Remote and Urban Air Quality: Surface Ozone in the Bay Area and White Mountains of CA

Abstract

Surface ozone concentrations are presented for seven sites: four from the White Mountains of California and three from the greater San Francisco Bay Area. The two highest elevation measuring sites in this study (White Mountain Summit = 4342 m, Barcroft Station = 3783 m) are believed to be the highest ground-level ozone measurements ever taken in North America. Ozone data were collected over a 4-week sampling period and analyzed via statistical software. It was found that ozone concentrations in the remote White Mountains of CA were consistently greater than those measured in the Bay Area, despite their distance from urban sources of primary pollutants. To explain this disparity, a variety of investigations are presented, including 72-hour HYSPLIT back-trajectories for an assessment of long-range transport, elevation trends, stratospheric intrusion, and fire impacts. Air quality was further investigated via passive sampling at the White Mountain sites; passive measurements for ammonia (NH₃), nitric acid (HNO₃), sulfur dioxide (SO₂) and ozone (O₃) indicate relatively good air quality.

1. Introduction

Ozone (O₃) is a triatomic allotrope of oxygen that is much less stable than the diatomic allotrope, O₂. Ozone, the primary component of smog, has been designated a criteria pollutant by the United States Environmental Protection Agency (EPA, 2011). While stratospheric ozone (the ozone layer) is beneficial because it prevents ultraviolet radiation from reaching the earth’s surface, ozone in the lower atmosphere (tropospheric ozone) is a highly reactive oxidizing agent that is detrimental to flora and fauna.

Health effects of ozone on the human population range from eye irritation to cell and tissue damage to permanent lung scarring from long-term exposure (Gryparis et al., 2004; Krupnick et al., 1990). According to the EPA, around 15,000 Americans die each year from air-borne pollutants, and exposure to ozone causes hundreds of thousands of acute asthma attacks (EPA, 2011). Plant symptoms include leaf mottling, burning and withering (Sikora, 2004).
The photochemical mechanism for ozone formation has been extensively studied (Crutzen et al., 1999; Sillman, 1999). The general reaction equation is as follows:

\[ \text{VOC} + \text{NO}_x + \text{sunlight (hv)} \rightarrow \text{O}_3 + \text{other pollutants} \]

Emissions of precursors for ozone formation, such as NO\(_x\) (NO\(_2\) + NO, nitrogen dioxide and nitric oxide, respectively) and volatile organic compounds (VOCs, e.g. isoprene), are typically greatest in urban areas due to human activities. Vehicular emissions and power plants are significant sources of nitric oxide and VOCs, respectively. Thus, ozone concentrations are often highest in urban environments. Additionally, warm and sunny weather favors ozone production.

In contrast, remote alpine sites are often used to assess changes in background ozone concentrations due to the absence of anthropogenic emissions. The EPA cites natural tropospheric background ozone concentrations around 10 ppb, but experimental measurements indicate background ozone levels in the Northern Hemisphere to be between 25-45 ppb, and rising (EPA, 2011; Vingarzan, 2004). Elevated ozone has also been observed in remote alpine areas where long-range transport can play a prominent role (Burley and Ray, 2007). Thus, it is of crucial import to investigate ozone concentrations in remote areas to determine the pollution levels for locations typically thought to possess pristine air.

This paper presents ozone data collected in the White Mountains over a four-week period during the months of July and August 2011 and compares them to data from three urban Bay Area sites (San Francisco, Concord, and Livermore). Sampling sites range from an elevation of 3 m (San Francisco) to 4342 m (White Mountain Summit). Two of the sites in this study (Barcroft Station (BRS), White Mountain Summit (WMS)) are believed to be the highest ground-level ozone measurements ever conducted in North America. Ozone concentrations were found to be higher in the more remote White
Mountains region; to explain this disparity, several analyses are presented, including discussion of long-range transport, smoke plume impacts, stratospheric intrusion and elevation gradients.

Passive sampling data for nitric acid (HNO$_3$), ammonia (HN$_3$), and sulfur dioxide (SO$_2$) are also presented for the WMRS sites to provide an assessment of non-ozone pollution. The passive data at the two higher elevation sites of BRS and WMS are believed to be the highest passive sampling measurements ever conducted in North America.

