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## Summertime ozone at Mount Washington: Meteorological controls at the highest peak in the northeast

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[1] This study examined the synoptic and regional-scale meteorological controls on summertime O<sub>3</sub> at Mount Washington, the highest peak (1910 m) in the northeastern United States. Analysis of air mass transport to Mount Washington was conducted for the summers of 1998–2003 using backward trajectories. Distinct patterns in air mass history were revealed using this approach that helped explain extreme variations in O<sub>3</sub> mixing ratios. Most enhanced ( $\geq 90$ th percentile) and depleted ( $\leq 10$ th percentile) O<sub>3</sub> events were short-lived and spread out over the summer months. Enhanced O<sub>3</sub> events at Mount Washington were generally associated with westerly transport, while depleted events corresponded to northwesterly transport. Periods of O<sub>3</sub> greater than 80 ppbv during nighttime periods coincided with westerly (71%) and southwesterly (29%) transport. Periods of elevated O<sub>3</sub> commonly occurred during regional warm sector flow or on the western edge of a surface anticyclone. Our analysis also identified a stratospheric contribution to a small percentage ( $\sim 5\%$ ) of extreme O<sub>3</sub> events at the site, but more evidence is required to establish the significance of the contribution to background O<sub>3</sub> levels in this region.

**INDEX TERMS:** 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 3364 Meteorology and Atmospheric Dynamics: Synoptic-scale meteorology; 3307 Meteorology and Atmospheric Dynamics: Boundary layer processes; **KEYWORDS:** tropospheric ozone, New England, trajectories

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### 1. Introduction

[2] It is recognized that current ozone (O<sub>3</sub>) levels are having a negative effect on both ecosystems and human health in rural northern New England. Biomonitoring programs in the northeast indicate that symptoms of O<sub>3</sub> damage on native vegetation are prevalent in areas with high O<sub>3</sub> levels [Moss *et al.*, 1998; Smith *et al.*, 2003]. Complementary fumigation studies have confirmed that the symptoms observed in the field are the result of O<sub>3</sub> exposure [Orendovici *et al.*, 2003]. Recent modeling work also suggests that O<sub>3</sub> exposure may be limiting nitrogen-induced carbon sinks in forests of the northeastern U.S. [Ollinger *et al.*, 1997, 2002]. In the realm of human health, an epidemiological study of adults hikers on Mount Washington, located in northern New Hampshire, showed a decline in respiratory function that correlated with O<sub>3</sub> exposure [Korrick *et al.*, 1998].

[3] High altitude sites are often used to assess background O<sub>3</sub> conditions. They are presumed to be relatively free from the influence of local emissions [Bronnimann *et al.*, 2000], and the associated NO titration [Kley *et al.*, 1994]. Mountain monitoring sites are also considered to be representative of regional O<sub>3</sub> [Cooper and Moody, 2000]. Mount Washington is the highest mountain in the northeastern United States ( $\sim 1910$  m), and therefore provides a unique opportunity to study the air chemistry and meteorology of New England. Transport to this site varies in response to different synoptic-scale wind regimes under the predominant westerly flow. Climatologies at lower elevations are subject to inversions [Lefohn and Manning, 1995] and are thus less representative of advected air masses. The collocation of O<sub>3</sub> monitoring sites near the base and at the summit of Mount Washington provides a unique opportunity to explore the temporal behavior of the boundary layer and gain insight on the vertical distribution of O<sub>3</sub>. There is a relatively long record (1987–2003) of summer O<sub>3</sub> at Mount Washington, so the data set provides a unique opportunity to

examine the patterns in  $O_3$  mixing ratios over a wide range of environmental conditions.

[4] The present study focuses on the differences in long-range transport between enhanced and depleted  $O_3$  periods, to understand the air mass history and source regions for high and low  $O_3$  episodes at Mount Washington. Backward trajectories and case studies were used to illustrate how  $O_3$  at Mount Washington is constrained by regional transport. This paper contrasts the diurnal variations in  $O_3$  between the base and the summit, and discusses background  $O_3$  levels and their relationship to stratospheric influences during summer months.

## 2. Methods

### 2.1. Study Area

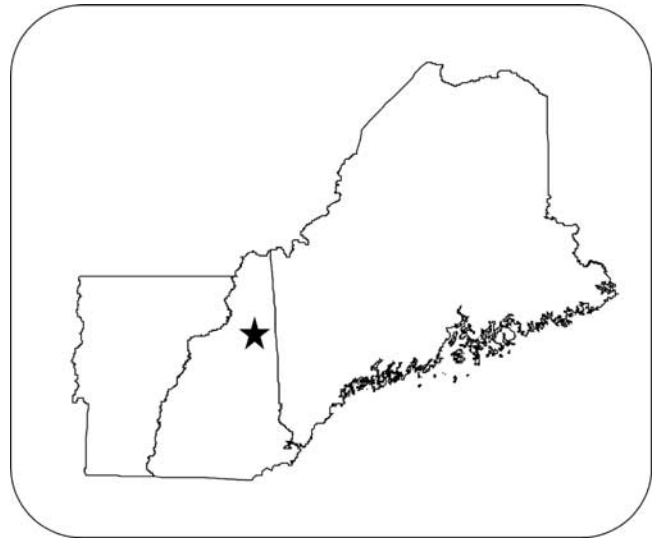
[5] Mount Washington (44.27°N, 71.30°W) is the highest peak in the northeastern United States, and is located in the 3035 km<sup>2</sup> White Mountain National Forest in northern New Hampshire (Figure 1). The tree line is approximately 600 m below the summit. Mount Washington is a valuable site for both air quality and meteorological research because it lies in the path of the major air mass routes that effect the northeast.

[6] There is a relatively long record of  $O_3$  for this site, as the Appalachian Mountain Club (AMC) has been collecting  $O_3$  data at the summit of Mount Washington and at a nearby lower elevation site (Camp Dodge) during summer since 1987. Camp Dodge (457 m) is located approximately 9 km from the summit of Mount Washington, slightly north of the base of the mountain. In this paper, the Camp Dodge monitoring site is referred to as the base site. These sites are currently part of the U.S. Environmental Protection Agency (EPA) and New Hampshire Air Resources Division (NHARD) Network. The Atmospheric Investigation, Regional Modeling, Analysis and Prediction (AIRMAP) network, based at the University of New Hampshire, has been collecting year-round data at the summit since 2001. This study focuses on recent summers 1998 to 2003, but a general description of earlier data is included for reference.

[7] Many vehicles and an antique coal fired locomotive make their way to the summit most summer days. It should be noted that cars are not allowed on the actual summit where the  $O_3$  measurements were conducted. There is occasional evidence of  $O_3$  titration from local nitric oxide (NO) emissions; however, these events are usually very short-lived (minutes) and sporadic. These local sources have a negligible influence on the hourly averaged long-term data set.

### 2.2. Ozone Data

[8] Ozone mixing ratios were measured at the summit of Mount Washington using unmodified Thermo Environmental, Model 49C UV photometric  $O_3$  analyzers (Franklin, Massachusetts) with a detection limit of 1 ppbv. Instrument zeroing and calibration was achieved as described by *DeBell et al.* [2004b]. One-minute averaged  $O_3$  data for summers 2001 to 2003 were obtained from the AIRMAP database ([airmap.unh.edu/data/index.cfm](http://airmap.unh.edu/data/index.cfm)). Carbon monoxide (CO) was also measured [*DeBell et al.*, 2004b] during summers 2001 to 2003. One-hour average  $O_3$  data collected at the summit of Mount Washington by the AMC were used



**Figure 1.** Location of Mount Washington.

for summers 1987–2002. Ozone data from both sources during overlapping summers 2001 and 2002 were highly correlated and  $AMC = 0.9409 * AIRMAP + 0.0542$  with  $r^2 =$  of 0.87, which indicates that the data are comparable within about 6%. It should be noted that these instruments are not exactly co-located on the summit and use separate inlets of different design. AIRMAP uses a high flow large diameter inlet mounted at least 50 m away from the AMC low flow 6.35 mm Teflon tubing inlet. The AIRMAP inlet is 15 m above the summit surface whereas the AMC inlet is only a few meters above the surface. Both inlets face into the predominantly westerly flow. The difference between the  $O_3$  measurements of the two instruments is likely attributed to their inlet characteristics.

[9] Hourly meteorological observations for the summit were provided by the Mount Washington Observatory. The meteorological data included hourly measurements of temperature, dew point, visibility, sky cover, wind speed, and wind direction. In addition, four pressure readings were provided daily.

### 2.3. Trajectory Calculation

[10] Trajectories were calculated with the Hybrid Single Particle Lagrangian Integrated Trajectories (HY-SPLIT) model [*Draxler*, 1999; *Draxler and Rolph*, 2003] using meteorological data from the Eta Data Assimilation System (EDAS) Archive. The EDAS archive grid covers the continental US after 1997, has a horizontal resolution of about 80 km and a vertical resolution of 22 pressure surfaces between 1000 and 50 hPa. HYSPLIT trajectory error normal to the predominant direction of the flow has been determined to be 10–30% of the distance traveled after 24 hours [*Draxler and Hess*, 1998]. A trajectory is not representative of the path of an air parcel within the planetary boundary layer (PBL) because the parcel quickly loses its identity through turbulent mixing processes [*Stohl*, 1998]. However, the model is adequate to classify regional-scale air mass motions in which local-scale winds are embedded.

