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Ozone Concentration Characteristics at a High-Elevation Forest Site

G. Wooldridge, K. Zeller, and **R. Musselman**

With 9 Figures

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Summary

Atmospheric ozone concentrations have been monitored at a subalpine forest ecosystem site, 3180 m above mean sea level (msl), and at a 2680 m msl forest-steppe ecotone site 15 km to the southeast. Ozone concentrations were monitored at three heights above the ground on a 30m tower at the higher elevation site, and on a 10m tower in a large meadow downwind of this site.

The research reported here concentrates on the data for the first six months of 1990–1994. The diel amplitude of ozone concentrations is very small in winter, increasing as the seasons advance to June. Following snowmelt in late May or June, the nighttime minima decrease under the forest canopy. The highest monthly mean ozone concentrations occur in April or May, depending on the year. Episodal high concentrations were recorded during spring months when upper level atmospheric low pressure troughs and cut-off low centers occurred. These contributions peak in May, and add about 10% to normal May background ozone concentrations, varying widely from year to year. Spectral representations of ozone concentrations, illustrate the suppression of the diel peak during spring months, when stratospheric-tropospheric intrusion patterns show no significant diel cycle.

1. Introduction

The ozone concentration in the atmosphere at a given point depends upon a complexity of phenomena. In addition to the photochemical reactions, which may be significantly affected by anthropogenic factors (Chameides and Lodge, 1992), atmospheric processes in the stratosphere and troposphere contribute significantly to near-surface ozone concentrations. The best documented stratospheric-tropospheric mechanism that contributes to ozone concentrations in the lower troposphere is known as "tropopause folding", which may produce stratospheric intrusions. This mechanism has been described by Danielsen (1980) and Danielson and Hipskind (1980).

Intrusions of ozone occur most frequently in middle latitudes during spring and early summer months, when dry, ozone-rich air flows on long downward trajectories into the middle or lower troposphere. These layers of high ozone concentrations have been detected at the earth's surface (Arlette, 1958; Lisac et al., 1993). On other occasions, the layer of ozone-rich air may be diluted by turbulent mixing in the mid- to lower troposphere, resulting in prolonged, enhanced ozone concentration episodes (Davies and Schuepbach, 1994).

Austin and Follows (1991) estimated that stratospheric intrusions are the source of 25% of the observed ozone mixing ratio at 300 hectoPascal (hPa) altitudes during late winter and spring months in middle latitudes. They estimated that the intrusions occur in short-lived events once or twice a month. Mean concentrations over 60 ppb

correlate well with the 500 hPa flow pattern of a high pressure ridge and an associated low-level thermal trough (McKendry, 1994).

Analyses of the ozone data presented here have concentrated on the first six months of the years of 1990–1994, and to a lesser extent on the months of July and August, 1992–1993. We are interested in the changes from the winter regime of January and February into the spring and early summer months, and the contribution of stratospheric intrusions to surface ozone concentrations at a remote, high-elevation site.

1.1 Ozone "Signatures"

The diel and short-term characteristics of surface tropospheric ozone concentrations have been categorized into three groups: (1) Urban; (2) Rural; and (3) Remote. Urban characteristics are strongly affected by the timing and concentration of anthropogenic precursors of ozone, and generally result in a maximum in the afternoon and a minimum during early morning hours. Due to reactions involving nitrogen oxides from fossil fuel combustion and soils, the early morning minimum may approach zero in large cities. Peak concentrations exceeding ambient air quality standards may occur in mid- to late afternoon. Significant annual trends can usually be detected in urban ozone data, with the highest concentrations occurring in mid- to late summer.

"Rural" ozone data might better be termed "rural and urban-affected", because of advected urban plumes that affect concentration characteristics at distances up to 150 km or more (Zeller et al., 1977; Stocker et al., 1993; Mueller, 1994). Urban effects can be found in stations at elevations over 1000 m msl (Aneja and Zheng, 1992), particularly where large urban centers exist in proximity to mountainous terrain. Sillman et al. (1993) reported urban effects over a wide region, with elevated O_3, NO_x, and volatile organic carbon levels within a broad plume over Lake Michigan at distances of 300 km from the major industrial center of Chicago.

Ozone concentration characteristics at remote sites have received less attention that at urban or rural sites. Ideally, remote sites are beyond the reach of urban plumes or other anthropogenic effects. The high Alpine station (3569 m msl) at the Jungfraujoch in Switzerland shows small seasonal variations in ozone. Extreme values are not generally observed there in averaging periods of an hour or longer (Wunderli and Gehrig, 1990), but infrequent sharp peaks sometimes have exceeded the measurement range of ozone monitors.

