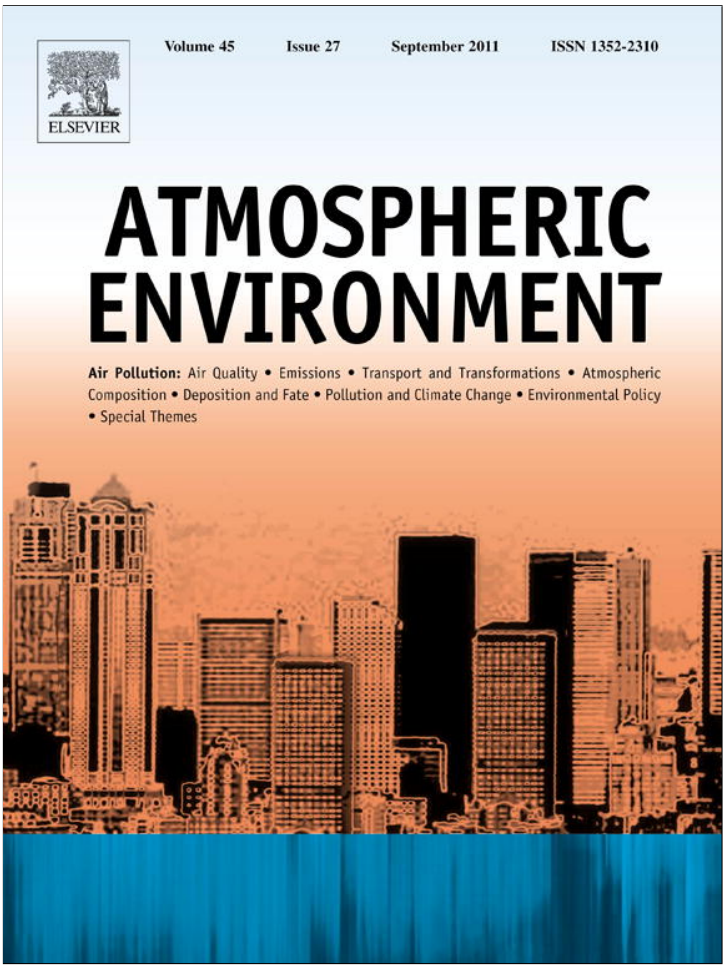

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Surface ozone in the White Mountains of California

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ABSTRACT

Surface ozone concentrations are presented for four high-elevation sites along a north–south transect along the spine of the White Mountains and a fifth site located at lower elevation approximately 15 km to the west on the floor of the Owens Valley. The ozone data, which were collected from mid-June through mid-October of 2009, include results from two sites, White Mountain Summit (4342 m elevation) and Barcroft Station (3783 m), that are believed to be higher in elevation than any previously investigated sampling locations in North America. Average daily ozone values from the five sampling sites display similar day-to-day and week-to-week temporal fluctuations, which suggest that the sites are experiencing the same regional-scale background patterns in air quality and meteorology. Ozone concentrations increase with increasing elevation, consistent with findings from prior studies in Europe and North America. A linear elevation gradient of $+0.0042$ ppb m^{-1} is obtained for July 15–August 15, but analogous gradients for August 15–September 15 and September 15–October 15 show reduced linearity and possibly the onset of a plateau in ozone concentrations for elevations above 2000 m. Average diurnal cycle magnitudes decrease with increasing elevation, falling from ~25–35 ppb for the Owens Valley site to ~3–7 ppb at three of the four high-elevation sites. Diurnal cycle magnitudes decrease (or remain roughly constant) at the non-Summit sites during the progression from mid-July to mid-October, but the magnitude of the diurnal cycle at the Summit increases from ~3 ppb to ~7 ppb over this same time frame. This latter result is inconsistent with results from previous investigations at other alpine sites, and may indicate the presence of local, topography-influenced mixing dynamics that are unique to the White Mountains. High hourly ozone concentrations at White Mountain Summit are found to correlate with 72-hour HYSPLIT back-trajectories that reflect enhanced levels of ozone transport from polluted regions (such as the Central Valley of California) or meteorological conditions that are favorable for ozone production. Low ozone concentrations at the Summit are found to correlate with HYSPLIT back-trajectories that reflect reduced levels of ozone transport from polluted areas or meteorological conditions that are unfavorable for ozone production.

1. Introduction

Ozone is one of the main components of photochemical smog and has been designated as a criteria pollutant by the U.S. Environmental Protection Agency (EPA, 2010). The photochemical processes that regulate tropospheric ozone have been extensively studied; readers who wish to review the pertinent details are directed to the comprehensive tutorial from Crutzen et al. (1999). Emissions of ozone precursors, such as NO_x ($=NO + NO_2$) and volatile organic compounds (VOCs), are usually associated with human activities such as transportation or industry, and ozone concentrations tend to be highest in urban environments (e.g. Los Angeles) that have both (i) elevated concentrations of the requisite precursors and (ii) warm, sunny weather that favors the kinetics of the photochemical formation sequences. Elevated ozone concentrations have also been observed in more remote alpine areas, where long-range transport of ozone from urban source regions and/or downward mixing of ozone-rich air from above – rather than local photochemical production – can play a significant role (Bytnerowicz et al., 2003; Burley and Ray, 2007; Chevalier et al., 2007; Cristofanelli et al., 2010; Senik and Elansky, 2001; Grigorieva and Polischuk, 2005; Wooldridge et al., 1997).

Because remote alpine measurements are frequently unaffected by local anthropogenic emissions, they have been used to assess changes in regional or global background ozone (Jaffe and Ray, 2007; Oltmans et al., 2006). In recent years a number of studies – most of which have emphasized coastal data from surface-based monitors

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Table 1
Sampling locations and timelines.

Site	Elevation (m)	Latitude	Longitude	Start	End	Sampling period (day-of-year)
Owens Valley Lab	1237	37.3602	−118.3297	Jun 9	Oct 18	160 to 291
USFS Cabins	2224	37.2729	−118.1480	Jun 10	Oct 18	161 to 291
Crooked Creek	3088	37.4990	−118.1719	Jun 9	Oct 16	160 to 289
Barcroft Station	3783	37.5831	−118.2372	Jun 9	Oct 17	160 to 290
White Mtn. Summit	4342	37.6342	−118.2557	Jul 14	Oct 20	195 to 293

or vertical profiles from ozonesondes – have examined background ozone concentrations entering western North America (Cooper et al., 2010; Oltmans et al., 2008; Jaffe et al., 2003; Weiss-Penzias et al., 2006). The majority of these studies have detected a long-term increase in springtime ozone entering the North American continent. Vingarzan (2004) conducted a comprehensive review of global background ozone levels and trends and concluded that, for mid-latitudes in the northern hemisphere, background ozone was in the range of 20–45 ppb, and was rising by 0.5–2.0% per year.

This paper presents surface ozone data measured in the White Mountains of California during the summer and early fall of 2009. Sampling elevations (above mean sea level) ranged from 1237 m on the floor of Owens Valley to 4342 m at the summit of White Mountain Peak. These results represent the first reported measurements of ozone in the White Mountains, and the data from White Mountain Summit and Barcroft Station are believed to be the highest elevation surface-based ozone concentrations ever recorded in North America.

2. Experimental methods and procedures

2.1. Ozone monitors, measurement protocols

Ozone concentrations were measured using Model 202 Ozone Monitors from 2B Technologies, which employ UV absorption (Beer's Law) at a wavelength of 254 nm. Ambient air was sampled approximately 2–3 m above ground level via a 2.5 m length of 6.35 mm (0.25 inch) o.d. Teflon tubing. The sampling inlet consisted of a downward-facing 47 mm diameter Teflon filter holder equipped with a 1–2 μm Teflon filter membrane, which was shielded from precipitation by a plastic rain shield. For the measurements at Crooked Creek Station the ozone monitor was positioned on a bench in an unheated tool shed, with the sampling line passing through a small hole in the wall to the inlet mounted above the roof. For all other locations the ozone monitor was placed in a weatherproof plastic case. Power for the ozone monitors was provided either by the local AC power grid (Crooked Creek, Barcroft) or by a 12-volt solar power system consisting of a photovoltaic solar panel, a lead-acid battery, and a solar charge controller. Ozone concentrations were measured every 10 s, and were automatically recorded into internal monitor memory as 5-minute averages. These 5-minute averages were subsequently downloaded from the ozone monitors and converted into hourly averages. The hourly averages then underwent additional processing to yield either daily averages or average diurnal cycles for each sampling location.