[11] Back trajectories from Mount Washington were calculated at 0700, 0900, 1900, and 2100 UTC (0200, 0400,

**Table 1.** Summer (May–September) O<sub>3</sub> Statistics for the Summit of Mount Washington Based on All Available Hourly Averaged Data<sup>a</sup>

Year	Mean, ppbv	Median, ppbv	Maximum, ppbv	90th Percentile, ppbv	10th Percentile, ppbv
1987	43	40	108	66	27
1988	53	47	148	88	27
1989	48	47	134	64	32
1990	39	38	100	58	23
1991	44	40	105	68	28
1992	42	40	97	57	28
1993	41	39	88	57	26
1994	43	42	86	60	27
1995	44	44	92	60	30
1996	46	46	101	62	31
1997	44	42	105	63	29
<b>1998</b>	<b>45</b>	<b>43</b>	<b>86</b>	<b>63</b>	<b>29</b>
<b>1999</b>	<b>45</b>	<b>45</b>	<b>100</b>	<b>63</b>	<b>28</b>
<b>2000</b>	<b>40</b>	<b>39</b>	<b>85</b>	<b>56</b>	<b>27</b>
<b>2001</b>	<b>47</b>	<b>45</b>	<b>87</b>	<b>67</b>	<b>31</b>
<b>2002</b>	<b>47</b>	<b>45</b>	<b>128</b>	<b>69</b>	<b>34</b>
<b>2003</b>	<b>49</b>	<b>48</b>	<b>98</b>	<b>64</b>	<b>35</b>

<sup>a</sup>This study primarily focuses on the 6-year period 1998–2003 (as indicated by boldface type). AMC data were used for 1987–2000. AIRMAP data were used for 2001–2003. The highest mean and median O<sub>3</sub> mixing ratios in the recent years (1998–2003) were measured at Mount Washington during summer 2003.

1400, and 1600 EST or 0200 and 0400 LT, and 1400 and 1600 LT) for summers (May–September) 1998–2003. The trajectories were calculated in 2-hour time steps for 72 hours back in time. Missing data or transgression of the EDAS grid boundaries caused some of the trajectories to truncate prematurely. Additional trajectories were run 120 hours back in time using FNL meteorological data from the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) archive to further investigate periods of interest when rapid transport from the north forced the trajectories off the EDAS grid in a short time period.

[12] Trajectories were initialized from a constant 1200 m above model ground level at Mount Washington. The trajectories were initialized above the ground because the EDAS model defines the terrain significantly below the actual altitude of Mount Washington. The backward trajectories were initialized at a constant elevation because when a large number of trajectories are analyzed and averaged, errors associated with vertical displacement tend to be small [Poirot and Wishinski, 1996; Brankov *et al.*, 1998].

#### 2.4. Trajectory Grouping and Analysis

[13] To take account of complex diurnal circulations associated with mountainous terrain, trajectories were broken into two groups: (1) nighttime, trajectories initialized at 0700 and 0900 UTC and (2) afternoon, trajectories initialized at 1900 and 2100 UTC. These two groups were analyzed separately to prevent grouping afternoon trajectories arriving under well-mixed boundary layer conditions with nighttime trajectories influenced by stable nocturnal boundary layer development. The timing of the nighttime trajectory initialization was chosen to coincide with the typical time of the highest observed O<sub>3</sub> mixing ratios at Mount Washington.

[14] Trajectories were paired with the average O<sub>3</sub> mixing ratio surrounding their corresponding initialization time. For summers 1998–2000, when only hourly averaged O<sub>3</sub> data were available, the trajectories were paired with a 3-hour average O<sub>3</sub> mixing ratio surrounding the initialization time. For example, a 3-hour average surrounding 0700 UTC

averaged the data from 0600, 0700 and 0800 UTC. So there is overlap of 1 hourly averaged value between adjacent odd hour averages for these summers. For summers 2001–2003, when 1-min averaged data was available, the trajectories were paired with a 2-hour averaged O<sub>3</sub> mixing ratio. For example, the 0700 UTC O<sub>3</sub> value was an average of 1-min averaged data from 0600–0759 UTC. This averaging limited the effects of short periods with missing data.

[15] Ozone trajectory pairs were sorted with respect to O<sub>3</sub> mixing ratios, and enhanced and depleted groups were determined. Trajectories for enhanced events corresponded to O<sub>3</sub> levels  $\geq$  the 90th percentile while depleted ones referred to O<sub>3</sub> levels  $\leq$  the 10th percentile for all six summers. Enhanced or depleted O<sub>3</sub> events were identified separately for the nighttime and afternoon initialization times. Trajectories corresponding to midrange O<sub>3</sub> levels (10th–90th percentile) were examined, but not in the same detail. NCEP surface analyses available at <http://nndc.noaa.gov/?http://ols.ncdc.noaa.gov/cgi-bin/nndc/buyOL-006.cgi?FNC=ch> were used along with NOAA Daily Weather Maps [National Oceanographic and Atmospheric Administration (NOAA), 1998–2003] to examine the meteorological features coincident with arrival time of trajectories at the summit.

### 3. Results and Discussion

#### 3.1. Ozone Characteristics at Mount Washington

##### 3.1.1. Summertime Seasonal O<sub>3</sub> Comparisons

[16] Annual statistics for O<sub>3</sub> at Mount Washington are given in Table 1. The mean and median hourly average O<sub>3</sub> mixing ratios for the summer seasons 1987–2003 ranged from 38 to 53 ppbv. The mean O<sub>3</sub> mixing ratios measured at Mount Washington are consistent with summer data from similar altitudes and latitudes in the U.S. and Europe [Logan, 1985, 1989]. Mean O<sub>3</sub> mixing ratios calculated for summers 1986 to 1988 for Mount Mitchell, NC (~2036 m) and Commissary Ridge, NC (~1760 m) ranged from 50 to 66 and 49 to 52 ppbv respectively [Aneja *et al.*, 1991]. Monthly mean O<sub>3</sub> at 800 hPa, (approximately 10 hPa

**Table 2.** Summer (May–September) Maximum 1- and 8-Hour Average O<sub>3</sub> for the Summit and Base of Mount Washington<sup>a</sup>

Year	Maximum 1-Hour Average Ozone, ppbv		Maximum 8-Hour Average Ozone, ppbv	
	Mount Washington Summit	Base of Camp Dodge	Mount Washington Summit	Base of Camp Dodge
1987	108	103	97	85
1988	148	98	134	92
1989	134	80	124	65
1990	100	95	79	72
1991	105	103	91	93
1992	97	99	89	86
1993	88	89	81	71
1994	86	83	77	77
1995	92	79	83	72
1996	101	67	79	63
1997	105	102	100	80
1998	86	85	82	76
1999	100	89	92	79
2000	85	69	75	65
2001	87	91	85	85
2002	125	86	110	81
2003	98		78	

<sup>a</sup>AMC data were used for both sites for 1987–2002. AIRMAP data were used for the summit of Mount Washington for 2003. The highest 1-hour maximum O<sub>3</sub> mixing ratio in recent years was measured in summer 2002. A 1-hour average O<sub>3</sub> mixing ratio over 0.12 ppmv, the primary 1-hour NAAQS for O<sub>3</sub>, had not been recorded at this site since 1989. The lowest seasonal hourly maximum O<sub>3</sub> mixing ratio during the 6-year study period was measured during summer 2000.

lower than Mount Washington) at Trinidad Head, CA, Boulder, CO, and Wallops Island, VA ranged from approximately 50 to 70 ppbv [Newchurch *et al.*, 2003]. Average summer O<sub>3</sub> mixing ratios at sites in the Alps ranged from 33 ppbv at low altitudes to 50 ppbv at 3600 m [Bronnimann *et al.*, 2000].

[17] The seasonal maximum 1-hour O<sub>3</sub> average ranged from 85 ppbv (2000) to 148 ppbv (1988). The maximum 1-hour and 8-hour average O<sub>3</sub> mixing ratios for each year for the summit and base of Mount Washington are presented in Table 2. Over the past 17 summers, the base of Mount Washington had 7 seasons where the maximum 8-hour average O<sub>3</sub> mixing ratio reached or exceeded 0.08 ppmv, the new primary National Ambient Air Quality Standard (NAAQS) for O<sub>3</sub>. The new 8-hour standard increases the importance of long-range transport and background O<sub>3</sub> amounts. Comparatively the summit had 12 seasons where this criteria was met. Figure 2 shows the number of days each year that had maximum 8-hour average O<sub>3</sub> mixing ratios  $\geq 0.08$  ppmv.