1.2 Forest-Ozone Interactions

For the purposes of the investigations reported here, stratospheric-tropospheric intrusions were assumed present when near-surface ozone concentrations exceeded 60 ppb for a period of ten hours or more, concurrent with low relative humidity values. These criteria were used to exclude occasional midday values that exceeded 60 ppb during late spring and summer months. The presence of very dry air at the beginning of high ozone concentrations suggests downward trajectories of air from the stratosphere or upper troposphere.

Large coherent eddies over the rough top of a forest result in the penetration of gaseous constituents of the atmosphere downward into the canopy. Strong turbulent transport during windy conditions brings pollutants into the lower canopy and trunk space resulting in concentrations that are only slightly lower than above the canopy (Bohm, 1991).

Forests function as a continuous sink for the deposition of ozone. Ozone is deposited on forest vegetation and soil surfaces by passive absorption and by active stomatal uptake into leaf tissue. Fluxes of ozone into forest canopies depend on the atmospheric concentrations of ozone, the surface area of leaf and soil exposed, the wetness of the surfaces, and the stomatal conductance of leaf tissue. This deposition to forests is much reduced in winter months when the forest canopy and soils are covered with ice or snow.

Ozone effects on forest vegetation originate with injury at the cellular level on leaf tissue, and manifest themselves as reductions in growth if the exposure is sufficient to exceed detoxification or repair (U.S. *E*nvironmental *P*rotection *A*gency (EPA), 1986). The magnitude of this impact on a regional or national basis remains unknown, since the seasonal and daily patterns of surface ozone are highly site specific, and plants vary in their susceptibility to ozone injury. Ozone concentrations of 60 ppb and 70 ppb have been sug-

gested as critical levels for cumulative impact indices for exposure of agricultural crops (Lee et al., 1989). Additionally, the timing and intensity of the ozone intrusions vary, and plant susceptibility varies according to the growth stage of a given plant species. The importance of ozone concentrations in plant response has been reviewed by the EPA. In fumigation experiments, Keller and Hasler (1987) found no significant changes in plant growth at low ozone concentrations, but changes were severe at concentrations between 100 and 300 ppb. The concentration of the exposure is an important component of damage (Musselman et al., 1994).

2. Observations and Analyses

The meteorological and ozone data which form the basis of the research reported here were recorded at two sites in the Rocky Mountains of Southeastern Wyoming, U.S.A. The *G*lacier *L*akes *E*cosystem *E*xperiments *S*ite, (GLEES), is located at 3170–3450 m elevation in the Snowy Range on the Medicine Bow National Forest, 55 km west of Laramie, Wyoming, at 41°22′3″ latitude and 106°15′30″ longitude (Fig. 1). The GLEES comprises an alpine/subalpine experimental ecosystem where baseline data are collected on landscape habitats, floristics, geology, soils, aquatics, atmospheric environment, hydrology, and snow (Musselman, 1994). A southeastern extension of the GLEES includes a subalpine fir and Engelmann spruce forest in which the 30-m Brooklyn tower, located at an elevation of 3180 m, is used to measure meteorological variables and ozone concentrations.

A second ozone monitoring site was located 15 km southeast of the GLEES, near Centennial, Wyoming. This site was an EPA National Dry Deposition Network (NDDN) site, and part of the EPA Clean Air Status and Trends Network (CASTNET). The site elevation of 2680 msl is 500 m lower than the GLEES, in an ecotone of sparse coniferous trees and grasslands. It is designated here as the Centennial NDDN site. In August, 1991 this monitoring station was moved to a large subalpine meadow, about 150 m southwest of the GLEES Brooklyn tower site, and 70 m downwind from the edge of the forest. This site is designated as the Brooklyn NDDN location. The NDDN ozone sampling height is 10 m above the surface (Zeller and Hehn, 1994). Ozone monitoring at the Brooklyn NDDN and the Centennial NDDN sites was conducted in accordance with EPA NDDN standards.