2.2. Sampling locations and timeline

Ozone monitors were deployed at five different locations ranging in elevation from 1237 to 4342 m above mean sea level.

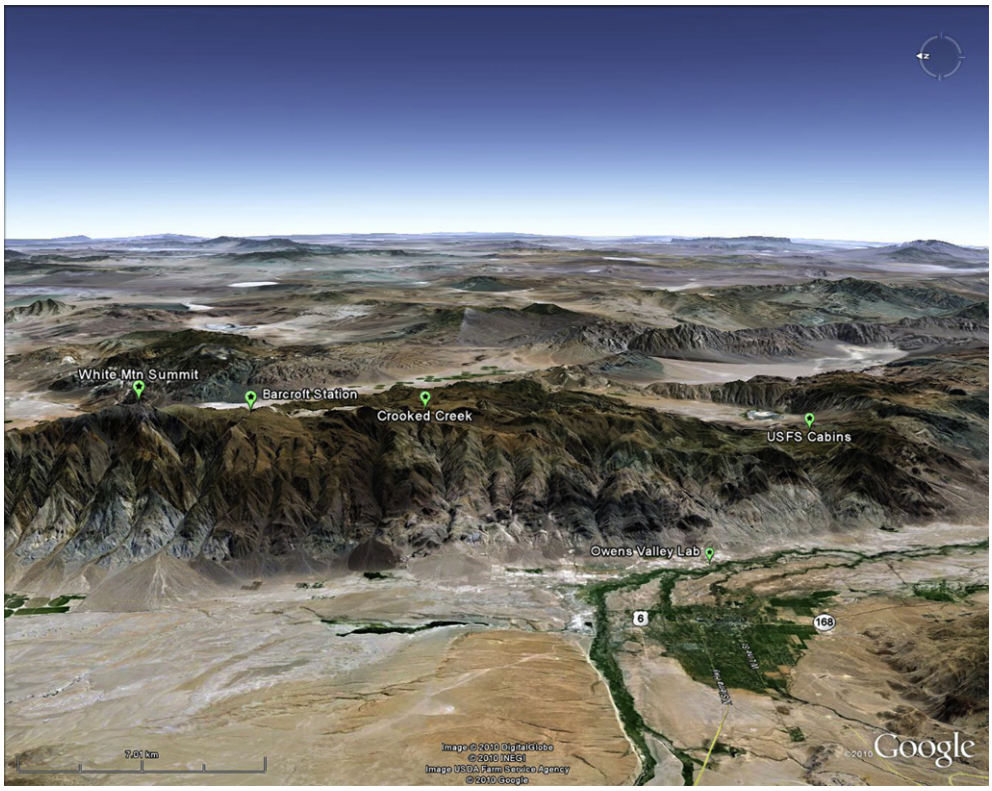

Fig. 1. Map of the five sampling sites utilized in this study. Corresponding latitude/longitude/elevation data for each sampling site are presented in Table 1.

These locations are summarized in Table 1, and a map of the sampling sites is presented in Fig. 1. Table 1 also contains the starting and ending dates for data collection at each site. To facilitate comparisons according to a common timeline, only the hourly data corresponding to 00:00 Pacific Standard Time (PST) on June 15 (day-of-year = 166.0000) through 23:00 PST on October 15 (day-of-year = 288.9583) are used to calculate average diurnal cycles and single-point averages. The ozone data for White Mountain Summit start approximately one month later than the other four sites because access to the Summit laboratory was blocked by snow until mid-summer.

2.3. Calibration of the ozone monitors

The ozone monitors used in this study were calibrated against a NIST-traceable Thermo Scientific 49i Ozone Analyzer standard at the 2B Technologies facility in Colorado before being deployed to the field. While 2B claims an overall accuracy and precision (1σ) of 1.5–2.0 ppb for a Model 202 monitor measuring ambient ozone concentrations between 0 and 100 ppb, previous fieldwork under similar conditions in Yosemite National Park (Burley and Ray, 2007) and at other locations in the Sierra Nevada mountains suggests that the uncertainty associated with field-deployed monitors is somewhat higher. All of the measurements presented here correspond to an estimated precision of ±5 ppb and an estimated accuracy of ±5%. Readers interested in a more detailed treatment of field-based assessments of monitor performance are directed to the discussion in Burley and Ray (2007).

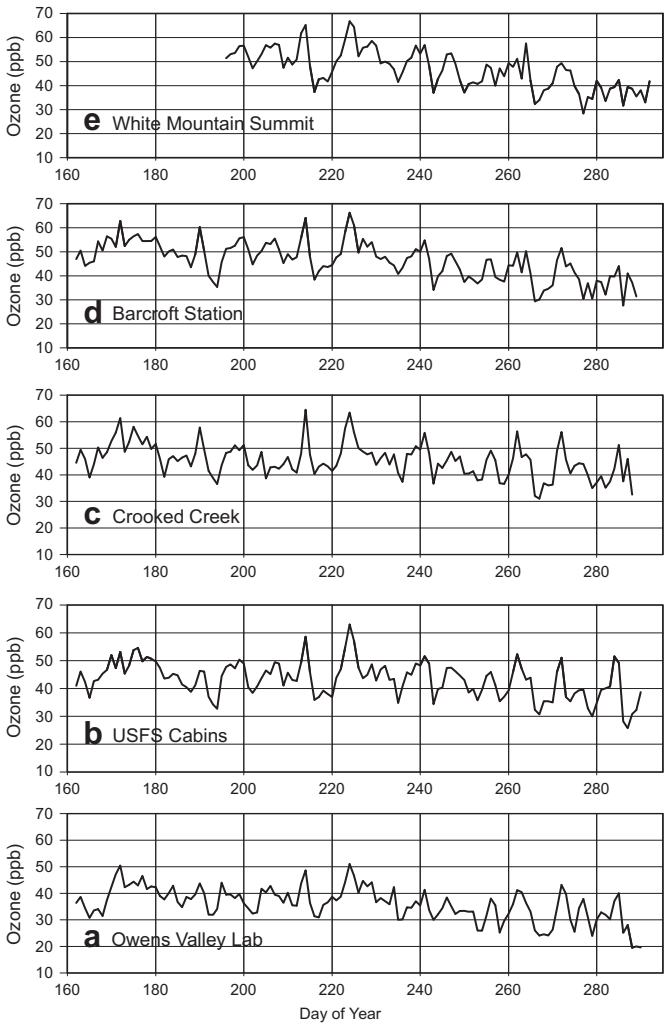

Fig. 2. Time-series plots of the daily average ozone concentrations (ppb) measured at the five sampling locations. The x-axis represents the day of year value (e.g., day 160 = June 9th; day 280 = October 7th). Fig. 2a (bottom) through 2e (top) corresponds to Owens Valley Laboratory, USFS Cabins, Crooked Creek, Barcroft Station, and White Mountain Summit, respectively.