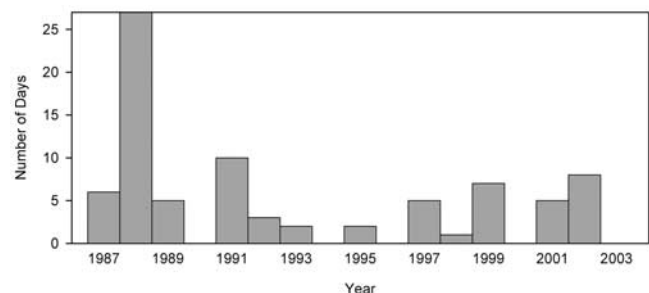
[18] The seasonal hourly average mean and median O<sub>3</sub> for the base of the mountain was normally 15 ppbv lower than at the summit for summers 1987–2002. Mean O<sub>3</sub> concentrations at similar latitudes in Europe have been shown to increase along slopes up to elevations of 2000 to 2300 m above sea level [Werner *et al.*, 1999], which is comparable to the height of Mount Washington. As expected from earlier work at a set of high-elevation sites in the eastern U.S. [Lefohn *et al.*, 1990] and in the southern Appalachians [Aneja *et al.*, 1991], the summit of Mount Washington generally received a greater exposure to higher O<sub>3</sub> levels than the base during the period from May to September.

[19] Cumulative frequency distributions and histograms of average hourly O<sub>3</sub> at the summit and base of Mount Washington for day and night periods are presented on the same scale in Figure 3. Differences in O<sub>3</sub> exposure between the summit and the base are reflected in the two sets of

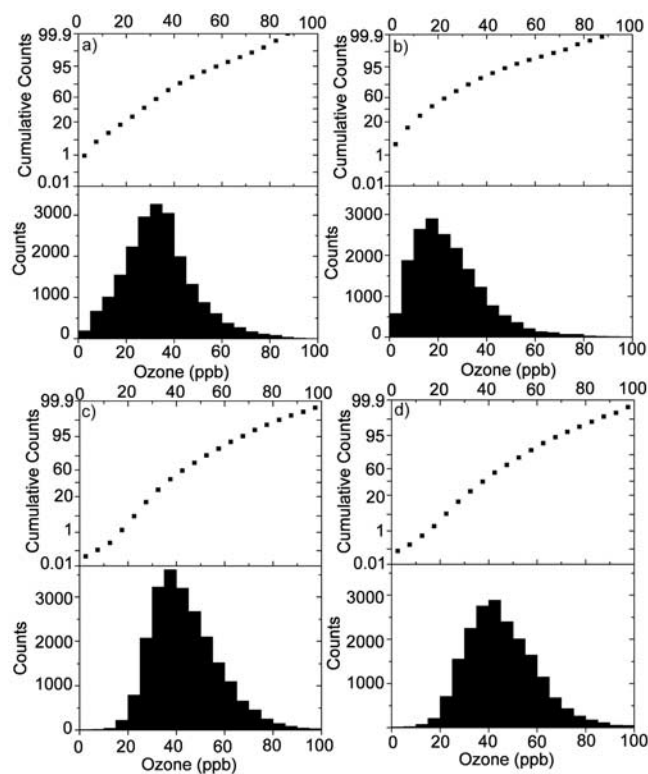
histograms. There was a low frequency of O<sub>3</sub> mixing ratios less than 30 ppbv at the summit, and the base/summit contrast is especially large at night. The daytime data at the summit (Figure 3c) was somewhat skewed toward higher mixing ratios, and slightly less Gaussian shaped than histograms of daytime O<sub>3</sub> distributions at other elevated sites in Europe and the eastern United States [Kley *et al.*, 1994]. We speculate that this is because Mount Washington is located more directly downwind of urban source regions and is slightly lower than the locations studied by Kley *et al.* [1994]. It is also possible that because of the high wind speeds characteristic of the summit of Mount Washington, any O<sub>3</sub> deposition is immediately compensated for with a fresh O<sub>3</sub> supply.

### 3.1.2. Diurnal O<sub>3</sub> Behavior

[20] Consistent with mountain sites, Mount Washington usually experiences a reversed diurnal cycle compared to lower elevation sites, with O<sub>3</sub> mixing ratios typically peak-



**Figure 2.** Number of days each summer with daily maximum 8-hour average O<sub>3</sub> greater than 80 ppbv at the summit of Mount Washington. The year 1988 stands out with 27 days where the maximum 8-hour average O<sub>3</sub> mixing ratio was  $\geq 0.08$  ppmv. Since 1998, the number of days each year with 8-hour averages  $\geq 0.08$  ppmv has ranged from 0 in 2000 and 2003 to 8 in 2002.



**Figure 3.** Cumulative frequency distributions and histograms of hourly  $O_3$  at the base of Mount Washington for (a) daytime hours, 0600–1800 LT and (b) nighttime hours, 1800–0600 LT. Cumulative frequency distributions and histograms of hourly  $O_3$  at the summit of Mount Washington for (c) daytime hours, 0600–1800 LT and (d) nighttime hours, 1800–0600 LT.

ing after midnight [Hill and Allen, 1994]. However, the summit does occasionally experience a secondary afternoon  $O_3$  peak when convective boundary layer growth over surrounding lower elevation regions results in the height of the mixed layer reaching the summit.

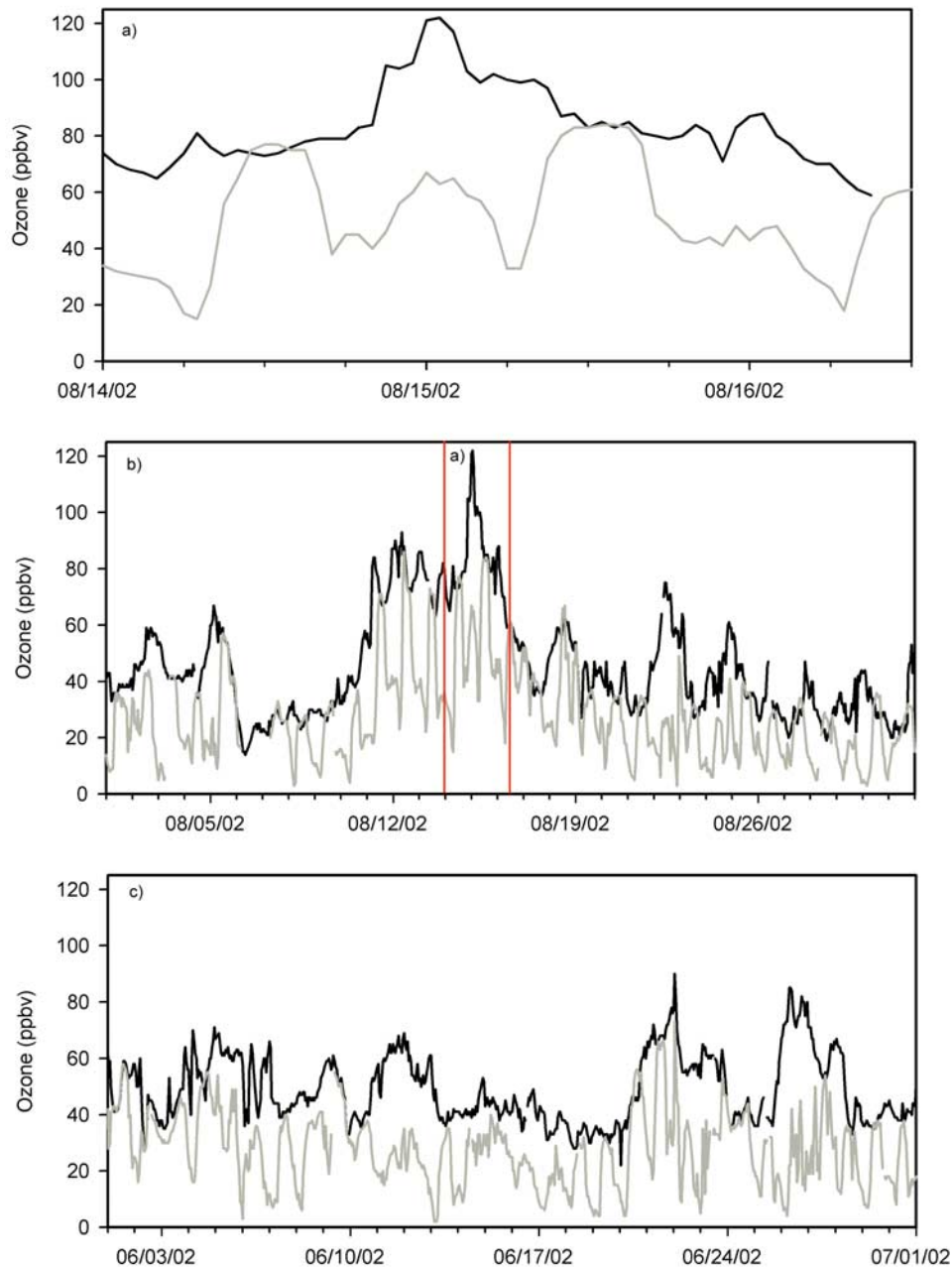
[21] In the following section, we use a major enhanced  $O_3$  event to provide an example of the diurnal cycle of  $O_3$  at the summit and base of Mount Washington, and to show that diurnal variation at this site is driven to a large degree by boundary layer dynamics. Figure 4a presents an  $O_3$  time series for the base and summit of the mountain for the period from 0000 eastern daylight time (EDT) 14 August 2002 to 1200 EDT 16 August 2002. This period was part of a major  $O_3$  event, which persisted for 6 consecutive days (Figure 4b) and has been described in more detail for sites in southern New Hampshire by Angevine *et al.* [2004]. This event occurred during a period of southwesterly flow, and was terminated by the passage of a cold front. The high  $O_3$  during this period was likely the result of chemically processed  $O_3$  rich air transported to New Hampshire [Angevine *et al.*, 2004; Griffin *et al.*, 2004]. Ozone at the summit peaked at about 0200 EST on 15 August 2002. The high  $O_3$  on 15 August was accompanied by elevated CO, which was  $\sim 260$  ppbv.