The main basis of the work reported here is ambient ozone concentrations above the canopy, and in the trunk space below the level of foliated lateral branches of the subalpine fir-Engelmann spruce forest at the Brooklyn tower (location 1, Fig. 1). The Brooklyn NDDN station (location 2 in Fig. 1) has provided ozone and wind data for comparison with the tower data taken above the forest canopy. The Centennial NDDN data

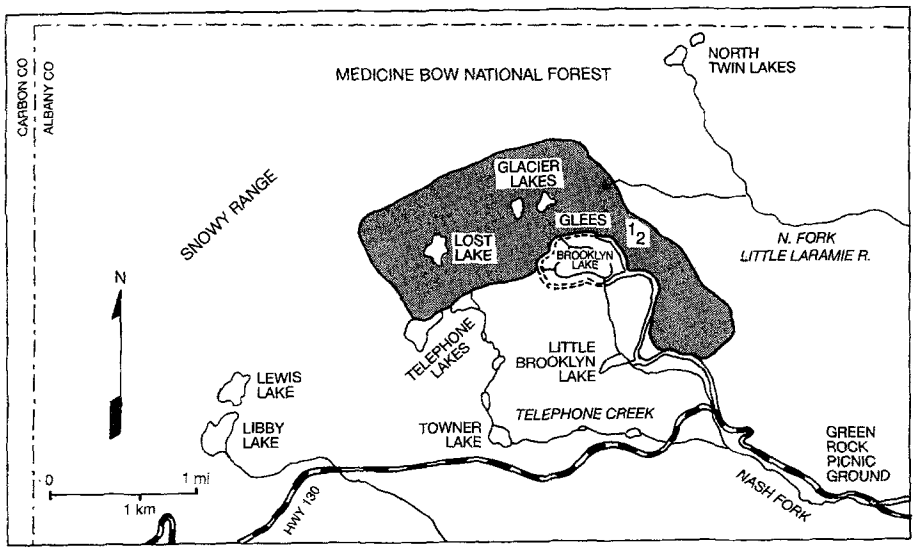

Fig. 1. Location of the GLEES. The experiment site and its southeast extension are in black. The Brooklyn tower and NDDN sites are marked as 1 and 2 respectively

allows a comparison of ambient ozone concentrations as a function of elevation.

The wind climate at the GLEES has been determined through an analysis of tree deformation (Wooldridge et al., 1992) and from continuous wind speed and direction data measured at two locations at the GLEES. Winds blow predominantly from the west and west-northwest over the GLEES and at the Brooklyn tower location, with an annual average speed of 8 ms^{-1} 13 m above the canopy. Easterly winds seldom occur, and have not been recorded at speeds greater than 15 ms^{-1}. Although thunderstorms occur frequently during summer months, the accompanying winds do not appear to be a significant factor in the wind climatology. Precipitation falls mostly as snow, and produces a winter ground cover varying from zero over bare ground at exposed points to more than five meters depth in drifts. The spatially averaged seasonal snow accumulation measured at the GLEES is about 2 m in depth. As spring snowmelt progresses, bare ground first appears during late May at locations near the Brooklyn tower site. Snowmelt is usually complete by late June, with a few drifts remaining until midsummer in protected areas.

The ozone measurements at all levels and sites at the GLEES were made with Thermo Electron Corporation (TECO) Series 49 U.V. photometric ambient ozone analyzers. Calibrations have been completed following EPA quality assurance protocols. The severe nature of the temperature, wind, and snow climate at the tower sites makes it difficult to maintain a continuous record with high data capture rates. This is particularly true at the top of the 30-m tower. Heights of the TECO sampling tubes on the Brooklyn tower were changed at times between 3, 23, and 30 m above the ground to support intensive periods of ozone deposition research near that site. The 23 and 30 m heights were in the turbulent air flow above the 17-m tall forest canopy.

2.1 *Brooklyn NDDN and Centennial NDDN Sites*

Figure 2 demonstrates a substantially different diel behavior of ozone concentrations between the monthly means for each hour at the Centennial NDDN site for 1990–1991 and those at the Brooklyn NDDN site for 1992–1993. The January mean diel trace shows little variance between

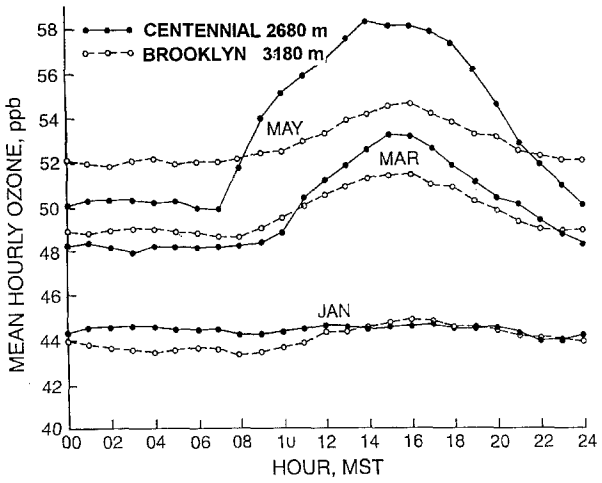

Fig. 2. Two-year averages of Centennial NDDN (solid lines) and Brooklyn NDDN (dashed lines) for 1990–1991 and 1992–1993 respectively

night and day at either site. By March the amplitude of the mean diel trace at the Centennial NDDN site was greater than at the higher Brooklyn site; the nighttime values at Centennial were lower, and the daytime peaks were higher.

