Environmental Applications and Display system (READY) Website <<http://www.arl.noaa.gov/ready/hysplit4.html>>. NOAA Air Resources Laboratory, Silver Spring, MD.
- Van Ooy, D.J., Carroll, J.J., 1994. The spatial variation of ozone climatology on the western slope of the Sierra Nevada. *Atmospheric Environment* 29, 1319–1330.