[22] The entire episode from 10 to 16 August 2002 can be seen in Figure 4b. Mount Washington experienced damp-

ened diurnal variation and higher average  $O_3$  during this period compared to the base. Ozone mixing ratios at the summit remained over 60 ppbv for the duration of the event, while the base recorded lower nocturnal mixing ratios of approximately 25 ppbv. The pattern noted at the summit is commonly attributed to isolation from surface deposition or nocturnal compensation by downward transport from the tropospheric  $O_3$  reservoir [Angle and Sandhu, 1986; Zaveri *et al.*, 1995]. Periods of downward transport are often associated with high wind speeds, which induce turbulence. During this particular episode, winds were consistently higher at night, with maximum speeds ranging from 11 to 23 m/s. The diurnal  $O_3$  patterns observed at Mount Washington agree with those at other high elevation locales, such as Green Knob, NC (1573 m), Whiteface Mountain, NY (1480 m), Sutton, Quebec (845 m) and other sites in the southern and eastern U.S. [Berry, 1964; Worth *et al.*, 1967; Mohnen *et al.*, 1977; Aneja *et al.*, 1991, 1994a; Hayden *et al.*, 2003]. These sites typically show minimal influence from the nocturnal inversion, with  $O_3$  mixing ratios peaking during the nighttime hours.

[23] The base normally experiences higher  $O_3$  in the afternoon and lower  $O_3$  during the night; however, during this period a nocturnal  $O_3$  spike was also measured at the base. The secondary nocturnal  $O_3$  peak at the base was 67 ppbv on 15 August 2002. This feature appeared occasionally in the  $O_3$  record, and based on results from a different location [Salmond and McKendry, 2002], is hypothesized to be the result of  $O_3$  transported to this site from layers aloft during periods of turbulence. Wind speeds at the summit exceeded 15 m/s, which supports the presence of turbulent transport during this time period. Secondary  $O_3$  maxima near midnight have been observed at a low elevation site in the Green Mountain National Forest in nearby Vermont and at other remote locations in the U.S. [Logan, 1989].

[24] Wind speed at the summit of Mount Washington was examined during periods with nocturnal  $O_3$  (2100–0500 LT) at the base above and below 40 ppbv. This bracketing captured the majority of the nocturnal  $O_3$  spikes. Nighttime periods with  $O_3$  greater than 40 ppbv had significantly higher mean wind speeds than their depleted counterparts. The mean wind speed at the summit during periods with base  $O_3$  greater than 40 ppbv was  $16 \pm 0.3$  m/s ( $N = 570$ ). During nocturnal periods with  $O_3$  less than 40 ppbv, the mean wind speed was  $10 \pm 0.1$  m/s ( $N = 4968$ ). This likely indicates that mechanically driven turbulence due to wind shear was causing  $O_3$  from aloft to penetrate the stable nocturnal inversion thus causing the  $O_3$  to rise at the base. It is possible that the high wind speeds causing this mechanically driven turbulence resulted from the development of a nocturnal jet. Low-level jets have core wind speeds between 10 and 15 m/s, with wind speeds increasing after sunset and reaching a maximum near midnight [Zhang *et al.*, 2001]. The summit and base  $O_3$  mixing ratios converged during the afternoons, suggesting deep boundary layer development each day of the event. During afternoons with vigorous heating, vertical exchange and mixing promoted similar  $O_3$  mixing ratios at the summit and base. Afternoon convergence of summit and base  $O_3$  mixing ratios was not common during cooler periods. Figure 4c presents an  $O_3$  time series for



**Figure 4.** Ozone time series based on hourly data provided by the AMC for the summit (black) and base (gray) of Mount Washington for (a) 0000 EDT 14 August 2002 to 1200 EDT 16 August 2002, (b) August 2002, and (c) June 2002. The ticks indicate local midnight in Figures 4b and 4c. The ticks are every 6 hours in Figure 4a. Data for 15 August exemplify the higher  $O_3$  mixing ratios often experienced at the summit relative to the base of the mountain. AIRMAP data for the period showed that the summit reached a maximum 1-hour average  $O_3$  mixing ratio of 128 ppbv. The maximum 1-hour averages at the base on the afternoons of 14 and 15 August were 77 and 84 ppbv, respectively.

both the summit and the base in June 2002. The average temperature for New Hampshire during this month was  $16.5^\circ\text{C}$  and there was 15.7 cm of precipitation. The average temperature for New Hampshire for August 2002 was  $20.7^\circ\text{C}$  and total monthly precipitation was 9.1 cm (<http://met-www.cit.cornell.edu/monitor.html>).

Comparison of Figures 4b and 4c shows that there was generally afternoon  $O_3$  convergence in August. However, in June the afternoon summit and base  $O_3$  mixing ratios were generally disconnected, likely indicating lower mixed layer heights during this month. Afternoon convergence has also been noted at two nearby sites in Sutton, Quebec,

**Table 3.** Description of O<sub>3</sub> Episodes

Description of Episode	Enhanced Episodes, %	Depleted Episodes, %
Stand alone event characterized by 1 enhanced/depleted afternoon or nighttime period	57	44
Enhanced/depleted afternoon period followed by an enhanced/depleted nighttime period or vice versa	9	14
Two successive afternoon or nighttime periods of enhanced/depleted O <sub>3</sub>	15	16
Enhanced/depleted O <sub>3</sub> persisting for more than 2 days	20	24

located ~220 km northwest of Mount Washington [Hayden *et al.*, 2003]. The summertime daytime mixed layer has typical depths of 1–2 km in the northeast [Holzworth, 1967], and thus boundary layer fluctuations at least partially drive diurnal O<sub>3</sub> variations at the summit of Mount Washington which can be located either above or below the mixed layer.

[25] *Moody et al.* [1998] determined the height of the mixed layer over Harvard Forest from the National Meteorological Center Nested Grid Model (NGM) temperature profiles for the years 1990–1993. They noted that there was not a large difference in the monthly averaged mixed layer height between June and August. However, average temperatures for Massachusetts and New Hampshire for June 2002 were colder than in the months of June during the 4-year study period for Harvard Forest. In addition, average temperatures in Massachusetts and New Hampshire during August 2002 were warmer than during the years 1990–1993 (<http://metwww.cit.cornell.edu/monitor.html>). Thus the effects of seasonal differences in mixed-layer development may have been accentuated during June and August 2002.

### 3.2. Enhanced and Depleted O<sub>3</sub> Events on the Summit

[26] Enhanced O<sub>3</sub> periods were identified as O<sub>3</sub> levels  $\geq$  90th percentile for afternoon or nighttime periods respectively. The 90th percentiles for night and afternoon periods were 65 and 62 ppbv respectively; the respective 10th percentiles were 30 and 31 ppbv. Successive afternoon and nighttime enhanced O<sub>3</sub> periods were grouped into episodes to identify the persistence of enhanced O<sub>3</sub> at Mount Washington (Table 3). Only ~20% of the episodes were characterized by high O<sub>3</sub> persisting for 2 days or more. This distribution clearly shows that most high O<sub>3</sub> periods at Mount Washington during the 6 summers 1998–2003 were spread out across the season and were not part of a small number of several-day events. The longest period of enhanced O<sub>3</sub> persisted for 6 consecutive days. This was the 11–16 August 2002 event discussed in 3.1.2 and presented in Figure 4. Two other notable events occurred in close succession, lasting 4 and 5 days respectively, from 1 to 4 May 2001 and from 8 to 12 May 2001. The long-range transport during these periods has been discussed previously by *DeBell et al.* [2004b] as they coincided with AIRMAP measurements of an Asian dust event in the northeastern U.S.

[27] A similar analysis was performed for depleted events (Table 3). The longest period of depleted O<sub>3</sub> persisted for approximately 4.5 days and took place from 12 to 16 July 2001. During this event a surface cyclone centered over southern Quebec transported cool clean air from Canada to New Hampshire. In summary, most of the depleted and enhanced events were spread out over the summertime period. Periods of extremely depleted or enhanced O<sub>3</sub>

lasting more than 2 consecutive days comprised ~20% of the total number of episodes.