2. Methods and Procedure

2.1 Portable Ozone Monitors and Measurements

Surface ozone concentrations were measured via portable 2B Technologies Model 202 ozone monitors. Lightweight (2.1 kg) and having low power consumption (≈4 watts), the 2B monitor is well-suited for long-term monitoring at remote locations where AC power is unavailable. Solar were used to provide power at all White Mountain sites, except Crooked Creek where local AC power was utilized. The ozone monitors were installed in a weather-proof plastic case equipped with rechargeable 12 V lead-acid a solar charge controller, as displayed in Figure 1.

Figure 1: Solar Box with 2B O$_3$ monitor
Air samples were collected at a height around 2 m through a 47 mm diameter Teflon filter that was shielded by a plastic rain cover. Air samples passed through this inlet and travelled along an inert length of 6.35 mm diameter Teflon tubing to the ozone monitor. Ozone concentrations were measured at 10-second intervals and logged within the ozone monitor as 5-minute averages. These data were downloaded roughly four weeks after the initial deployment utilizing a serial port-USB adaptor cable and then converted into hourly averages for analysis via statistical software (e.g. Microsoft Excel, JMP).

2.2 Ozone Monitor Calibration

2B Technologies calibrated the ozone monitors utilized in the White Mountains study prior to deployment for the summer of 2011. 2B Technologies claims a precision and accuracy rating greater than 1.5 ppb for ambient ozone concentrations between 0-100 ppb (roughly 2%), but calibration at Saint Mary’s College of California prior to deployment revealed the accuracy closer to between 3-5 ppb (roughly 5%) (Ozone concentrations for calibration purposes were measured at 10-second intervals and the collected data logged as five-minute averages, so as to simulate actual deployment). Data were collected over two days at the same location (Saint Mary’s College) to allow identical air samples for comparison purposes. The calibration results are depicted in Figure 2.

![Figure 2: Pre-deployment calibration results](image)

Calibration results indicate an accuracy of roughly +/-3 ppb between the monitors used for the White Mountains study; the ozone monitor for OVL (#887) seems to read low by roughly 2 ppb, whereas the other three monitors remain consistently within 2 ppb of one another.
2.3 Sampling Details

Site details for the White Mountain sampling locations are provided in Table 1 and Figure 3, along with the start and end dates for the data collected.

Table 1: Site Locations and Timelines

<table>
<thead>
<tr>
<th>Site Abbreviation</th>
<th>Site Abbreviation</th>
<th>Elevation (m)</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Start Date</th>
<th>End Date</th>
<th>Sampling Period (day of year)</th>
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<td>August 16</td>
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Figure 3: Sampling Locations in the White Mountains, Summer 2011. Fig.3A: close up of deployment sites, 1=WMS, 2=BRS, 3=CC, 4=OVL; Fig.3B: The White Mountains.
2.4 HYSPLIT back-trajectories and Smoke Overlays

2.4.1 HYSPLIT

To assess long-range transport of ozone and its impact on measurements collected at White Mountain Summit (WMS), back-trajectory calculations were conducted via the online version of the HYSPLIT model (Draxler and Rolph, 2010). Utilizing the 40 km EDAS (Eta Data Assimilation System) archived meteorological data, 72-hour run time trajectories were calculated for selected ozone concentration maxima and minima with arrival heights of 300, 500 and 1000 m.

2.4.2 Smoke Overlays

Satellite images of smoke plumes were obtained from the National Oceanic and Atmospheric Administration (NOAA). Hazard Mapping System Fire Products (HMS) were downloaded as Google Earth files via the National Environmental Satellite Data and Information Service (NESDIS). These images were used in conjunction with HYSPLIT back-trajectories to investigate fire effects on ozone measurements in the White Mountains.

2.5 Online Data

2.5.1 Meteorological Data from the WMRS website

To analyze various atmospheric phenomena (e.g. stratospheric intrusion) and better understand the causes of low and high ozone concentrations, local meteorological data were obtained from the White Mountain Research Station (WMRS) website (wmrs.edu).