The May ozone data at Centennial shows a larger diel amplitude, with nighttime values about 2 ppb lower and the midday values about 3 ppb higher than for March. For the Brooklyn site, the diel amplitude in May differed little from that for March. The difference between these sites and the lag in the diel pattern at the higher elevation site are probably due to differences in dates of snow cover and snowmelt. At the higher location, snow cover is much deeper and more wide-spread except for occasional wind-swept patches; snowmelt occurs between late May and late June. At the lower Centennial site snow cover is generally thinner and more patchy, with snowmelt occuring much earlier.

The mean monthly values of ozone concentrations for the two NDDN stations differed only slightly during the winter and early spring months, but during the two years at the Centennial (lower) site the monthly mean for May was 1.2 ppb higher than for the following two years at the Brooklyn (upper) site. This is much less than the 10 ppb diurnal amplitude increase found by Stocker et al. (1995) for bare vs snow-covered ground at a rural grassland site in Northeastern Colorado.

2.2 *Ozone Concentrations over the Forest Canopy*

For some months of 1993, the ozone sampling height on the Brooklyn tower alternated each half-hour between 23 m and 30 m above ground level (agl), and later was maintained at 30 m agl. The data taken at 23 m differed less than one ppb from those taken at 30 m within the same hour, which was within the accuracy of the instrument. Consequently, these data were all assumed to represent the ozone concentrations above the canopy.

The diel traces of the hourly ozone concentrations over the forest canopy at the Brooklyn tower site (dashed lines in Fig. 3a and 3b) illustrate the progression from January to June of 1993. March is not included due to missing data for 16 days of that month at the Brooklyn tower; the months shown have been normalized with the Brooklyn NDDN data (solid lines). The highest monthly mean values were measured during April and May, with a slightly lower value for June. The mean diel amplitude increases slightly until May, when it reaches 3.8 ppb.

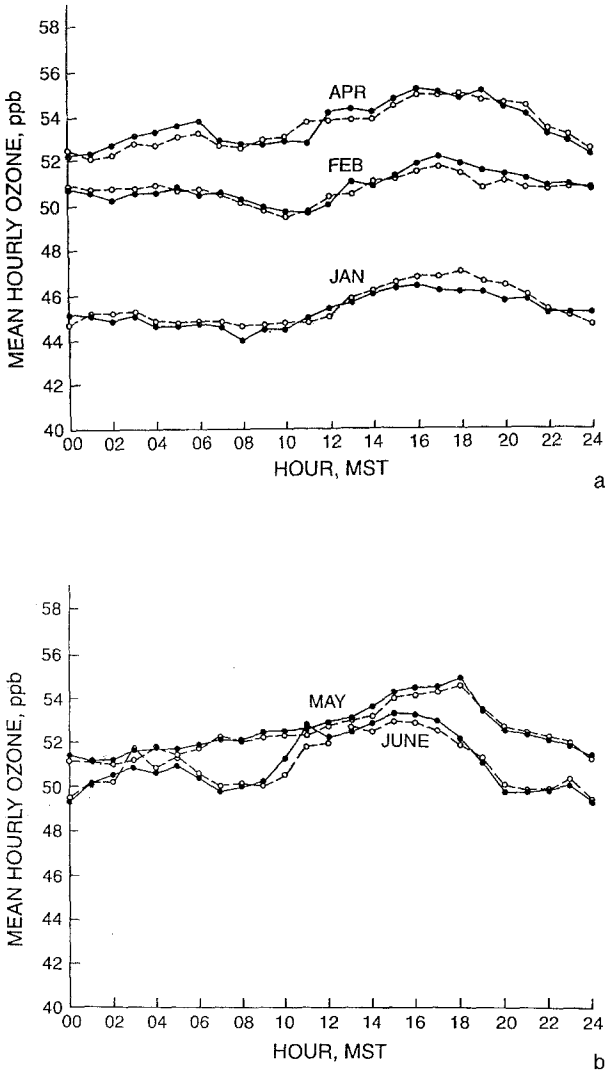

Fig. 3a, b. Comparison between mean diel ozone values for Brooklyn tower over the canopy (dashed lines) and Brooklyn NDDN (solid lines) for 1992. Figure 3a represents January, February, and April; Fig. 3b represents May and June

2.3 *Concurrent 30-m Brooklyn Tower and Brooklyn NDDN Data*

Since the average tree canopy top at the Brooklyn tower site is 17 m above the ground, the NDDN data can be used henceforth as a surrogate for ozone values over the top of the canopy. By imposing the Brooklyn NDDN data (solid lines) on the Brooklyn tower data (dashed lines) in Fig. 3a and 3b, one can see that the differences are nowhere greater than 1 ppb, and mostly only a few tenths of one ppb.