### 3.3. Transport Analysis of Enhanced and Depleted O<sub>3</sub> Events

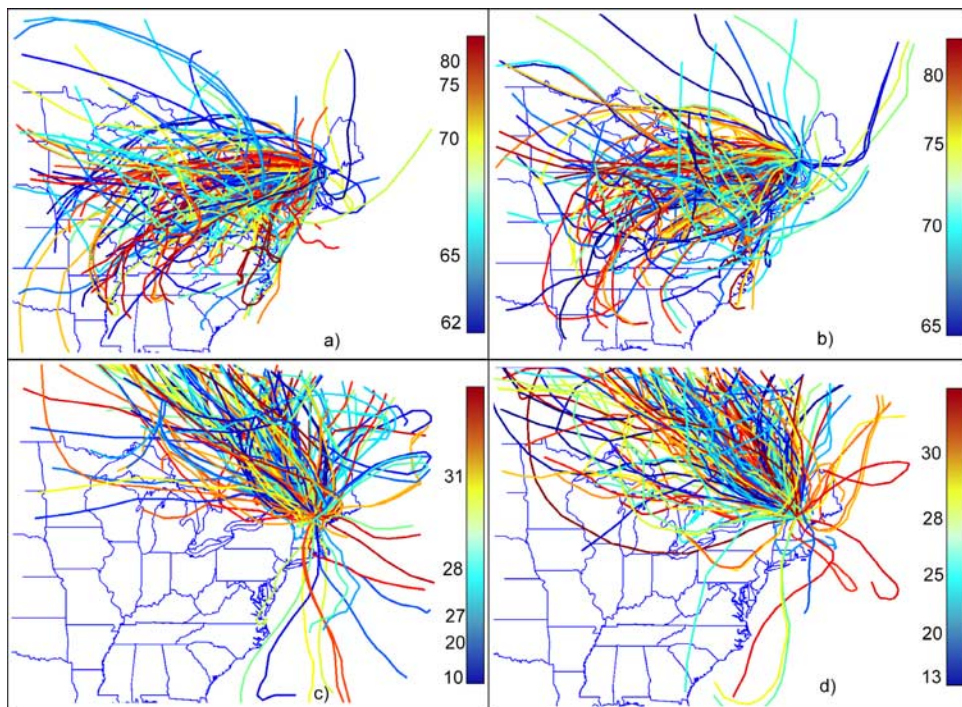
[28] For both afternoon and nighttime enhanced O<sub>3</sub> the corresponding trajectories were predominantly from the west and southwest (Figure 5). In agreement with the trajectories, enhanced events had a strong westerly or southwesterly local wind component, while depleted events were most commonly associated with northwesterly local winds. The color scales in the trajectory plots indicate the average O<sub>3</sub> mixing ratio upon arrival of the air mass at Mount Washington. Note that the color scale changes in each plot to reflect the different range of O<sub>3</sub> mixing ratios in each category. About 5% of the trajectories in both the enhanced afternoon and night periods with northerly or northeasterly components were identified, and this subset will be discussed in section 3.5.2.

[29] Night trajectories corresponding to 2-hour average O<sub>3</sub> mixing ratios  $\geq$  80 ppbv at Mount Washington represented the top 20% of the nighttime enhanced group and the top 2% of all nighttime periods. Nighttime trajectories were used to study this enhanced subset because the majority of high O<sub>3</sub> occurred during this period; there were only 7 afternoon trajectories associated with O<sub>3</sub>  $\geq$  80 ppbv. A plot of this most enhanced subset (Figure 6) showed that these trajectories followed two main paths: westerly or southwesterly. These events were associated with local wind in a small range from 225–300 degrees and wind speeds  $>$  5 m/s. With the exception of four episodes, the coincident synoptic conditions fell into two repetitive surface and 850 hPa patterns.

[30] The southwesterly trajectories corresponded to a distinct ridge of high pressure at 850 hPa, with the ridge axis located off the coast. This ridge was paired with an elongated surface warm sector over New England. The exact position of the surface cyclone ranged from east of the Great Lakes to north of New Hampshire. The southwesterly trajectories typically corresponded to surface isobars parallel to the east coast. The surface patterns associated with southwesterly flow correlated with synoptic conditions described as Atlantic return or moist tropical. This type of flow is found in the warm sectors of midlatitude cyclones and on the western side of surface anticyclones as they move out over the Atlantic [*Merrill and Moody*, 1996; *Moody et al.*, 1996; *Cooper et al.*, 2001a]. Atlantic return flow is typically characterized by warm temperatures and high relative humidity. A surface synoptic climatology of the Mount Washington area showed that this pattern dominates in summer [*Gillman et al.*, 2002].

[31] The westerly trajectories were consistently paired with a more dampened ridge at 850 hPa, with the ridge axis located over New England. The center of the surface





**Figure 5.** Back trajectories from Mount Washington (1998–2003) corresponding to (a) afternoon enhanced ( $\geq 62$  ppbv), (b) night enhanced ( $\geq 65$  ppbv), (c) afternoon depleted ( $\leq 31$  ppbv) and (d) night depleted ( $\leq 30$  ppbv)  $O_3$  periods. The color scales indicate the average  $O_3$  mixing ratio upon arrival at Mount Washington. Note that the color scale is different for each map to reflect the different range of  $O_3$  mixing ratios in each category.

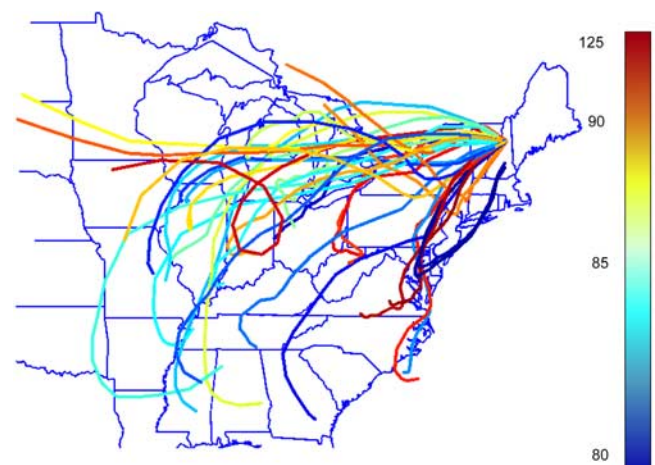
anticyclone was located over the Carolinas or off the coast. Again, the position of the surface cyclone and the associated warm sector changed as it moved toward the east, with similar ranges as above. Westerly trajectories were paired with surface isobars perpendicular to the east coast. Similar synoptic conditions corresponded to the afternoon trajectories associated with  $O_3 \geq 80$  ppbv.

[32] *Merrill and Moody* [1996] observed that warm sector flow delivered the most polluted air masses to the Maritime Province regions during the North Atlantic Regional Experiment (NARE). In their analysis of the meteorology during NARE, *Moody et al.* [1996] showed that warm sector transport delivered pollution from the industrial/urban areas of the eastern U.S. to the western North Atlantic. Their analysis also confirmed that the preceding upper level flow patterns often provided a mechanism for natural stratospheric  $O_3$  enhancements in upwind areas of the upper troposphere. We found one potential example of this phenomenon for the enhanced subset of  $O_3 \geq 80$  ppbv, and it is discussed in section 3.5.2.

[33] Less than 10% of the enhanced events were associated with surface anticyclones centered over New England (Table 4). Over 55% of the enhanced  $O_3$  periods occurred while New Hampshire was located in the warm/moist sector of a surface cyclone. This scenario was associated with a concurrent surface anticyclone centered over the mid-Atlantic States or the Carolinas approximately half the time. The presence of a surface anticyclone often preceded the enhanced  $O_3$  at Mount Washington, rather than being coincident with it. This may distinguish ozone events at Mount Washington from those at lower elevations in the

mid-Atlantic region. The highest  $O_3$  mixing ratios were often measured when New England was on the western side of the anticyclone, during periods of southwesterly or westerly flow.

[34] Arrival of approximately 70% of the depleted  $O_3$  trajectories at this site was associated with regional precipitation, conditions not conducive to  $O_3$  formation. Depleted  $O_3$  events were generally coupled with precipitation associated with a cold front. Passage of a cold front generally brings clean Canadian air from the northwest to the region.



**Figure 6.** Nighttime backward trajectories corresponding to  $O_3$  mixing ratios  $\geq 80$  ppbv when arriving at Mount Washington.

**Table 4.** Percentage of Trajectories in Enhanced and Depleted Groups Associated With a Particular Synoptic Feature Coincident With the Initialization Time<sup>a</sup>

	Ozone $\leq$ 10th Percentile		Ozone $\geq$ 90th Percentile	
	Night	Afternoon	Night	Afternoon
Descending from above 700 hPa	11	18	29	43
Ascending/predominantly below 850 hPa	49	36	40	33
Surface anticyclone centered over New England	16	26	7	9
New Hampshire in warm sector	2	5	62	57
Concurrent surface anticyclone over mid-Atlantic states or Carolinas	8	7	26	32
Regional-scale precipitation on arrival	72	74	32	26

<sup>a</sup>The number of cases in each group were as follows: ozone  $\leq$ 10th percentile: 177 night, 174 afternoon; ozone  $\geq$ 90th percentile: 170 night, 152 afternoon.

Previous work has shown that surface flow behind cold fronts is typically low in O<sub>3</sub> [Cooper and Moody, 2000].