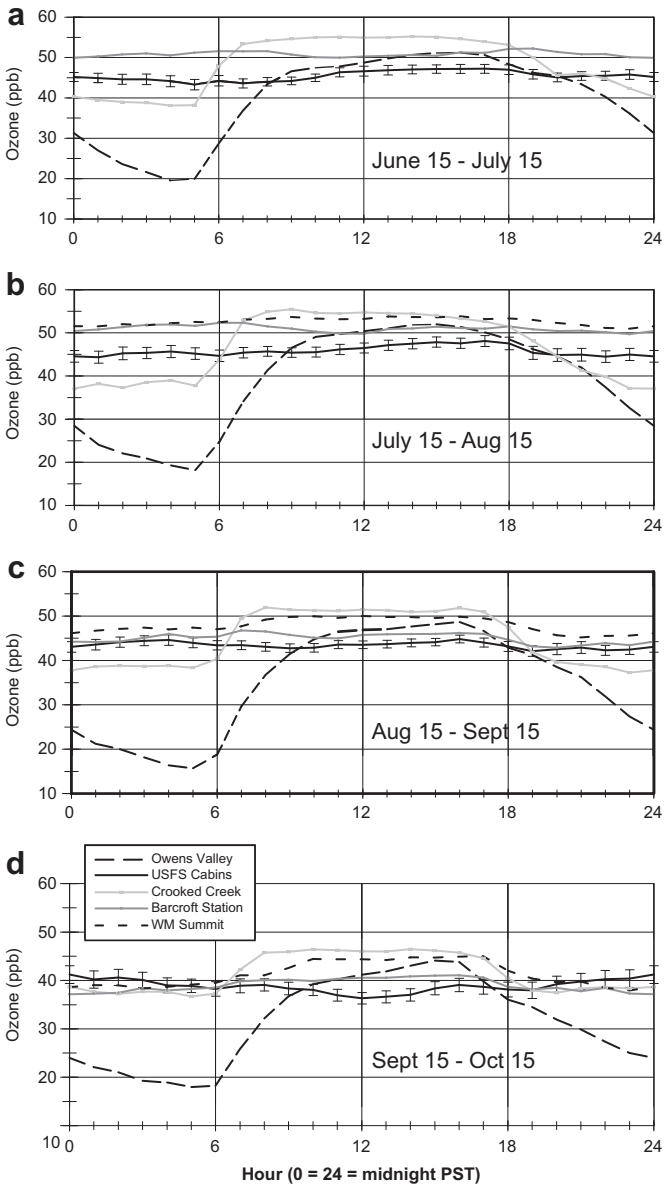

Fig. 3. Average diurnal cycles of observed ozone (ppb) for one-month periods between June 15 and October 15. Fig. 3a (top) through 3d (bottom) correspond to averaging periods of June 15–July 15, July 15–August 15, August 15–September 15, and September 15–October 15, respectively. Representative uncertainties (±1 standard deviation of the mean) are included for the USFS Cabins site; uncertainties at the other sites – which are of similar magnitude – have been omitted to improve clarity.

2.4. Wind rose data for White Mountain Summit

In order to assess the influence of local meteorological conditions on the ozone data from White Mountain Summit, monthly wind rose diagrams compiled for this location by the Western Regional Climate Center (WRCC, 2010) were downloaded from the

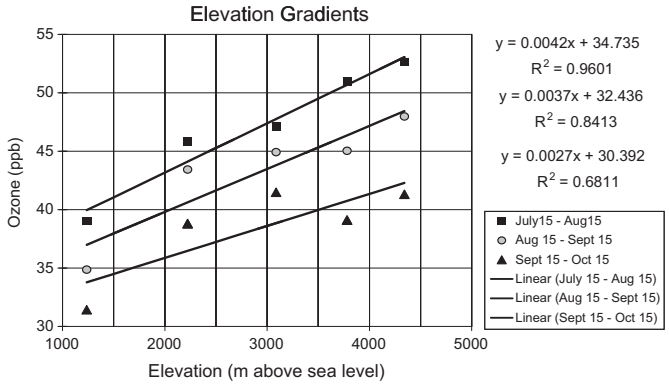

Fig. 4. Elevation-based trends in the monthly average ozone data. The squares, circles, and triangles represent the data for July 15–August 15, August 15–September 15, and September 15–October 15, respectively.

weather page of the White Mountain Research Station web site (WMRS, 2010). The wind rose data correspond to six years (2004–2009) of observations for the months of June, July, and August, and seven years of observations (2003–2009) for the months of September and October.

2.5. HYSPLIT back-trajectory calculations

The regional-scale transport patterns responsible for bringing elevated (or reduced) ozone concentrations to these remote sites were investigated by conducting back-trajectory calculations with the online version of the HYSPLIT model (Draxler and Hess, 1997, 1998; Draxler, 1999; Draxler and Rolph, 2010; Rolph, 2010). Calculations were performed using the 40 km EDAS (Eta Data Assimilation System) archived meteorological data, with a run time of 72 h and an arrival height of 500 m AGL. Some calculations with arrival times corresponding to the beginning or mid-point of any given month had shorter run times because of restricted data availability. The limited spatial resolution of the HYSPLIT calculations restricts the back-trajectory analysis to regional-scale effects, so that localized mixing dynamics – which may play a significant role, given the sharply-contoured alpine topography of these high elevation sites – are not resolved in the back-trajectories.

3. Results

3.1. Daily averages – time-series plots

Daily average ozone values (calculated from the hourly data) for the five sampling locations are presented as stack plots in Fig. 2. All five sampling sites display similar temporal trends, which suggest that all of the sites are experiencing the same regional-scale background patterns in air quality and meteorology. The measured ozone concentrations tend to increase in magnitude with increasing elevation, and the day-to-day variability in the daily values is somewhat higher for the higher elevation sites.

3.2. Diurnal cycles

Average diurnal cycles corresponding to month-long sampling periods are shown in Fig. 3, along with representative uncertainties (±1 standard deviation of the mean) for the USFS Cabins site. Analogous uncertainties for the other sampling sites, which are very similar in magnitude to those observed for the USFS Cabins site, are not included in Fig. 3 so as to reduce clutter and improve legibility. The data in Fig. 3a–d correspond to June 15–July 15 (day-of-year = 166 to 196), July 15–August 15 (day-of-year = 196–227), August 15–September 15 (day-of-year = 227–258), and September 15–October 15 (day-of-year = 258–288), respectively. While all five sites experience similar ozone maxima between the hours of 10:00 to 17:00 PST, substantially different concentrations are measured at other hours, resulting in diurnal variations that vary widely in overall magnitude. The Owens Valley site exhibits the largest diurnal variability, with ozone concentrations rising from an early morning minimum below 20 ppb to an afternoon maximum in the range of ~43 to ~52 ppb. Crooked Creek shows a smaller diurnal variability, with early morning minima slightly below 40 ppb and afternoon maxima in the range of ~ 45 to ~ 55 ppb. The other three sites display much smaller diurnal variations, with ozone concentrations remaining mostly constant throughout the day.

A number of general trends become apparent in the progression from early summer (Fig. 3a, June 15–July 15) to early fall (Fig. 3d, September 15–October 15). The mid-day maxima decline from an approximate range of 45–55 ppb to 35–45 ppb. The site-to-site variability in the evening data (i.e. 20:00 to 06:00 PST) becomes much smaller, with all of the sites except Owens Valley yielding essentially identical nighttime ozone concentrations in Fig. 3d. And the diurnal cycle for White Mountain Summit evolves from no diurnal variability in Fig. 3b to a ~ 7 ppb difference between mid-day and evening values in Fig. 3d. A concurrent increase in the diurnal variability is not seen at the other sites; Barcroft Station and the USFS Cabins remain relatively flat, while Crooked Creek and Owens Valley Lab see a marked decrease in the magnitude of the diurnal variability.

3.3. Average ozone concentrations: elevation gradient

Average ozone concentrations as a function of site elevation are presented in Fig. 4 and Table 2. The average values for each sampling site are calculated from the same hourly data used to prepare Fig. 3b–d, and have been separated into the same one-month periods. All three sampling periods indicate that average ozone concentration increases with elevation, but the linearity of

Table 2
Average ozone (ppb) as a function of elevation.