2.4 *Brooklyn Tower 3-m Data*

Prior to raising the Brooklyn tower sampling intake to heights above the forest canopy, it was located at a height of 3 m above the forest floor. The years of 1990 and 1991 have been combined into one set of data, and the average monthly mean diel traces are shown in Fig. 4 for each of the first six months. These contrast with the diel traces of ozone concentrations measured over the canopy (see Fig. 3a and 3b). The diel amplitudes increase during May and June, and reach 11 ppb in June. Part of this may be due to snowmelt dates (June 9 in 1990, June 15 in 1991, May 22 in 1992, and June 23 in 1993) at the tower location, but the diel amplitude reached nearly 7 ppb in May, well before snowmelt. Most of the increased amplitude was due to lower nighttime values of ozone, which decreased more than 15 ppb below winter values by June below the canopy. The abrupt drop in nighttime ozone concentrations in June occurred when snowmelt was nearly complete, and the soil temperatures had risen. The daytime ozone values by June were in the same range as the daytime values above the canopy in June of 1993, but they had decreased 6 ppb from the spring maximum. Zeller and Hehn (1994) have also noted a dramatic change in ozone fluxes at the Brooklyn tower after snowmelt.

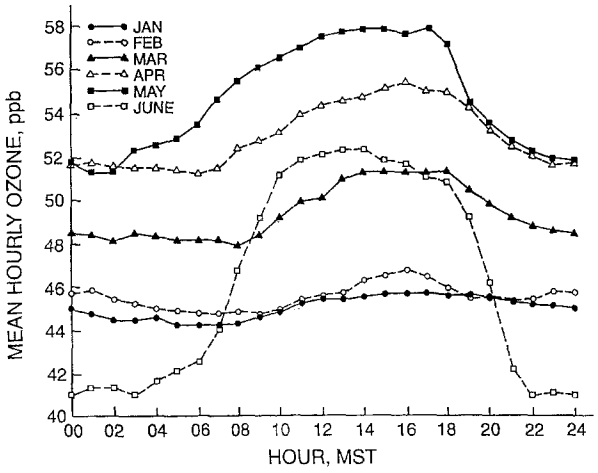

Fig. 4. Mean diel ozone values for January through June, averaged for 1990 and 1991, at 3 m above the surface at the Brooklyn tower

2.5 *High Ozone Level Episodes*

High concentration episodes were apparent in the data recorded above and below the forest canopy at the Brooklyn tower site. Episodes were present at the 3-m height (1990–1991) in intensity and duration approximately equal to those recorded at the 30-m height (1992–1993). This indicates little resistance of the canopy to the intrusions of ozone, particularly during strong downdrafting in sweeps of air from over the top.

Table 1 lists the number of episodes estimated (Est.) using the criteria discussed for stratospheric instrusions, i.e. with ozone concentrations greater than 60 ppb for ten hours or more and associated low relative humidities. The criterion for verification (Ver.) required the passage of a cutoff low pressure center between Central Colorado and Central Wyoming. The mean values of the monthly ozone concentrations for 1990–1991 are taken from the 3-m height on the Brooklyn tower, and from the 10-m Brooklyn NDDN site for 1992–1994.

The estimated number of high-ozone episodes assumed to be stratospheric intrusions averaged three in April, four in May, and slightly more than two in June. None were observed during the months of January or February, and few during March. Episodes persisted for periods of several days on occasion, and concentrations reached 85 ppb. The relative humidity of the air dropped to less than 25% toward the beginning of an intrusion, and rose afterward. The winds were generally northwesterly, at speeds of 8 to 13 ms^{-1} over the forest canopy.

2.6 *Contributions of Stratospheric Intrusions to Ozone Levels*

A relationship between the number of stratospheric intrusion events for any given year and the mean ozone concentrations during the months of April, May, and June can be seen in Table 1. It appears that the constraints of the location of the cut-off low specified in the criteria are restrictive, since trajectories may be quite different from one intrusion event to another.