[35] Patterns in vertical transport suggest that enhanced O<sub>3</sub> at Mount Washington is at least partially influenced by subsidence of higher O<sub>3</sub> levels (e.g., 50–60 ppbv) characteristic of the free troposphere [Logan *et al.*, 1999], and is subject to pollution transported long distances. Forty-three percent of the Mount Washington afternoon enhanced O<sub>3</sub> trajectories descended from above 700 hPa during the previous 72 hours, while only 18% of corresponding depleted trajectories descended from this elevation (Table 4). The free troposphere has been shown to have a dominating influence on O<sub>3</sub> at other elevated sites in the eastern region of the U.S. and Europe, such as Mount Mitchell, NC (1950 m) and Zugspitze, Germany (2690 m) [Kley *et al.*, 1994]. Although a large portion of the afternoon enhanced trajectories indicated minimal surface interaction, the average height of enhanced trajectories did not become greater than the average altitude of the depleted trajectories until 42 hours back in time. The average horizontal position of the daytime enhanced trajectories at 42 hours back in time was 41.4°N, 81.7°W. The difference in the average altitudes was greatest ( $\sim$ 730 m) at 72 hours back in time.

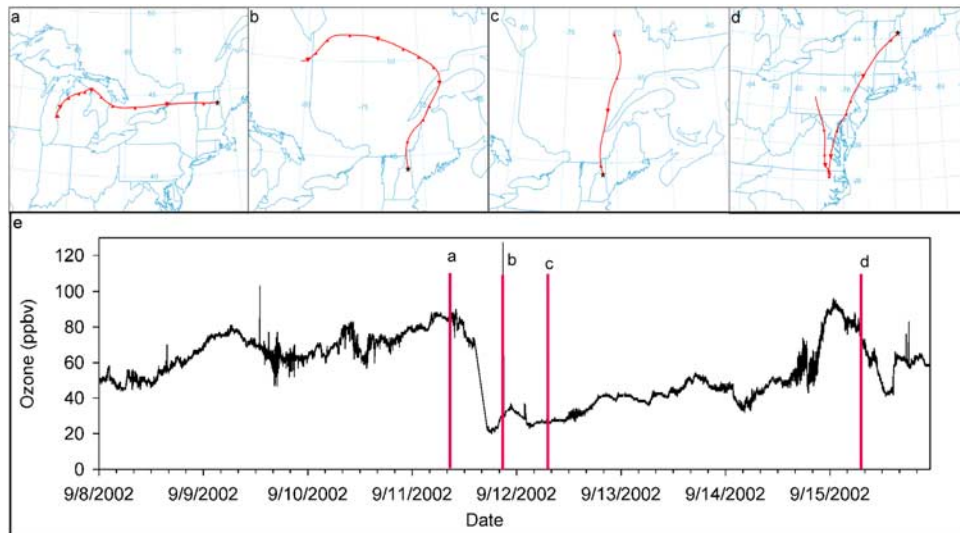
[36] Twenty-nine percent of the nighttime enhanced O<sub>3</sub> trajectories and 11% of the depleted trajectories arriving at Mount Washington descended from 700 hPa or above. There was a smaller percentage (29% versus 43%) of enhanced nighttime trajectories descending from the free troposphere than for the afternoon period. The average altitude of enhanced trajectories was greater than their depleted counterparts after 28 hours back in time. The average horizontal position of enhanced nighttime trajectories was 42.3°N, 78.8°W at 28 hours back in time, which placed the “average” enhanced trajectory south of the western edge of Lake Ontario, near Buffalo, NY. Enhanced/depleted trajectories differed by 525 m at 72 hours back in time. The corresponding average horizontal position of afternoon enhanced trajectories 28 hours back in time was 41.9°N, 79.1°W. These trajectories suggest that lofted pollution from the urban/industrial regions of the midwest surrounding the Great Lakes is impacting northern New Hampshire.

[37] A higher percentage of depleted trajectories for both night and afternoon periods ascended to Mount Washington or remained below 850 hPa than for enhanced trajectories. However, the differences in these percentiles were small. Near surface flow and the associated dry deposition (R. Talbot *et al.*, Diurnal characteristics of surface-level O<sub>3</sub> and other important trace gases in New England,

submitted to *Journal of Geophysical Research*, 2004) likely played a role in some of the depleted events, but this analysis indicates that near surface flow was also associated with a large percentage of enhanced events (Table 4). These results highlight the need for tracer data (e.g., isoprene) to determine whether O<sub>3</sub> arriving at the summit is associated with local sources via near surface flow or with descending flow from aloft.

[38] Our analysis indicates that periods of enhanced O<sub>3</sub> at high elevation sites in New England often occurred when anticyclones move offshore. During these periods, New Hampshire was located on the backside of the high or in the warm sector of an approaching surface cyclone. The synoptic situation generated a condition where major pollution sources most likely originated along the eastern seaboard or in the midwest. This finding agrees with recent AIRMAP modeling results which have shown that O<sub>3</sub> episodes in New England commonly occur under conditions of strong southwesterly synoptic flow [Mao and Talbot, 2004a], and with observations during NARE [Moody *et al.*, 1996]. It also agrees with previous modeling work that has demonstrated that O<sub>3</sub> episodes in New England are likely to occur when surface anticyclones stagnate over the region or are immediately offshore for more than 3 consecutive days [Jacob *et al.*, 1993]. Previous back trajectory calculations at 850 hPa for several high elevation sites in the northeastern U.S. also indicated that most sites were influenced by upwind urban and industrial source areas in midwestern states during high O<sub>3</sub> episodes [Aneja *et al.*, 1994b].

[39] The westerly and southwesterly transport corridors that were associated with the highest O<sub>3</sub> ( $\geq$ 80 ppbv) at Mount Washington correlate with the W and SW trajectory clusters calculated for Harvard Forest [Moody *et al.*, 1998]. Despite differences in site characteristics between Mount Washington and Harvard Forest and different study periods, the highest O<sub>3</sub> mixing ratios in summer at both sites were associated with regional-scale transport from the west under deep boundary layers. Also in accordance with results from Harvard Forest, the lowest O<sub>3</sub> during the summer season was associated with northwesterly transport. Results from this analysis indicate that high O<sub>3</sub> at Mount Washington is also associated with southwesterly transport. Moody *et al.* [1998] found relatively low average O<sub>3</sub> and total reactive nitrogen (NO<sub>y</sub>) in the SW trajectory cluster for Harvard Forest. However, the SW trajectory cluster did bring generally polluted air to Harvard Forest, characterized by enhanced mixing ratios of CO, nitrogen oxides (NO + NO<sub>2</sub>), and acetylene, suggesting O<sub>3</sub> titration and or lower photochemical production under cloudy conditions. Warm



**Figure 7.** Back trajectories initialized at (a) 0900 UTC 11 September, (b) 2100 UTC 11 September, (c) 0700 UTC 12 September, and (d) 0700 UTC 15 September. (e) One-minute averaged O<sub>3</sub> for Mount Washington from 8 to 16 September 2002 (UTC).

sector flow ahead of an advancing cold front is one of the most common synoptic conditions in northern New England during summer [Gillman *et al.*, 2002]. We observed some of the highest O<sub>3</sub> at Mount Washington during these conditions, but our analysis did not quantify the average O<sub>3</sub> during all days with this type of flow regime.

[40] The base of Mount Washington also experienced elevated O<sub>3</sub> during periods of elevated O<sub>3</sub> at the summit during southwesterly flow. One example of this is the O<sub>3</sub> episode referenced in Figure 4 that occurred during August 2002. However, the O<sub>3</sub> enhancements were generally less at the base than at the summit, except during afternoon periods when there was convergence of base and summit O<sub>3</sub> mixing ratios. This pattern suggests that O<sub>3</sub> enhancements in this region during periods of southwesterly flow are not limited to the free troposphere, but are more pronounced there. There are no large NO sources located near the base monitoring site, thus most of the O<sub>3</sub> depletion would be associated with deposition.

### 3.4. Case Study: 8–15 September 2002

[41] In this section we present a case study we identified to illustrate the point that summertime O<sub>3</sub> at Mount Washington is constrained by regional-scale meteorology. The O<sub>3</sub> data for the period from 8 to 15 September 2002 is an example where changing synoptic conditions caused O<sub>3</sub> mixing ratios to shift rapidly from enhanced to depleted levels. Trajectories initialized from the summit at different times are shown in Figures 7a through 7d. Figure 7e presents the 1-min averaged O<sub>3</sub> time series for Mount Washington during this period.

[42] From 8 to 11 September westerly transport (Figure 7a) resulted from a surface high pressure system centered south of New England paired with a relatively flat upper level ridge. Ozone mixing ratios at Mount Washington remained elevated (>60 ppbv) during most of this period. During this time a surface low pressure system was approaching from the west while tropical storm Gustav

was moving toward the north along the east coast. The rapid decline in O<sub>3</sub> mixing ratios on 11 September (Figure 7b) coincided with the passage of a cold front, which shifted winds from westerly to northerly. We hypothesize that the peak in O<sub>3</sub> that followed the shift was either associated with local lightning strikes on the summit or with rapidly descending air. Ozone production processes in thunderstorms are a topic of debate and beyond the scope of this paper [Martin *et al.*, 2000; Zahn *et al.*, 2002]. The low pressure system approached from the west and combined with Gustav as it moved off the coast of Maine. As a result, strong northerly flow continued through 12 September on the western side of Gustav (Figure 7c). As Gustav continued to move off to the northeast, surface high pressure developed over the midwest moved toward the east, and eventually out over the Atlantic. New England returned to southwesterly warm sector flow on 15 September (Figure 7d) and O<sub>3</sub> mixing ratios returned to enhanced levels near 80 ppbv.