Site	Elevation (m)	July 15–Aug. 15		Aug. 15–Sept. 15		Sept. 15–Oct. 15	
		Ave.	Std. err.	Ave.	Std. err.	Ave.	Std. err.
Owens Valley Lab	1237	39.01	0.50	34.87	0.49	31.43	0.47
USFS Cabins	2224	45.83	0.27	43.43	0.22	38.80	0.31
Crooked Creek	3088	47.08	0.41	44.93	0.32	41.48	0.33
Barcroft Station	3783	50.98	0.27	45.03	0.26	39.11	0.30
White Mtn. Summit	4342	52.68	0.28	47.97	0.28	41.32	0.33
Slope (ppb m^{-1})		0.0042		0.0037		0.0027	
R-squared value		0.9601		0.8413		0.6811	

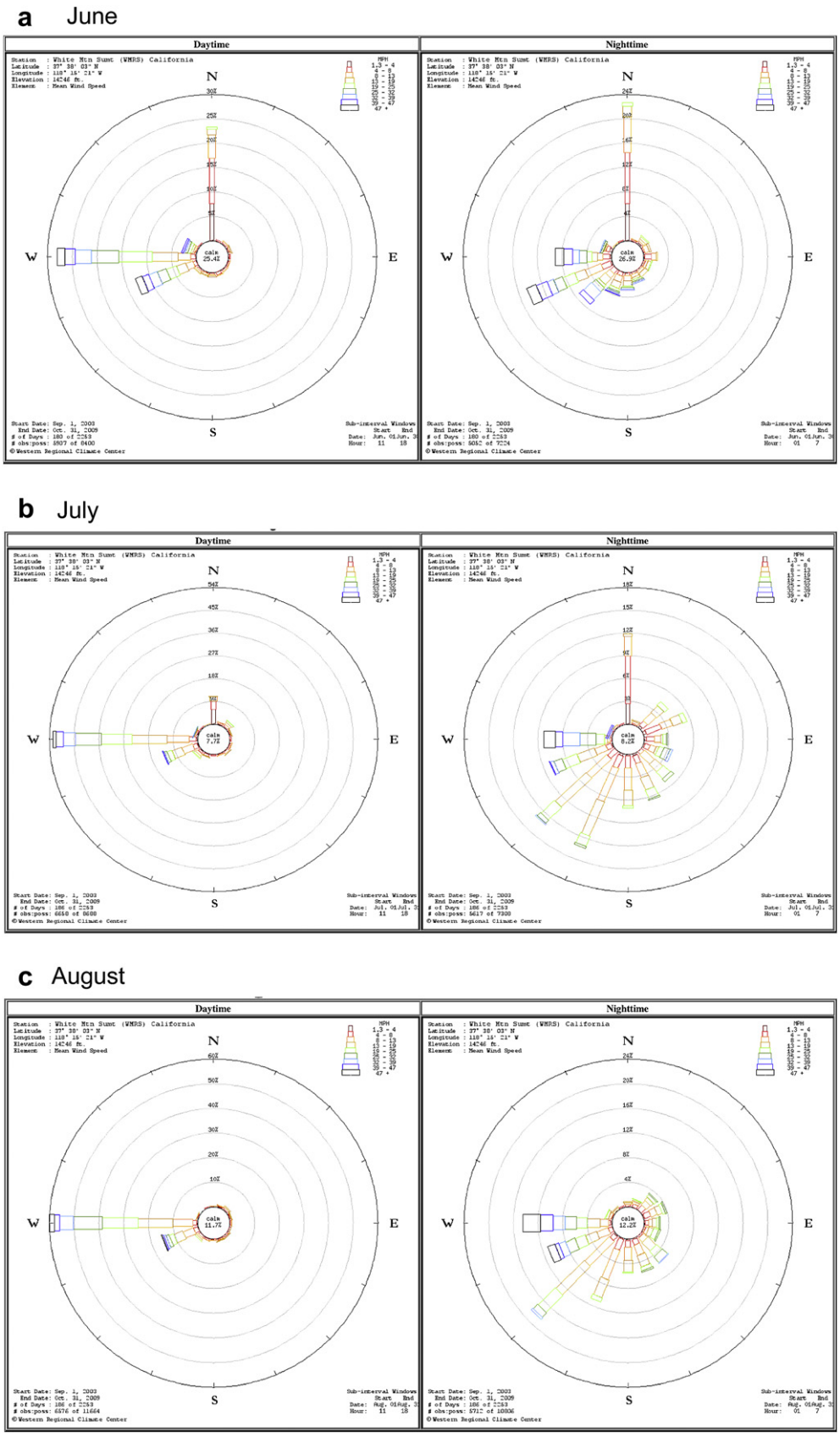

Fig. 5. Wind rose plots for White Mountain Summit. Fig. 5a–e corresponds to June, July, August, September, and October, respectively, and represent either six years (2004–2009; June, July, August) or seven years (2003–2009; September, October) of data collection.

the relationship decreases markedly as one progresses from the July 15–August 15 period ($R^2 = 0.9601$) to August 15–September 15 ($R^2 = 0.8413$) and September 15–October 15 ($R^2 = 0.6811$). The overall slope of the elevation gradient decreases as the sampling period moves from July 15–August 15 (slope = 0.0042 ppb m^{-1}) to August 15–September 15 (slope = 0.0037 ppb m^{-1}) and September 15–October 15 (slope = 0.0027 ppb m^{-1}). A similar regression analysis of the June 15–July 15 results, which lack data from White Mountain Summit, yields a slope of 0.0043 ppb m^{-1} and an R^2 value of 0.9818, nearly identical to that obtained for July 15–August 15. This latter regression has been omitted from Fig. 4 since it does not include data from the Summit site.

The preliminary elevation gradient data shown in Fig. 4 may indicate a seasonal shift from a linear relationship across the entire elevation range for mid-summer (July 15–August 15), to an incline at lower elevations followed by a plateau for elevations above 2000 m in early fall (September 15–October 15). Year-round measurements are needed to confirm the preliminary results presented here and ascertain possible seasonal shifts in the elevation dependence for fall, winter, and spring.

3.4. Wind rose results

The local wind rose climatology data for White Mountain Summit, presented in Fig. 5, indicate that winds are primarily from the north or west during daytime hours, and from the north or west – southwest at night. The months of July, August and September are dominated by daytime approaches from due west, when daytime heating of Owens Valley air – and subsequent upslope flows – are strongest. Differences between daytime and nighttime data become more significant during the months of July, August, and September, but decline substantially in October, when daytime and nighttime observations are nearly identical.

4. Discussion

4.1. Unique sampling site characteristics

The measurement locations utilized in the present study possess a number of unique features for an analysis of surface ozone in an alpine environment. The overall increase in elevation – more than