2.5.2 Bay Area Data from CARB

To compare ozone concentrations in the White Mountains to those in more urban locations, hourly ozone values for three sites (Concord, San Francisco, and Livermore) were downloaded from the California Air Resources Board website (CARB, 2011).
2.6 Passive Sampler Data

Passive samplers of the Ogawa design (Roadman et al., 2003) were used to collect data for HNO$_3$, NH$_3$, SO$_2$ and O$_3$ at the four sites in the White Mountains. Samplers were mounted ~2.5m above ground on wooden posts. Ambient air diffused through filters saturated with the specific chemicals needed for each particular measurement. For NH$_3$, the filters were coated with citric acid; ammonia reacts with citric acid on the filters, producing ammonium citrate. After water extraction, the ammonium ion (NH$_4^+$) concentration in the filter extract was determined colourimetrically and the ambient NH$_3$ concentration was calculated based upon a comparison of passive samplers against collocated annular denuder systems (Koutrakis et al., 1993). This analysis and computation was conducted by the United States Forest Service (USFS), as was the placement and installation of passive sampler equipment. For a more detailed discussion of the passive sampling method, see Bytnerowicz et al., 2005 and Bytnerowicz et al., 2002.

3. Results

3.1 Daily Averages

Daily average ozone values were calculated for the four White Mountain sampling. As displayed in Figure 4 below, all four sites demonstrate similar trends over the four week sampling period; this indicates similar patterns of air quality and meteorology for all four sites. Measured ozone concentrations increase in magnitude with elevation (see Elevation Gradient) and the variability in values is slightly larger for the higher elevation sites.
Figure 4: Time-series plot of daily average ozone for four White Mountains Sampling Sites. The x-axis represents the day of year value (e.g. day 198 = July 17th; day 229 = August 18th)

3.2 Diurnal Cycles

The average diurnal cycles presented in Figure 5 correspond to the entire four-week sampling period. While all four sites demonstrate similar ozone maxima from 10:00 to 17:00 PST, significantly different concentrations occur at other hours. Owens Valley Lab (OVL) shows the strongest diurnal dependence, with ozone concentrations increasing from early morning minima near 13 ppb to afternoon maxima of nearly 52 ppb. Crooked Creek (CC) exhibits a weaker – but still clear – diurnal pattern with early morning minima around 35 ppb and afternoon maxima in the range of 52-54 ppb. The two higher elevation sites (BRS and WMS) produce only minute diurnal variability, remaining relatively constant and never deviating more than +/- 2.5 ppb.

Figure 5: Average Diurnal Cycles for Observed Ozone between July 18th and August 17th
3.3 Bay Area versus WMRS

A comparison of select Bay Area monitoring sites (Arkansas Street, San Francisco (SF), Treat Boulevard, Concord (CCD), and Rincon Avenue, Livermore (LVR)) and the WMRS sites is provided in Figure 6. Table 2 provides site details for the Bay Area locations.

Table 2: Summary Site Information for Bay Area Ozone

<table>
<thead>
<tr>
<th>Site</th>
<th>Site Abbreviation</th>
<th>Elevation (m)</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Start Date</th>
<th>End Date</th>
<th>Sampling Period (Day of Year)</th>
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</thead>
<tbody>
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<td>-122.0264</td>
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<td>Aug 17th</td>
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<td>LVR</td>
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<td>-121.7842</td>
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<td>Aug 17th</td>
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<td>SF</td>
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<td>37.7661</td>
<td>-122.3991</td>
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</table>

Despite the remoteness of the White Mountains sampling sites, the daily average ozone at all four WMRS sites is higher than all three urban counterparts, including Livermore, which typically displays the highest ozone values in the Bay Area (CARB, 2003). Figure 7 presents the average diurnal cycles for the Bay Area sites juxtaposed against the WMRS sites. Concord and Livermore demonstrate large diurnal dependences whereas San Francisco only fluctuates between around 17 and 22 ppb.
Figure 7: Average diurnal cycle comparison for urban and rural sites 2011; urban sites Livermore (LVR), Concord (CCD), San Francisco (SF) and remote alpine sites Owens Valley Lab (OVL), Crooked Creek (CC), Barcroft Station (BRS), and White Mountain Summit (WMS)

4. Discussion

A variety of factors are responsible for the elevated ozone values observed in the White Mountains relative to the lower values observed in the Bay Area. The discussion in this paper will address some general background issues for the Bay Area and White Mountains sites, and then offer four potential explanations for the observed discrepancies.

4.1 General Background: White Mountain Sites

The disparity between diurnal cycles for the four sampling sites of the White Mountains may be the result of topographical differences. Whereas White Mountain Summit and Barcroft Station are well exposed to the free troposphere and likely experience well-mixed air, Crooked Creek and Owens Valley Lab are situated in depressions that allow ozone depletion during nocturnal hours. Crooked Creek Research Station is positioned in a shallow valley enclosed by relatively steep peaks on three sides with and a gap to the south and Owens Valley Lab is positioned at the north end of Owens Valley. While the combination of transported ozone and thorough mixing maintain elevated ozone concentrations throughout day- and night-time hours at WMS and BRS, the reduced evening mixing at calmer, sheltered
sites (CC, OVL) allows dry deposition and destruction of ozone formed during the day, producing the lower night-time values observed at these locations.