Intrusion-related ozone data from 1990–1991 at the 3-m level on the Brooklyn tower and 1992–1994 at the 10-m NDDN Brooklyn site are assembled in Table 2. N60 designates the number of hourly values with ozone concentrations equal to or greater than 60 ppb during stratospheric intrusion events in the months designated, N70 the number equal to or greater than 70 ppb, and

Table 1. *The Number of Ozone Intrusion Episodes and the Mean Monthly Ozone Concentrations for the First Six Months of 1990-94 at the Brooklyn Site*

Year	1990			1991			1992			1993			1994		
Mo.	Est.	Ver.	Mean ppb	Est.	Ver.	Mean ppb	Est.	Ver.	Mean ppb	Est.	Ver.	Mean ppb	Est.	Ver.	Mean ppb
Jan.	0	0	44.0	0	0	45.7	0	0	43.0	0	0	45.3	0	0	45.1
Feb.	0	0	45.3	0	0	45.8	0	0	44.9	0	0	50.8	0	0	50.5
Mar.	1	1	50.6	0	0	48.4	0	0	49.4	0	0	49.0	1	1	54.3
Apr.	2	1	53.3	4	3	55.2	3	2	52.8	3	2	52.7	3	3	55.6
May	3	2	53.3	4	4	56.3	1	1	52.7	4	3	52.6	7	3	58.1
June	2	1	47.8	2	1	46.1	3	3	51.7	2	2	51.1	3	3	52.2

Table 2. *The Number of Hourly Ozone Values in ppb Above Certain Thresholds, and Sums of Ozone Dosages Above Those Thresholds for the Spring Months of April and May at the Brooklyn Site*

	1990	1991	1992	1993	1994
April	N60: 40	N60: 172	N60: 133	N60: 93	N60: 127
	S60: 134	S60: 533	S60: 598	S60: 158	S60: 368
May	N60: 141	N60: 179	N60: 127	N60: 117	N60: 309
	S60: 677	S60: 859	S60: 533	S60: 35	S60: 1453
April	N70: 0	N70: 10	N70: 18	N70: 0	N70: 8
	S70: 0	S70: 38	S70: 36	S70: 0	S70: 31
May	N70: 6	N70: 16	N70: 0	N70: 0	N70: 33
	S70: 3	S70: 27	S70: 0	S70: 0	S70: 136
April	N80: 0	N80: 0	N80: 0	N80: 0	N80: 0
May	N80: 0	N80: 0	N80: 0	N80: 0	N80: 5
	S80: 0	S80: 0	S80: 0	S80: 0	S80: 14

N80 the number equal to or greater than 80 ppb. S60 = Sum(C − 60), where C is the ozone concentration in ppb for each hour during an intrusion event, and similarly for S70 and S80.

Table 2 illustrates the variability in the number and intensity of intrusions during the spring months of April and May over five years of ozone records. In April, 1990, when only two stratospheric intrusions were identified at the 3-m level, no concentrations of ozone greater than or equal to 70 ppb were recorded. In May, 1990, while three events were indicated and two were verified, only six hours occurred with hourly concentrations equal to or slightly greater than 70 ppb; however, the mean monthly values exceeded those for 1992 and 1993. During the spring months of 1991, more than twice as many intrusions were verified, with a total of 351 hours over 53 days of ozone concentrations equal to or greater than 60 ppb and 26 hours equal to or greater than 70 ppb. Since seven and one-half days of data were missing for the month of May, the numbers for 1991 may have been greater than indicated on Table 2.

The ozone concentrations recorded during the month of May, 1994 indicate more frequent and stronger stratospheric-tropospheric intrusions than during the same month of any of the preceding four years. The 500 hPa synoptic charts (not shown here) revealed a persistent low pressure trough across the Southwestern U.S., with frequent cut-off low pressure centers.

2.7 Stratospheric-Tropospheric Ozone Contributions

The contributions to near-surface ozone concentrations by stratospheric intrusions into the lower troposphere have been quantified for the five-year period through application of the following assumptions: (1) The contributions occurred during intrusions identified through criteria presented above; (2) The background level was reached eight or more hours after an intrusion, and ended six or more hours prior to the next intrusion; (3) The contribution consisted of the sum of the multiple of each hourly ozone value over a certain threshold and its excess over the background; and (4) the "diffusive" period that follows values equal to or greater than 60 ppb were not included in the calculations. The underestimate resulting from (4) may not be negligible, but probably does not lead to a major error. These calculations, presented below in Table 3, can be considered as minimum