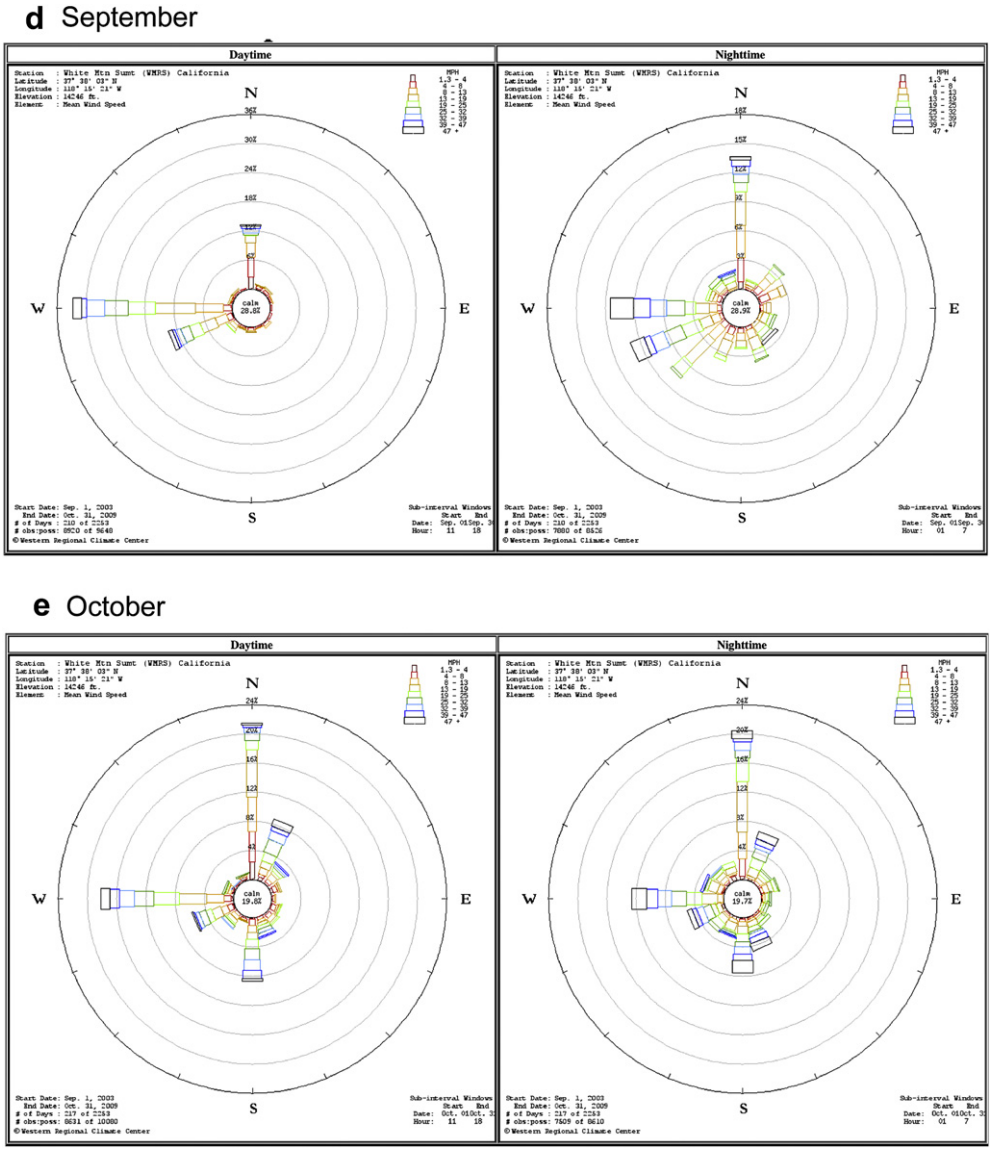

Fig. 5. (*continued*).

3100 m – is substantial, and the site at the summit of White Mountain Peak is the highest elevation scientific research facility in North America. The four sites located along the spine of the White Mountains lie along a north–south transect that is approximately 40 km in length, rising from an elevation of 2244 m (USFS Cabins) to 4342 m (White Mountain Summit). The fifth site is situated at an elevation of 1237 m at the northern end of the Owens Valley, located roughly 15 km west of the north-south transect and 3 km from the eastern edge of Owens Valley. The study region is approximately 375 km north of downtown Los Angeles, 270 km south of Reno, 370 km southwest of San Francisco, and 300 km northwest of Las Vegas. Four of the sites – all except USFS Cabins – host basic meteorological measurements (temperature, wind speed and direction, etc.), with data available online from the Western Regional Climate Center (WRCC, 2010). These latter four sites comprise the White Mountain Research Station (WMRS), which is a multi-campus research unit of the University of California Office of Research (WMRS, 2010).

The high elevation of the sampling locations and their remote location – approximately 45 km east of the eastern crest of the Sierra Nevada Mountains and hundreds of kilometers distant from major urban areas – make them excellent choices for the measurement of regional background ozone. Most measurements of alpine ozone in California have taken place on the western slope of the Sierra Nevada – and at significantly lower elevations – which can be heavily impacted by pollution transported upslope from California's Central Valley (Bytnerowicz et al., 2003). There have been relatively few measurements of ozone in the eastern Sierra Nevada (Burley and Ray, 2007), and no prior measurements in the White Mountains.

4.2. Comparisons to other high elevation measurements

Ozone mixing ratios at alpine sites are strongly influenced by a number of factors, including proximity to urban sources of ozone precursors, seasonal variability, local topography, and the frequency of downward mixing of ozone-rich air from the stratosphere. These complications make it difficult to make direct comparisons between different measurement sites. The comparisons presented here will emphasize sites that are located either at extremely high elevations (~3000 m or above) or at slightly lower elevations but in locations that are not likely to be influenced by regional emissions of ozone precursors.

4.2.1. European sites

Ozone concentrations at high elevation alpine sites have been investigated for many decades at locations including Jungfraujoch (3580 m) and Zugspitze (2960 m) in the Alps and Kislovodsk (2070 m) in the Caucasian Mountains along the eastern border of Europe. A good summary of the western European data is provided by Chevalier et al. (2007), who report average values of 51.5 ppb (Zugspitze), 51.4 ppb (Sonnblick, 3106 m), and 53.3 ppb (Jungfraujoch) for measurements from 2001 through 2004. These results are similar to those reported by Bronnimann et al. (2000), who obtained 50.2 ppb at Jungfraujoch for 1992–1998. More recent Jungfraujoch data are presented by Balzani Loov et al. (2008), who separate the 2005 data into seasonal averages. They report summer and fall values of 54 and 47 ppb, respectively, and an overall yearly average of 52 ppb. These values are slightly higher than the earlier measurements from Sandroni et al. (1994), who report a Jungfraujoch value of 50 ppb for July 1991. The Kislovodsk results, in contrast, are somewhat lower than those from Jungfraujoch, with ozone mixing ratios ranging from 42.2 ppb (2001–2004 average; Tarasova et al., 2009) to 45–46 ppb (spring and summer monthly averages for 1989–1990 and annual medians for 1991, 1992, 1995, and 1998; see Yelansky and Senik, 1995; Senik and Elansky, 2001). The lower mixing ratios measured at Kislovodsk likely reflect its more remote location, 2600 km due east (but 1500 m lower in elevation) than Jungfraujoch.

The ozone mixing ratios reported in these European studies are consistent with the 2009 summertime data for Barcroft Station and White Mountain Summit (see summary of average values in Table 2). In addition, the elevation gradient of $+0.003$ ppb m^{-1} reported by Chevalier et al. (2007) for measurement locations above 1200 m is similar in magnitude to the gradients observed in the White Mountains, which range in value from $+0.0042$ to $+0.0027$ ppb m^{-1} (Table 2, Fig. 4). It should be noted, however, that these latter values correspond only to mid-summer to early fall observations from a single year, while those from Chevalier et al. (2007) represent four full years of data.

4.2.2. Asian sites

In contrast to Europe, relatively few alpine measurements have been reported for Asian locations. Ozone mixing ratios have been reported for the Pamir Mountains (1400 to 4000 m) in Central Asia, Mondy in eastern Siberia (2006 m), Mount Waliguan (3816 m) on the Qinghai-Tibetan Plateau in western China, and the Nepal Climate Observatory – Pyramid (5079 m) in Nepal. Surface ozone values have also been reported for the summit region of Mount Everest at elevations ranging from 5676 to 8848 m (Semple and Moore, 2008), but with very limited temporal coverage consisting of two measurements per day for the latter half of May 2005.

The results from the Pamir Mountains (Grigorieva and Polischuk, 2005) are for summertime data collected in 1996 and display diurnal variability qualitatively similar to that observed in the current data for Owens Valley Laboratory, but with nighttime values of 5–10 ppb at night and daytime maxima of ~35 ppb. The Mondy data cover the period of 1997–1999, with June to August averages in the range of 40–42 ppb, and September to November averages of 39–41 ppb (Pochanart et al., 2003). The average mixing ratio recorded at Mount Waliguan in the spring and summer of 2003 is somewhat higher at 58 ppb, which reflects the influence of both anthropogenic emissions of ozone precursors (Wang et al., 2006) and stratosphere-to-troposphere exchange (Ding and Wang, 2006). The data from the Nepal Pyramid covers the period of March 2006 to February 2008 and yields an overall ozone concentration of 49 ppb, but with substantial variability between seasons (Cristofanelli et al., 2010). The Pyramid measurements have the distinction of being the highest elevation long-term ozone data recorded to date, at any location.