4.2 General Background: SF Bay Area Sites

Concord and Livermore demonstrate large diurnal variability, with morning minima around 15 ppb and afternoon maxima approaching 40 and 45 ppb for Concord and Livermore, respectively. These diurnal patterns are typical of urban areas due to the photochemical kinetics of ozone formation. While during daylight hours photons catalyze the formation of ozone from precursors such as NO$_2$, fresh NO emissions at night actually deplete ozone formed during the day via titration by the reaction:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

Dry deposition during calmer night-time conditions also decreases ozone formed during the day. The combination of these factors, coupled with the lack of photons for ozone formation, results in the strong diurnal cycles observed for Livermore and Concord.

San Francisco, on the other hand, demonstrates a very slight diurnal dependence, from early morning minima around 17 ppb to afternoon maxima near 22 ppb. Although the urban environment of San Francisco undoubtedly produces sufficient precursors for ozone concentrations well above 20 ppb and night-time emission of NO is likely sufficient for titration, insufficient solar radiation during daytime hours due to thick fog during the summer season may hinder ozone formation, lending the low values and lack of variability observed in the diurnal cycle. Likely the most important factor, clean on-shore air flow limits large ozone pollution build-up in San Francisco.

4.3 Long-range Transport

Back-trajectory analysis of the data from White Mountain Summit suggests that most of the ozone being measured in the White Mountains results from long-range transport rather than local
production. These results are not altogether unexpected given previous analyses (Burley and Ray, 2007), and long-range transport is further validated as the primary ozone source by both the remote location (removed from urban sources of precursors) and the small magnitude of the diurnal cycle.

HYSPLIT trajectories are essential to assessing the impact of long-range transport because they produce a detailed image of where the sampled air mass has been. This provides useful insight into the causes of low or high ozone values. For example, high ozone back-trajectories often spend extended periods of time over land, particularly the central valley or urban areas, such as Fresno, Bakersfield or Los Angeles. Additionally, HYSPLIT trajectories provide detailed time delineations so other events (e.g. fires) can be viewed accurately in conjunction with the moving air mass. Each point distributed along the line of the back-trajectories provided below corresponds to one hour within the course of the 72-hour trajectory.

Due to its uniquely high elevation and exposure to the free troposphere, White Mountain Summit (WMS) is used as the primary focus of all HYSPLIT back-trajectory calculations and analyses; Barcroft Station (BRS) displays similar HYSPLIT results which are not shown here. Figure 8 shows representative HYSPLIT images for high and low ozone values. Figures 8A and 8B depict back-trajectories corresponding to high ozone values. Both high ozone back-trajectories pass through metropolitan areas (e.g. Bakersfield, Fresno, and Sacramento) and remain over land for nearly the entire 72 hours. Additionally, Fig. 8B shows the 300 m trajectory (red) stagnating over Bakersfield for roughly 24 hours. On the other hand, figures 8C and 8D correspond to low ozone values and display the characteristic onshore flow and minimal time spent over polluted areas on their more direct path to WMS. While figure 8D almost mirrors the path of 8B, a characteristically high ozone value, inspection of the HYSPLIT back-trajectories reveals the lower values possessing trajectories that neatly avoid the urban centers of Sacramento and Reno whereas the higher ozone values’ trajectories pass straight through both cities.
Fig. 8A: Aug. 11, 2011; O$_3$ (high) = 72.6 ppb; trajectories pass through Sacramento and Reno.