Table 3. *Contributions by Stratospheric-Tropospheric Intrusions to Near-Surface Ozone Concentrations at the GLEES for May, 1990–1994*

1990	5.4%
1991	11.0%
1992	8.0%
1993	5.4%
1994	18.0%
Five-year mean	9.6%

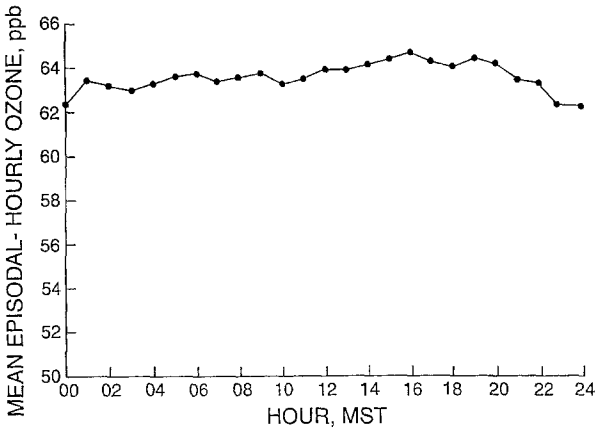

Fig. 5. Mean diel ozone concentrations for intrusion episode days, averaged for April and May at 3-m height on Brooklyn tower (1990–1991) and at 10-m height at Brooklyn NDDN (1992–1993)

contributions of stratospheric intrusions to the near-surface ozone concentrations.

2.8 Diel Patterns of mean Hourly Ozone Values for Episode days

Over the four-year period of 1990–1993, days in April and May on which stratospheric intrusions were identified and assembled in order to estimate the degree to which intrusions were a function of the hour of the day. These "mean intrusion days" for the Brooklyn site are shown in Fig. 5 above. No preference is found for stratospheric intrusion episodes as a function of the hour of the day. If the stratospheric intrusion event data were removed from the concentration data shown in Fig. 3a and 3b, the diel characteristics would remain the same except for a reduction in the mean hourly values for the months of April and May. This provides evidence that the high ozone concentrations during these events are not a result of diurnal photochemical generation.

2.9 Relative Humidity and Ozone Concentrations During Intrusions

A scatter diagram of the May, 1994 ozone concentrations (Fig. 6) indicates a general increase in concentration as relative humidities have decreased to low levels. These data relate to separate physical processes. The process of interest here is stratospheric-tropospheric intrusions and their penetration downward into the forest canopy. The scatter diagram also contains concentration data exceeding the mean value due to photochemical production during fair-weather days. The set of data identified by the intrusion criteria is that included in box A; the set assumed due to photochemistry is included in box B. The intersection of the sets includes data related to both processes.

Intrusion events begin with low humidities, concurrent with rising ozone concentrations (see Fig. 7, 21 May to 24 May, 1994). In most cases, as the ozone reaches higher values, the humidity over the sparse forest canopy rises to intermediate values. This results from the very strong turbulent mixing of air from layers above the forest canopy with air from below and within the canopy itself. That is, ozone-laden "sweeps" penetrate the forest canopy, and the slow, larger-area upward return flow brings moist air upward through and above the canopy. This deep mixing of the dry intrusion air from above and more moist air from below lasts for many hours during "bursts", with air above refreshed from the intrusion layer, while the relative humidity of the air immediately above the canopy increases from upward movement of air from below.

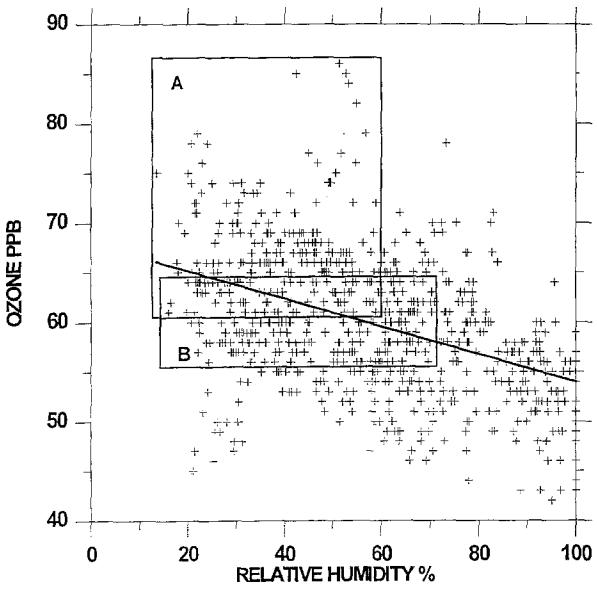

Fig. 6. Scatter diagram of hourly ozone concentrations vs relative humidity for the month of May, 1944 at the Brooklyn NDDN 10-m site. Box A includes ozone data during stratospheric-tropospheric intrusions; box B includes high daytime data not due to intrusions