Given the wide variability in the remoteness (and elevation) of these Asian sites, the spread in the observed ozone values is not surprising. The general trend that emerges is that the more remote locations in (Pamir Mountains, Mondy) tend to experience lower ozone concentrations. Extremely high elevation sites (Nepal Pyramid) or those sometimes exposed to anthropogenic emissions (Mount Waliguan) experience higher average ozone. The White Mountain ozone concentrations are generally higher than those observed at the more remote Asian locations but lower than the concentrations from Asian sites heavily influenced by stratospheric intrusions or anthropogenic emissions.

4.2.3. Mauna Loa

Mauna Loa Observatory, which is situated at an elevation of 3397 m on the Big Island of Hawaii, has an extensive record of surface ozone data extending back to September of 1973 (MLO, 2010). Because of its isolated location – at a high elevation in the middle of the Pacific Ocean, with good access to the free troposphere – the Mauna Loa data have been used extensively in studies on background ozone trends. An analysis by Vingarzan (2004)

Table 3
Maximum and minimum hourly ozone concentrations at White Mtn. Summit.

Rank	Ozone (ppb)	Date	Hour (PST)	Day of year	Trajectory approach	# Hours inland	Figure
Maximum values							
#1	73.7	Aug. 18	4:00	230.1667	From N	>72	6a
#2	72.8	Aug. 12	20:00	224.8333	From W	55	6b
#3	71.9	Aug. 13	5:00	225.2083	From S	>72	6c
#4	69.9	Aug. 2	9:00	214.3750	From W	42	
#5	68.8	Aug. 1	7:00	213.2917	From W	64	
#6	68.4	Sept. 21	21:00	264.8750	From N	70	
#7	67.8	Sept. 21	2:00	264.0833	From N	58	
#8	66.5	Jul. 26	18:00	207.7500	From S	>72	6d
Minimum values							
#1	14.4	Oct. 15	0:00	288.0000	From W	11	7a
#2	17.4	Oct. 18	20:00	291.8333	From NW	62	
#3	18.8	Oct. 5	2:00	278.0833	From NW	30	7b
#4	20.6	Oct. 4	8:00	277.3333	From NW	48	
#5	23.3	Oct. 6	22:00	279.9167	From N	>72	7c
#6	24.7	Sept. 30	3:00	273.1250	From NW	28	
#7	25.4	Aug. 4	7:00	216.2917	From SW	18	7d
#8	25.6	Sept. 7	7:00	250.2917	From W	42	

reported annual mean concentrations (for UTC = 10:00 to 18:00) in the range of 37–46 ppb over the period spanning 1992–2001. Oltmans et al. (2006) reported that the Mauna Loa ozone concentrations had increased by approximately $3.5 \pm 1.5\%$ per decade between 1973 and 2004, but with substantial seasonal (and year-to-year) variability. Hourly Mauna Loa data are readily available from the official observatory website (MLO, 2010); these values yield July 15–October 15 averages of 35.8 and 37.5 ppb, respectively, for 2007 and 2008, the two most recent years that are available. These values are notably lower than the corresponding mean of 47.4 ppb from White Mountain Summit for July 15–October 15 of 2009, likely reflecting the cleaner environment at the more remote Mauna Loa site. Comparison of daily average values for the July 15–October 15 timeframe indicates that the Mauna Loa ozone values remain essentially constant over this three-month period while the data from White Mountain Summit show a pronounced seasonal decline.

4.2.4. North American sites

Most of the surface ozone data measured in North America over the past 40 years have been collected in urban areas that are heavily impacted by anthropogenic emissions (EPA, 2010; CARB, 2010). While remote locations have, in contrast, received less attention, there has nonetheless been substantial recent interest in long-term trends in at remote sites. Much of the recent work has focused upon air masses entering the west coast of North America and the influence of long-range transport from Asia (Cooper et al., 2010; Oltmans et al., 2008; Jaffe et al., 2003); these investigations have relied primarily on data collected from coastal monitors. Other studies have examined trends at remote inland locations, some of which are at higher elevations (e.g., Jaffe and Ray, 2007). Many of the high-elevation datasets that are currently available for North America come from Rocky Mountain sites in Colorado or Wyoming that correspond to maximum elevations of ~3000–3500 m, which are somewhat lower than the elevations for Barcroft Station and White Mountain Summit.

Previous measurements at high elevation sites in the Rocky Mountains are in general agreement with the data from the White Mountains, but differ regarding the magnitude of the elevation gradient. Fehsenfeld et al. (1983) presented data from June 1980–July 1981 for the Niwot Ridge site (3048 m elevation) in Colorado, approximately 80 km northwest of Denver. Their data for July of 1981 indicate an average of approximately 47–48 ppb. Wooldridge et al. (1997) reported data for the first six months of 1990–1994 at a 3180 m elevation site located approximately 55 km west of Laramie, Wyoming. They obtained June averages ranging between 46.1 and 52.2 ppb. More recently, Brodin et al. (2010) conducted an extensive study along an elevation gradient in the Colorado Front Range Mountains. They reported surface ozone concentrations for seven sites ranging between 1608 and 3528 m in elevation, measured between September 2007 and August 2008. Their highest elevation site measured an average summertime (June–August, 2008) concentration of approximately 60 ppb, and an average fall (September–November, 2007) concentration of approximately 50 ppb. The ozone concentration data summarized in Table 2 for the White Mountains are similar to the results from Fehsenfeld et al. (1983) and Wooldridge et al. (1997), but 8–10 ppb lower than the highest elevation data from Brodin et al. (2010). The elevation gradients from the White Mountains, which range from 0.0042 to 0.0027 ppb m^{-1} (Table 2; Fig. 4), are significantly smaller than the gradients reported by Brodin et al. (2010), who observed a monotonic wintertime increase of 0.015 ppb m^{-1}, and a two-step increase during the summertime, with a gradient of 0.045 ppb m^{-1} between 1610 m and 1940 m, and a gradient of 0.056 ppb m^{-1} between 3350 m and 3530 m.

4.3. Diurnal cycles

The diurnal cycles presented in Fig. 3 show an elevation trend that is largely consistent with observations from previous alpine measurements. Most of the cycles in Fig. 3 display slightly enhanced ozone concentrations during daylight hours, which suggests that there is still some local photochemical production of ozone in the sampled air masses. (At many mountain locations daytime ozone concentrations are actually lower than nighttime values, an observation that may reflect extremely low concentrations of ozone precursors or photochemical destruction of ozone during daylight hours.) The amplitude of the diurnal cycle decreases with increasing elevation, falling from a magnitude of ~ 34 ppb for Owens Valley Laboratory to ~ 3 ppb for White Mountain Summit (Fig. 3b). This progression is not smooth, however, and the data for Crooked Creek (3088 m) have a larger diurnal cycle than those from the lower-elevation USFS Cabins site (2224 m). It is believed that the larger diurnal magnitude for Crooked Creek reflects its more secluded topography; the Crooked Creek site is located in a shallow depression that is likely more susceptible to the formation of a nocturnal inversion layer that could enhance the nighttime destruction of near-surface ozone via dry deposition. The