Fig. 8B: Aug. 11, 2011; O$_3$ (high) = 72.6 ppb; trajectories pass through Sacramento and Reno.
Figure 8: Representative HYSPLIT back-trajectories. 8A: Aug. 11, 2011; ozone hi = 72.6ppb; trajectories pass through Sacramento and Reno. 8B: Aug. 3, 2011; O$_3$ = 71.2ppb; trajectories pass through central valley, Fresno, Bakersfield. 8C: Aug. 13, 2011; O$_3$ = 38.3ppb. 8D: Aug. 15, 2011; O$_3$ = 44.3ppb
In order to look for general patterns, HYSPLIT calculations were performed for the twelve highest and lowest hourly ozone values for WMS. Summary information for these HYSPLIT back-trajectories is provided in Table 3. Averaging the Table 3 data indicates that ozone maxima result from trajectories typically spending greater time inland rather than cleaner onshore flow (Table 4). As Table 4 shows, 50% of the trajectories corresponding to days of high ozone demonstrate trajectories spending >72 hours inland – in some cases, these trajectories linger over emission-prone areas (e.g. the central valley) for much greater amounts of time (Figures 8A,8B).

High ozone trajectories typically approach in one of two ways, either from the Northwest or South. While an approach from the South is consistent with previous observations (Burley et al., 2011) and would have more exposure to pollute areas (e.g. lower central valley, Fresno, Bakersfield), an approach from the Northwest is typically associated with cleaner air. Closer inspection of these trajectories, however, reveals many of the NW trajectories passing first through the Sacramento metropolitan area up along interstate 80 to curve around through Reno before descending through western Nevada to WMS. With warm and sunny weather conditions, emissions from major freeways (e.g. I-80) and cities such as Sacramento can produce sufficient ozone to explain the high values measured at WMS (Figure 8A).

Trajectories for air with decreased ozone typically spends less time inland (Table 4) and is often characterized by strong onshore flow from the Pacific Ocean (Figures 8C, 8D). Only 19% of trajectories at WMS for low ozone values show trajectories spending >72 hours inland and some trajectories (Aug. 13, 15) spend as little as 20-30 hours over California before reaching WMS. The eddy-currents and stagnant air masses are much less pronounced for minima trajectories, with a few notable exceptions (See Smoke Influence, below).
Table 3: Maximum and minimum ozone concentrations at White Mountain Summit

<table>
<thead>
<tr>
<th>Rank</th>
<th>Hourly O3 (ppb)</th>
<th>Smin O3 hi (ppb)</th>
<th>Date</th>
<th>Hour (PST)</th>
<th>Day of Year</th>
<th>Trajectory Approach</th>
<th>Hrs inland (300m=red)</th>
<th>Hrs inland (500m=blue)</th>
<th>Hrs inland (1000m=green)</th>
<th>Thru Smoke</th>
</tr>
</thead>
</table>
| Maxima
| 1    | 72.6            | 77.2             | 8/11/2011    | 9:00       | 223         | NW                 | >72                    | >72                     | >72                      | No          |
| 2    | 71.2            | 75.8             | 8/3/2011     | 5:00       | 215         | S                 | >72                    | 61                      | 61                       | Yes         |
| 3    | 70.8            | 74.1             | 7/31/2011    | 2:00       | 212         | S                 | >72                    | >72                     | >72                      | No          |
| 4    | 70.6            | 76.1             | 7/30/2011    | 19:00      | 211         | S                 | >72                    | >72                     | >72                      | No          |
| 5    | 68.6            | 73.4             | 7/24/2011    | 6:00       | 205         | SW                | 52                     | 60                      | 67                       | No          |
| 6    | 68.1            | 70.3             | 7/20/2011    | 4:00       | 201         | NW                | >72                    | >72                     | 60                       | No          |
| 7    | 67.5            | 72.1             | 8/5/2011     | 9:00       | 217         | NW                | 57                     | 48                      | 60                       | Yes         |
| 8    | 67.6            | 71               | 8/10/2011    | 20:00      | 222         | NW                | 67                     | 64                      | 55                       | No          |
| 9    | 66.4            | 67.7             | 7/22/2011    | 7:00       | 203         | NW                | >72                    | >72                     | >72                      | No          |
| 10   | 65.9            | 67.8             | 8/4/2011     | 15:00      | 216         | SW                | 69                     | 69                      | 66                       | Yes         |
| 11   | 65.4            | 68.2             | 7/21/2011    | 6:00       | 202         | NW                | >72                    | 62                      | 62                       | No          |
| 12   | 64.5            | 68.2             | 8/8/2011     | 8:00       | 220         | NW                | >72                    | >72                     | >72                      | No          |

Minima

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Table 4: HYSPLIT Averages and Statistics

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<th>Avg. hours inland (300m)</th>
<th>Avg. hours inland (500m)</th>
<th>Avg. hours inland (1000)</th>
<th>%&gt;72hr inland trajectories</th>
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</table>

4.4 Stratospheric intrusion

While long-range transport is likely the most prominent cause for elevated ozone in remote, high elevation locations, stratospheric intrusion (SI) is another phenomenon that can produce high ozone concentrations (Clements et al., 2004). Stratospheric intrusion occurs at high elevations when warmer and more polluted air from above penetrates the lower troposphere in isolated bursts, causing single high ozone events of limited duration. Due to the brief nature of stratospheric intrusion, 5-minute
ozone averages were utilized for this investigation. Figure 9 shows a possible stratospheric intrusion for WMS and BRS.