## 3.5. Natural and Anthropogenic O<sub>3</sub> Contributions

### 3.5.1. Background O<sub>3</sub> Based on CO

[43] There are several different definitions and calculation methodologies used to identify and determine background O<sub>3</sub> [Lin *et al.*, 2000]. One approach to estimating background O<sub>3</sub> is by its correlation with relatively low CO mixing ratios [Trainer *et al.*, 1993]. This approach was used for the summers 2001–2003 because both CO and O<sub>3</sub> measurements were available during this period. The results are summarized in Table 5. Using AIRMAP data, the monthly background O<sub>3</sub> mixing ratios were calculated as the median O<sub>3</sub> value corresponding to the lowest 10th and 25th percentiles of CO mixing ratios. The percentiles were calculated separately for each month. The 10th percentile CO mixing ratios ranged from 110 to 154 ppbv, and the 25th percentile CO mixing ratios ranged from 119 to 166 ppbv. The background O<sub>3</sub> mixing ratios varied both monthly and interannually, and ranged from 31 to 50 ppbv during summers 2001–2003.

**Table 5.** Estimated Monthly Background O<sub>3</sub> Mixing Ratios Calculated As the Median O<sub>3</sub> Value Corresponding to the Lowest 10th and 25th Percentiles of CO Mixing Ratios for the Summit of Mount Washington<sup>a</sup>

	CO < 10th Percentile			CO < 25th Percentile		
	2001	2002	2003	2001	2002	2003
May	48	43	49	48	43	50
June	43	44	40	44	42	45
July	30	35	38	31	41	39
August	37	33	39	39	36	40
September	36	47	38	36	48	41

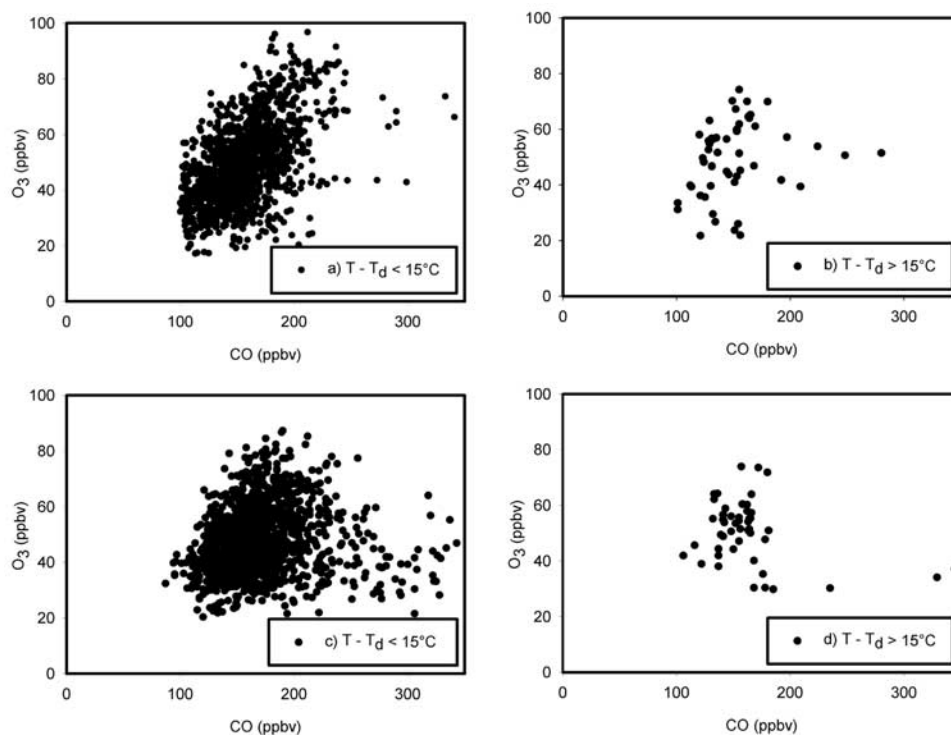
<sup>a</sup>AIRMAP data were used for these calculations. All values are given in ppbv.

[44] The range in background mixing ratios observed at Mount Washington is consistent with other work in the boundary layer and at sites in the lower free troposphere. Background O<sub>3</sub> at Harvard Forest, calculated by *Lin et al.* [2000] using the lowest 25th percentile CO data, ranged from 35 ppbv in the fall to 45 ppbv in the spring. *Bronnimann et al.* [2000] have shown that O<sub>3</sub> mixing ratios at elevated sites in the Alps converge to values around 40 ppbv during periods with low CO levels.

[45] Ozone versus CO was plotted for night and afternoon periods using AIRMAP data for summers 2001–2003, and these plots are presented in Figure 8. The number of data points available for each plot and the associated slope are given in Table 6. In general, positive O<sub>3</sub>/CO slopes may signify photochemical O<sub>3</sub> production, while negative slopes can indicate stratospheric contributions or O<sub>3</sub> destruction. An O<sub>3</sub>/CO slope of 0.3 is common for aged air masses in

the eastern U.S. [*Chin et al.*, 1994; *Mao and Talbot*, 2004b]. *Moody et al.* [1998] showed that the O<sub>3</sub>/CO slope for Harvard Forest data varied with air mass history. *Cooper et al.* [2001b] emphasized that the O<sub>3</sub>/CO slope of 0.3 generally observed for the eastern U.S. is dependent on rapid transitions in transport from different source regions.

[46] One signature of stratospheric air is high O<sub>3</sub> accompanied by low CO; however, data from NARE showed that enhancements in O<sub>3</sub> are often paired with small decreases in CO, and O<sub>3</sub> enhancements  $\leq 20$  ppbv are often accompanied by no significant change in CO mixing ratios [*Parrish et al.*, 1998]. Figure 8 distinguishes subsets of points by their associated dew point depression, with higher dew point depressions (Figures 8b and 8d) indicating a subsiding dry layer and a possible stratospheric component to the sampled air mass. These points indicate that subsiding dry airstreams have a mean O<sub>3</sub> of 51 ppbv (median of 53 ppbv).



**Figure 8.** Plots of O<sub>3</sub> versus CO using AIRMAP data for the summit for summers 2001–2003 for night (0700–1000 UTC) and day (1900–2200 UTC). The points are aggregated by dew point depression ( $T - T_d$ ). Points with corresponding dew point depressions less than 15°C are shown for (a) night and (c) day periods. Points with corresponding dew point depressions  $\geq 15^\circ\text{C}$  during (b) night and (d) day are shown. The number of points in each category is given in Table 6.

**Table 6.** Slope and Number of Points Plotted in Figure 8 Falling Under Each Dew Point Depression Bin<sup>a</sup>

	Night (0700–1000 UTC)		Day (1900–2200 UTC)	
	Slope	<i>n</i>	Slope	<i>n</i>
$T - T_d < 15^\circ\text{C}$	0.34	1516	-0.13	1566
$T - T_d \geq 15^\circ\text{C}$	-1.20	52	-0.099	57

<sup>a</sup>The number of points associated with dew point depressions  $\geq 15^\circ\text{C}$  make up approximately 3% of the total number of points.

Understanding the timing and magnitude of these dry air layers and their contribution to the background  $\text{O}_3$  is important to understanding how much additional  $\text{O}_3$  from anthropogenic sources is needed to elevate the  $\text{O}_3$  mixing ratios to unhealthy levels. The relative frequency of these dry air mass  $\text{O}_3$  events is low, but the fact that they deliver above background  $\text{O}_3$  on average should not be ignored. These may be indicative of the impact that upper-tropospheric  $\text{O}_3$  from stratospheric enhancements has on background levels.

### 3.5.2. Identification of a Stratospheric Influence on Enhanced Events

[47] The majority of backward trajectories arriving at Mount Washington for enhanced  $\text{O}_3$  conditions indicated westerly or southwesterly transport. Transport from these directions does not preclude a natural stratospheric  $\text{O}_3$  enhancement; however, identifying stratospheric influences is complicated by transport over industrialized/urban source regions. Twenty northerly or northeasterly trajectories were also associated with enhanced  $\text{O}_3$  levels, and these events were identified because the  $\text{O}_3$  enhancement was likely natural in origin. Ozone events with northwesterly trajectories extending north of the Great Lakes were also included here because results from the Program for Research on Oxidants: Photochemistry, Emissions and Transport (PROPHET) show that air from this Canadian region is generally associated with low  $\text{O}_3$  except during periods influenced by Canadian forest fires [Cooper *et al.*, 2001b]. Further investigation of the meteorological conditions associated with these trajectories led to the identification of several enhanced events with a likely stratospheric  $\text{O}_3$  component. Two of the northerly trajectories in the enhanced category were associated with forest fires located mainly north of  $52^\circ\text{N}$  in Quebec during July 2002 [DeBell *et al.*, 2004a].