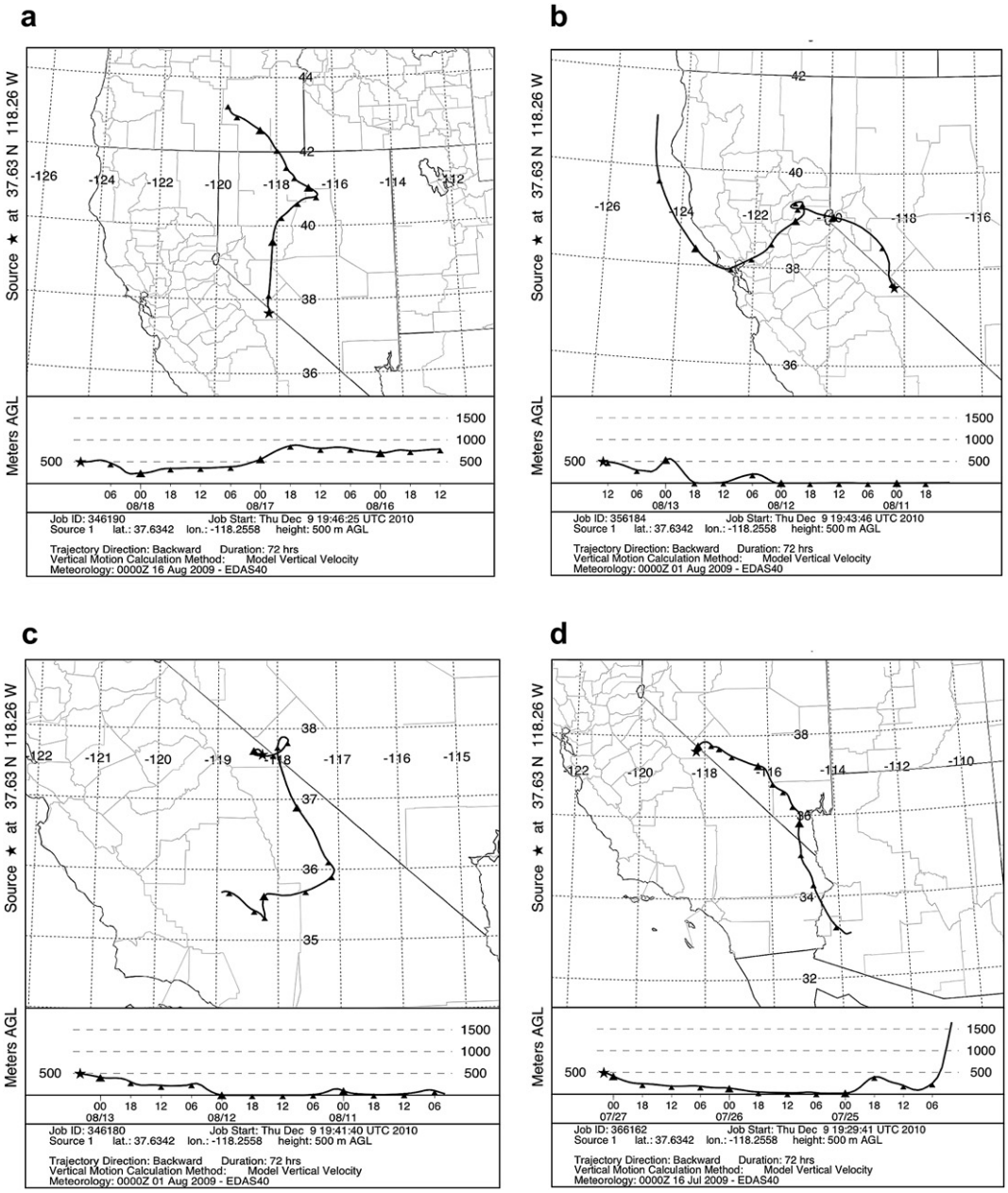

Fig. 6. HYSPLIT back-trajectory calculations for selected one-hour ozone maxima observed at White Mountain Summit. Please consult Table 3 for information regarding the corresponding ozone concentrations and Summit arrival times.

three other high-elevation sites, in contrast, are positioned on terrain that is moderately to severely sloped, where nocturnal inversion layers are less likely to occur. Wind speed data from Crooked Creek are lower at night compared to the values measured at Barcroft and White Mountain Summit, which supports this hypothesis (WRCC, 2010). This explanation is also consistent with the general observation of reduced site-to-site variability during the well-mixed hours of 10:00 to 18:00 PST.

The month-to-month evolution of the diurnal cycles in Fig. 3 includes a number of temporal trends, some of which are not presently well understood. Average ozone concentrations decline at all five measurement sites during this transition from early summer (June 15–July 15, Fig. 3a) to early fall (September 15–October 15, Fig. 3d), consistent with the arrival of cooler weather, declining solar fluxes, and reduced regional emissions of ozone precursors. The magnitudes of the diurnal cycles observed at Owens Valley Laboratory and Crooked Creek both decline, reflecting the reduction in photochemical activity. The spread in the nighttime ozone values (~20:00 to 06:00 PST) for the four highest-elevation sites decreases from a value of ~15 ppb for July 15–August 15 to ~5 ppb for September 15–October 15. The reason(s) for this latter decrease are not clear, and elucidating them may require high-resolution meteorological simulations that can accurately describe the localized transport dynamics present in the White Mountains. It is unlikely that this trend – which can be viewed as a decrease in the nocturnal ozone values being measured at the USFS Cabins, Barcroft Station, and White Mountain Summit while those measured at Crooked Creek remain essentially constant – is due to changes in local photochemical production, because (i) the observed changes are taking place during nighttime and (ii) none of these high-elevation sites have significant emissions of ozone precursors. Another mystery

that will likely require further analysis is the month-to-month evolution of the diurnal cycle for White Mountain Summit. The data for July 15–August 15 (Fig. 3b) have a diurnal magnitude of ~ 3 ppb, and similar diurnal magnitudes are observed at Barcroft Station and the USFS Cabins. As one progresses to August 15–September 15 (Fig. 3c) and September 15–October 15 (Fig. 3d), the magnitude of the diurnal cycle at the Summit increases (to ~7 ppb), which is usually indicative of an increasing contribution from photochemical production. This is a very intriguing result, since diurnal cycles at other high-elevation alpine sites have been observed to decrease from summer to fall (Brodin et al., 2010). In addition, the cycles for the USFS Cabins and Barcroft Station do not show the same trend as the Summit data. Further measurements – preferably year-round data – are needed to confirm this preliminary result and help distinguish between possible explanations.

4.4. Back-trajectory analysis of the data from White Mountain Summit

The hourly ozone data for the USFS Cabins, Barcroft Station, and White Mountain Summit are highly scattered, with large temporal variability. When these hourly values are averaged to yield the diurnal plots presented in Fig. 3, the scatter is substantially reduced and the resulting diurnal cycles that emerge have very small magnitudes (on the order of 3–4 ppb for the early part of the summer). These observations – coupled with the remote location of the White Mountain facilities, which are far removed from urban source emissions of ozone precursors – suggests that most of the ozone being measured in the White Mountains results from long-range transport, rather than local photochemical production. While preliminary HYSPLIT back-trajectory calculations were performed for all five of the measurement sites, the present discussion