![Time-series plot of 5-minute O₃ average (ppb) measured at WMS (top) and BRS (bottom); arrows indicate a possible stratospheric intrusion around 23:40 PST on 7/23/2011.](image)

To help assess the likelihood of stratospheric intrusion, co-located meteorological data were downloaded from the White Mountain Research Station (WMRS) website. While data are limited for WMS (only available through February 2011), Barcroft Station (BRS) has better coverage, so weather data from BRS were utilized for this analysis.

Stratospheric intrusion is often accompanied by upward spikes in both temperature and barometric pressure but a sharp fall in relative humidity (Cristofanelli et al., 2006). Figure 10 depicts weather data from BRS that confirm the likelihood of an intrusion event on the evening of July 23rd, 2011.
Figure 10: Meteorological data for Barcroft Station (BRS). Dates for data span from July 22nd – July 25th. Stratospheric intrusion time (July 23rd @ ~23:40 PST) is highlighted by black arrows. Top: Relative Humidity (%) demonstrates relative minimum at time of high O₃ event. Middle: Temperature (°F) displays relative spike at time of high O₃ event. Bottom: Barometric Pressure (in. Hg) demonstrates relative peak at time of high O₃ event.
4.5 Elevation Gradient

It has been previously observed that ozone concentrations tend to increase with increasing elevation (Chevalier et al., 2007). Ozone data from the summer of 2011 confirm this trend at White Mountain sampling sites as well as with the Bay Area sites (Figure 11). The relationship shows a very strong correlation ($R^2 = 0.966$) and a slope of +0.0077ppb per meter of elevation gain (Figure 11).

![Elevation Gradient](image)

\[
y = 0.0077x + 23.087
\]

$R^2 = 0.966$

Increase in ozone concentration with higher altitudes has been attributed to the stratification of the troposphere which results in variable ozone mixing. Previous investigations have noted that 1000 m marks a clear transition between the boundary-layer (= bottom of the troposphere, closest to the earth’s surface) and higher free-tropospheric areas for ozone (Chevalier et al., 2007). As the lowest elevation site at the White Mountains was greater than 1000 m (OVL = 1237 m), this potentially explains the increased ozone concentrations measured at the White Mountain sites as compared to the S.F. Bay Area. Additionally, background ozone concentrations are known to increase with height in the troposphere because ozone is eroded near the surface via deposition and titration that dominates the
boundary layer of the atmosphere. Thus, the 0.0077 ppb/m increase in ozone is not particularly surprising in the White Mountains.

4.6 Smoke Influence

Fire impacts on ozone are often less clear than other influences. Fire effects on ozone formation and depletion are notoriously situational and therefore difficult to summarize. Fires produce nitric oxide (NO) in large concentrations, which serves to titrate (remove) ozone previously formed (for details on ozone titration, see Sillman, 1999). Additionally, the smoke plumes of large fires often lead to decreased solar radiance, thereby hindering the photochemical formation of ozone. Despite these factors potentially decreasing atmospheric ozone, NO has a very short life-span and is quickly oxidized to NO2, one of the key precursors in ozone formation. In cases where smoke is blown downwind, elevated NO2 can result in increased ozone concentrations.