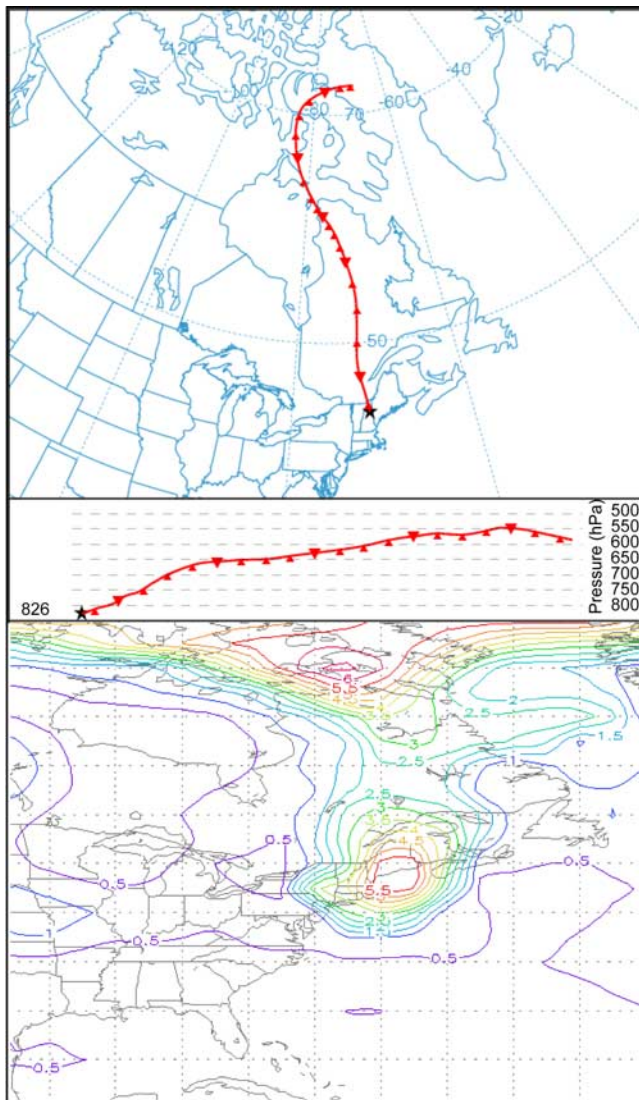
[48] Plots of potential vorticity (not shown) were produced from National Center for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalysis data that corresponded to periods covered by the back trajectories. Potential vorticity is conserved by isentropic transport and is a useful tracer of stratospheric air [Hoskins *et al.*, 1985]. There are strong isentropic potential vorticity (IPV) gradients between the troposphere and the stratosphere. IPV values greater than 1 are indicative of a stratospheric influence [Shapiro, 1980].

[49] The dew point depressions during events with suspected stratospheric influence ranged from 10 to  $41^\circ\text{C}$ . Using the trajectories from night and afternoon enhanced periods was not sufficient to identify all possible stratospheric influences, so the dew point depression was calculated for every hour for every summer. All depressions greater than  $10^\circ\text{C}$  were identified. A small percentage of the dry periods corresponded to enhanced  $\text{O}_3$ . Potential vorticity

plots for these periods were then created for comparison. A total of 10 events were identified where  $\text{O}_3$  was greater than 65 ppbv, dry air was present, and descending trajectories likely passed through areas of stratospheric influence. The average dew point depression of these events was  $23^\circ\text{C}$ . The average dew point depression of all other events was approximately  $3^\circ\text{C}$ .

[50] Only one enhanced event was associated with descending air passing through a region with a high potential for stratospheric tropospheric exchange as indicated by IPV plots, a coincident dew point depression  $>10^\circ\text{C}$ , and  $\text{O}_3$  reaching 80 ppbv. It was a nighttime event identified by a northerly trajectory in Figure 5b. Figure 9a is a backward trajectory initialized on 1 June 2001 from Mount Washington at 0900 UTC. The trajectory indicates rapid northerly descent from approximately 500 hPa toward the site. Contours of isentropic potential vorticity (IPV) on the 315K surface are shown in Figure 9b for 0000 UTC 31 May 2001. Figure 9 indicates that the air mass impacting Mount Washington on 1 June was likely located in a region with high potential for stratosphere troposphere exchange during the previous 48 hours. Between 0800 and 0900 UTC, the dew point temperature dropped from  $-2^\circ\text{C}$  to  $-14^\circ\text{C}$ . The dew point dropped further to  $-16^\circ\text{C}$  for approximately 3 hours before returning to  $0^\circ\text{C}$  at 1200 UTC. Dew points this low are uncharacteristic of regional summer air at the altitude of Mount Washington. Ozone at Mount Washington was 70–80 ppbv during this period, but CO was not enhanced. Surrounding monitoring sites at lower elevations did not experience this  $\text{O}_3$  peak, suggesting that the stratospheric air did not penetrate the stable nocturnal boundary layer. During this event, the stratospheric air followed the western edge of an upper level trough and then descended into a weak surface anticyclone over New England. This transport agrees with conceptual models [Danielson, 1980].

[51] It has been argued that the stratosphere does not frequently contribute to elevated surface  $\text{O}_3$  mixing ratios over large areas [Vieze *et al.*, 1983]. However, Cooper and Moody [2000] suggested that stratospheric  $\text{O}_3$  enhancements of the midtroposphere are common in the eastern U.S. and have the potential to impact the surface during conditions that are also favorable for photochemical  $\text{O}_3$  production. Parrish *et al.* [1993] showed that stratospheric and anthropogenic  $\text{O}_3$  contributions to the troposphere over the North Atlantic are comparable. However,  $\text{O}_3$  from the stratosphere enters the upper troposphere, and much of this  $\text{O}_3$  is lost prior to reaching the lower troposphere [Parrish *et al.*, 1993]. Moody *et al.* [1996] showed that the upper level flow patterns preceding the delivery of pollution in a surface warm sector often provided a mechanism for natural stratospheric  $\text{O}_3$  enhancements in upwind areas of the upper troposphere. We found a potential example of this phenomenon. Westerly descending trajectories impacted the summit



**Figure 9.** (a) A backward trajectory initialized on 1 June 2001 from Mount Washington at 0900 UTC and (b) contours of isentropic potential vorticity, a stratospheric tracer, on the 315°K surface are shown for 0000 UTC 31 May 2001. The units are  $\text{km}^2 \text{s}^{-1} \text{kg}^{-1} * 10^6$ . The panel between Figures 9a and 9b indicates the altitude of the trajectory in hPa.

on 27 June 2003 and  $\text{O}_3$  mixing ratios reached over 80 ppbv. Two days earlier a deep upper level trough was present west of the Great Lakes. The air impacting the summit on 27 June would have gone through this area. The dew point depression on the summit was small ( $<5^\circ\text{C}$ ) when  $\text{O}_3 \geq 80$  ppbv was measured; however, the levels remained enhanced for several hours and the dew point depression increased to  $10^\circ\text{C}$  several hours later. This suggests that natural enhancements upwind could have contributed to the background  $\text{O}_3$  burden and provided a base for photochemical contributions.

[52] The  $\text{O}_3$  record at Mount Washington suggests that the stratosphere does play a role in enhanced  $\text{O}_3$  at this site; however, the role is limited in summer and is not likely the

single source of  $\text{O}_3$  mixing ratios greater than 80 ppbv. This analysis has identified a stratospheric contribution to a small percentage of enhanced  $\text{O}_3$  events at this high elevation site; however, this analysis did not quantify the relative contributions of anthropogenic and stratospheric  $\text{O}_3$  sources. Stratospheric  $\text{O}_3$  was hypothesized to influence the summit during conditions also potentially conducive to photochemical  $\text{O}_3$  production, which make any relative contribution calculations difficult without additional measurements of anthropogenic and stratospheric tracers.

#### 4. Conclusions

[53] This study has identified the major synoptic conditions coincident with enhanced and depleted  $\text{O}_3$  at Mount Washington, the highest peak in the northeastern U.S. Enhanced  $\text{O}_3$  events at Mount Washington were generally associated with westerly and southwesterly flow, while depleted  $\text{O}_3$  events corresponded to northwesterly flow. During more than 50% of the periods with enhanced  $\text{O}_3$ , New Hampshire was located on the backside of an anticyclone, or in the warm/moist sector of an approaching surface cyclone. These synoptic conditions generated a situation where New Hampshire was downwind from major pollution sources along the eastern seaboard or in the midwest. Many periods of extreme  $\text{O}_3$  at Mount Washington were short-lived, frequently less than a day in length, and would not have been considered episodes under the definitions used in many previous studies. Several of the periods when enhanced  $\text{O}_3$  persisted at Mount Washington for two or more consecutive days were associated with a surface anticyclone, but the  $\text{O}_3$  peaked when strong synoptic flow returned as the center of the anticyclone moved off the coast. Stratospheric air does not appear to be a major  $\text{O}_3$  source during summer months at this site, but the relative contributions of stratospheric and anthropogenic sources are difficult to separate without tracer species to apportion sources.

[54] Mount Washington provides a unique opportunity to study air masses advected into the lower troposphere in New England. There is a relatively long record of summer  $\text{O}_3$  at this site, and with the advent of the AIRMAP network, data are now available year-round. Future research objectives should be to understand the link between climate and  $\text{O}_3$ , to quantify the relative contributions from anthropogenic and stratospheric  $\text{O}_3$  sources, and to characterize the seasonal cycle of  $\text{O}_3$  at this site.

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