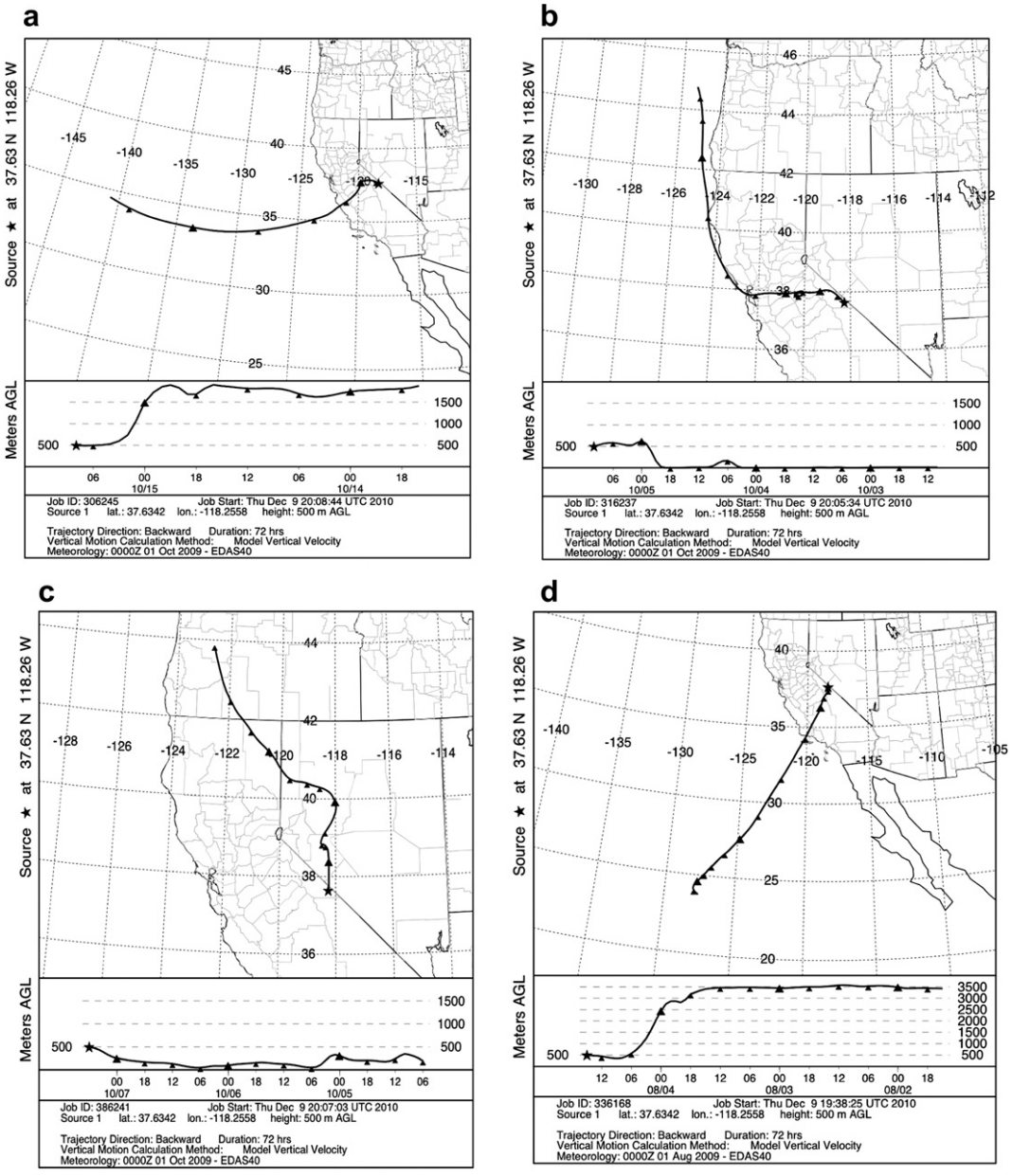

Fig. 7. HYSPLIT back-trajectory calculations for selected one-hour ozone minima observed at White Mountain Summit. Please consult Table 3 for information regarding the corresponding ozone concentrations and Summit arrival times.

shall be limited to results for White Mountain Summit because (i) its higher elevation and sharply defined local topography give it better access to the free troposphere compared to the other sites, and (ii) the limited horizontal resolution of the model does not adequately resolve meaningful distinctions between the four high-elevation sampling locations. Calculations were configured so that the arrival times would coincide with the eight highest – and eight lowest – hourly ozone values measured at White Mountain Summit across the entire measurement period. These hourly maxima and minima are summarized in Table 3, and representative back-trajectories are presented in Figs. 6 and 7.

The eight highest ozone maxima occur primarily during mid- to late summer, when production of regional background ozone is increased due to warmer temperatures and increased solar irradiance. Five out of the eight hourly maxima occur between day-of-year = 213 and day-of-year = 230 (Table 3), consistent with the trends observed previously in the daily average values (Fig. 2a). Back-trajectory calculations for these eight maxima indicate great variability in the direction of approach, with transport from the north (maxima #1, #6 and #7), west (maxima #2, #4 and #5), and south (maxima #3 and #8). Fig. 6a shows the back-trajectory corresponding to maximum #1 (northerly approach), while Fig. 6b–d shows the back-trajectories corresponding to maxima #2 (westerly approach), #3 (southerly approach), and #8 (southerly approach), respectively. The prevalence of northerly approaches is somewhat unexpected, given that previous work in the Sierra Nevada Mountains has shown that episodes of high ozone generally correlate with transport from the west or southwest, via upslope transport from the Central Valley. The northerly approaches observed for maxima #1, #6 and #7 do not pass through the Central Valley, but rather through remote portions of Oregon and Nevada. While exposure to pollution from the Central Valley (maxima #2 through #5) or Las Vegas (maximum #8, Fig. 6d), would appear to offer a straightforward explanation for five of the eight hourly maxima presented here, it cannot account for the three northerly approaches.

The eight lowest ozone minima occur primarily during late September to mid-October, consistent with the arrival of cooler weather and reduced solar irradiance. This period of time included a significant early-season winter storm on October 13–14 (day-of-year = 286–287), with heavy snowfall throughout the White Mountains. Analysis of hourly solar radiation data from White Mountain Summit and hourly precipitation data from Barcroft Station indicates, however, that the ozone minima in Table 3 are not coincident with this particular precipitation event, or with any other episodes of rain or snow that occurred during the sampling period. (The White Mountains generally receive very little precipitation compared to their Sierra Nevada neighbors, which are located approximately 45 km to the west.) Six out of the eight hourly minima occur between day-of-year = 273 and day-of-year = 291 (Table 3), consistent with the behavior observed in the daily averages (Fig. 2a). The back-trajectory calculations for the minima display approaches from the west (minima #1 and #8), northwest (minima #2, #3, #4 and #6), north (minimum #5), and southwest (minimum #7). Fig. 7a shows the back-trajectory corresponding to minimum #1 (westerly approach), while Fig. 7b–d shows the back-trajectories corresponding to minima #3 (northwesterly approach), #5 (northerly approach), and #7 (southwesterly approach), respectively.

The short-range wind rose data from Fig. 5 are generally consistent with the long-range back-trajectory results from Figs. 6 and 7. Both sets of data indicate that a significant fraction of air masses arriving at the Summit make their final approaches from the north, but with large overall variability. The upslope–downslope bimodal behavior that is observed at many alpine sites is largely absent from this high-elevation site.

The general picture that emerges from the analysis presented in Table 3, Fig. 6, and Fig. 7 is that ozone concentrations at White Mountain Summit reflect the behaviors of the corresponding back-trajectories. High hourly ozone concentrations generally correlate with slow-moving trajectories that have spent more time in inland regions, some of which are known to be highly polluted (e.g., the Central Valley of California). These slow-moving trajectories usually experience lower wind speeds and higher ambient temperatures, conditions that favor photochemical production of ozone. In some cases (Fig. 6b and c), these trajectories contain tightly wound loops that are suggestive of eddy current-type behavior that can promote the accumulation of locally produced ozone. Low hourly ozone concentrations generally correlate with fast-moving trajectories that have spent significantly more time offshore, and less time in polluted inland regions. These latter trajectories typically correspond to higher wind speeds and lower temperatures, conditions that are unfavorable for ozone production.

5. Conclusions

The data presented here represent the first measurements of surface ozone concentrations in the White Mountains of California, and include the two highest sampling elevations (4342 m and 3783 m) ever reported for a North American study. Measured ozone concentrations are in rough agreement with results from other high-elevation sites in Europe, Asia, and North America, and the general elevation-based trends that are observed in the data are mostly consistent with results from other alpine locations from around the globe. High ozone concentrations at White Mountain Summit are found to correlate with slow-moving back-trajectories that have spent more time inland and less time offshore, while low ozone concentrations are associated with fast-moving back-trajectories that have had limited exposure to polluted inland air. A number of features in the data – some of the month-to-month and spatial trends in the diurnal cycles – are not well understood, however, and further field work is needed in order to confirm these initial results and provide greater insight into seasonal trends. It is hoped that the preliminary analysis presented here will attract interest from modelers who can augment the relatively low-resolution HYSPLIT back-trajectories used here with higher-resolution calculations that will accurately reflect the unique local topography and mixing dynamics that are present in the White Mountains.

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