In conjunction with the HYSPLIT back-trajectories, smoke plumes corresponding to the dates of ozone maxima and minima were obtained and evaluated. Table 3 assessed back-trajectories in terms of their potential passage through a smoke plume (or not), but Table 5 provides a more general analysis of smoke influence on back-trajectories. Smoke appears to play a more prominent role in trajectories corresponding to ozone minima (50%) than ozone maxima (25%). Additionally, one third (33%) of the minima back-trajectories passed through smoke within a 16 hour window preceding the arrival of the trajectory at the summit. Only 8.3% of ozone maxima spent time in smoke within 16 hours of arriving at the summit. Two of the three trajectories displaying smoke influence for ozone maxima passed through smoke over 36 hours before the ozone high was measured, allowing a full day’s sun for photochemical ozone formation.
Table 5: Smoke Influence on ozone concentrations

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>% Through Smoke</th>
<th>Avg. Time Through Smoke</th>
<th>% Thru Smoke in 16 hr window before arrival</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxima</td>
<td>25%</td>
<td>5.11hrs</td>
<td>8.3%</td>
</tr>
<tr>
<td>Minima</td>
<td>50%</td>
<td>9.17hrs</td>
<td>33.3%</td>
</tr>
</tbody>
</table>

To consider a specific case, the smoke analyses for August 12, 2011 (the lowest ozone minima) will be discussed here as a representative example. As shown in Table 3, the lowest hourly ozone concentration (24.0ppb @ 5:00PST on Aug. 12th) corresponds to a back-trajectory spending >72hrs inland. The actual HYSPLIT trajectory is presented in Figure 12, below. Additionally, these trajectories all contain more stagnant behavior (red = 300m), southerly approach (blue, green = 500m, 1000m, respectively) and pass through polluted areas such as Fresno and the central valley (blue, green). These attributes collectively characterize high ozone concentrations rather than lower values.

Adding smoke plume overlays from NOAA, however, reveals heavy smoke as potentially responsible for the low values observed in the early morning hours. Figure 12 depicts all three trajectories passing through smoke within 16 hours of the measured ozone lows. For the 500 m and 1000 m trajectories (blue and green, respectively), this smoke passage occurred roughly between the hours of 12:00 PST and 20:00 PST of August 11th. This heavy smoke cover likely reduced solar radiance, leading to less ozone production on the afternoon before the measured low.

Additionally, the 300 m trajectory (red) spends the last 6 hours before the ozone low (23:00 PST on August 11th to 5:00 PST on August 12th) within the smoke plume. As mentioned previously, NO produced from the fire could titrate the ozone formed from the day previously, resulting in the minimum observed in the early hours before sunrise on August 12th. However, more data – particulate matter, NO, NO₂, VOCs, etc. – would be required to confirm this preliminary analysis.
Figure 12: HYSPLIT back-trajectory for Ozone low @ 5:00 PST on August 12th, 2011 with Smoke Plume overlay (green) for fires occurring on August 11th and 12th, 2011.

4.7 Passive Sampler Data: HNO$_3$, NH$_3$, SO$_2$, O$_3$

While the elevated ozone concentrations in the White Mountains coupled with the much lower values in the more urban Bay Area might suggest that overall air quality in the White Mountains is poor, passive sampler data for HNO$_3$, NH$_3$, and SO$_2$ indicate otherwise (passive samples collected and averaged from July 19th – August 3rd). High ozone from long-range transport, stratospheric intrusion and elevation gain seems to be the only indicator of poor air quality. The assessment of other pollutants by passive sampling (ammonia, nitric acid, sulfur dioxide) reveals relatively clean air at the four stations utilized in this study.
Table 6 presents the passive sampler data as 2-week averages for each site. The 2B technologies ozone monitor averages are provided for comparison with the passive sampler. Excepting Crooked Creek, the passive samplers demonstrate decent agreement with the 2B values.

Table 6: Passive Sampler Data 2011

<table>
<thead>
<tr>
<th>Site</th>
<th>HNO3 Avg. (µg/m³)</th>
<th>NH3 Avg. (µg/m³)</th>
<th>O3 Avg. (ppb)</th>
<th>SO2 Avg. (µg/m³)</th>
<th>Sample Period (day of year)</th>
<th>2B O3 Avg.(ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLANK</td>
<td>0.05</td>
<td>0.39</td>
<td>-0.25</td>
<td>-0.053</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OVL</td>
<td>0.90</td>
<td>1.88</td>
<td>37.29</td>
<td>0.268</td>
<td>199-214</td>
<td>38.5</td>
</tr>
<tr>
<td>CC</td>
<td>0.73</td>
<td>1.56</td>
<td>37.27</td>
<td>0.258</td>
<td>200-215</td>
<td>44.4</td>
</tr>
<tr>
<td>BRS</td>
<td>0.92</td>
<td>1.92</td>
<td>50.38</td>
<td>0.264</td>
<td>200-215</td>
<td>52.6</td>
</tr>
<tr>
<td>WMS</td>
<td>1.04</td>
<td>1.55</td>
<td>58.34</td>
<td>0.313</td>
<td>200-215</td>
<td>56.3</td>
</tr>
</tbody>
</table>

Nitric acid (HNO₃) and ammonia (NH₃) are not currently regulated by the EPA, so an assessment of air quality regarding these components somewhat difficult. Due to their high deposition velocity and reactivity, however, these pollutants are the major drivers of nitrogen dry deposition, or nitrogen eutrophication. In this process, the ecosystem is enriched with excess nitrogen which impacts species composition, favoring those plants with a high demand for nitrogen (Fowler et al., 1989). High concentrations of HNO₃ and NH₃ typically result from traffic, agricultural and industrial activities and waste management.

The concentrations of HNO₃ measured in the White Mountains (between 0.73 µg/m³ and 1.04 µg/m³) are much lower than concentrations (around 6-8 µg/m³) on the western slopes of Sequoia and Kings Canyon National Park in the Sierra Nevada (Bytnerowicz et al., 2002). Concentrations are extremely low compared to those measured in the highly polluted areas in southern California (Bytnerowicz et al., 1999).

Likewise, NH₃ concentrations are all relatively low, particularly at Crooked Creek and White Mountain Summit (values = 1.56 µg/m³, 1.55 µg/m³, respectively). All four sites display concentrations
markedly lower than those measured at Sequoia and Kings Canyon National Park (Btynerowicz et al., 2002). NH₃ concentrations at the remote White Mountain sites are equal to or lower than measurements obtained in remote regions (0-2 µg/m³) in the United Kingdom (Sutton, 2000). Higher concentrations of NH₃ typically result in areas of heavy agricultural use. Thus the relatively higher value obtained at Owens Valley Lab (1.88 µg/m³) is not surprising given its relative proximity to private cattle ranching and other activities in Owens Valley. The highest value for NH₃ appears at Barcroft Station (1.92 µg/m³), which may at first seem surprising given its remoteness and elevation of 3783m. This relatively elevated (but still low) NH₃ concentration may likely be explained by the presence of sheep being used in an experiment conducted by Loma Linda University just uphill from the sampling site. Given proper wind direction, the NH₃ from animal excrement could easily explain the higher values measured.

Unlike NH₃ and HNO₃, sulfur dioxide (SO₂) is a criteria pollutant and regulated by the EPA. Both controlled laboratory and epidemiology studies have shown that people with asthma and children are particularly sensitive to the effects of SO₂ pollution at concentrations as low as 0.25 ppm (655 µg/m³) (Koenig et al., 2000). SO₂ averages from the White Mountains are far below all of these EPA/CARB standards (including 24 hr standard of 260 µg/m³), indicating very low SO₂ concentrations.

5. Conclusion

Data collected during the summer of 2011 at the White Mountains sampling sites demonstrate ozone concentrations considerably greater than the urban sites within the S.F. Bay Area. Elevated ozone was found to correlate strongly with elevation and reflected the influence of long-range transport rather than local photochemical production. Although stratospheric intrusion events do occur at White Mountain Summit and Barcroft Station, these events were found to be relatively rare. Additionally, fire impacts may influence high or low ozone values, but more data and research would be required for a significant conclusion regarding the positive or negative effect of smoke on ozone measured at the
White Mountain sites during the summer of 2011. Tentatively, it seems increased smoke coverage played a larger role in decreasing ozone concentrations rather than providing precursors for increased ozone production over the four-weeks sampled in this study. Finally, while the majority of ozone values measured remain below EPA mandates (1 h average = 90 ppb), elevated ozone in remote locations such as the White Mountains remains a concern. It seems clear that long-range transport can result in quite high ozone concentrations even in pristine alpine areas much removed from pollution sources. For the best management strategies, investigations of pollutant concentrations cannot solely focus upon urban areas (e.g. the Bay Area), but must include a larger geographical range to account for secondary influences at other locations. Excluding O₃, measurements of other pollutants (e.g. SO₂) reveal that air quality in the White Mountains of California is generally good.

6. Acknowledgements

I would like to thank Dr. Burley for his support and guidance throughout this project. Additionally, I would like to thank Andrzej Bytnerwicz and the U.S. Forest Service for assistance in data acquisition. Finally, I would like to recognize John Cartwright from NOAA for his outstanding support regarding smoke image downloads as well as his endurance of endless pesky questions.
References