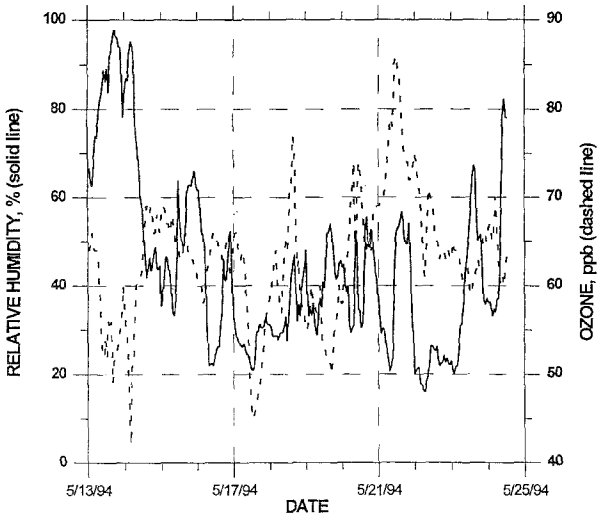

Fig. 7. Time lines of relative humidity (solid line) and hourly ozone concentrations (dashed line) for May, 1994 at the Brooklyn NDDN 10-m observation site

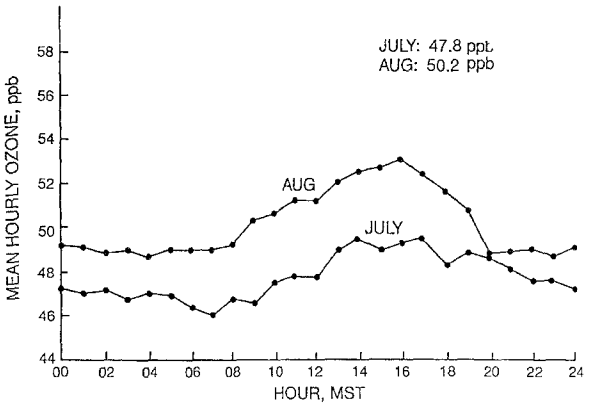

Fig. 8. Mean diel ozone values for July and August, 1992 at the NDDN Brooklyn site; sampling height is 10m

In set A of Fig. 6, groups of ozone concentration and relative humidity data can be traced from one burst to another during the period of 13–23 May, (Fig. 7) with ozone concentrations diminishing in intensity while the relative humidity increases. During the 22–23 May period, the strong intrusion causes concentrations to continue to increase while the relative humidity increases, and then falls again.

2.10 Summer Ozone Concentrations

The months of July and August, 1992 (Fig. 8) indicated a diel amplitude of the monthly mean hourly concentrations only slightly greater than for spring months. The September data for the same year suggest a mean value and diel amplitude similar to the month of July. Using the criteria set out for the spring months, there were no stratospheric intrusions during the summer of 1992. Some hourly concentrations exceeded 60 ppb during daytime hours but they were probably due to normal photochemical reactions, in contrast to the findings reported in Section 2.9 above. The monthly mean concentrations, except for August, resembled background concentrations for April and May of the same year.

2.11 Spectral Representations of Ozone Concentration Time Series

Spectral analyses have been applied to seasonal groupings of the ozone concentration data for winter, spring, and summer to illustrate the frequency distribution of meteorological events which contribute to the concentrations. The ozone data were separated by season to remove the trend effects of the transitional months of March and June. Next, the data for the winter, spring, and summer periods were detrended to attain near-stationarity (Kaimal and Finnigan, 1994).

2.11.1 Winter Season Ozone Spectra

A spectral analysis of the January-February Brooklyn 1993–1994 NDDN ozone concentration data (Fig. 9a) demonstrates a sharp diel peak. A broad peak is found near a two-and-one-half day period. This is probably due to the cloudy-fair weather sequences and the resultant suppression and enhancement of photochemical reactions during the passage of winter low pressure centers.

2.11.2 Spring Season Ozone Spectra

A spectral analysis of the April-May ozone concentration data for the same years (Fig. 9b) indicates very weak diel variances, and a broad peak near three- to four-day periodicities. The longer-frequency peak is considered to be due to the sequence of "bursts" of high ozone concentrations. These bursts appear in the data from two to four times in a longer sequence of generally high ozone levels (see Fig. 7 for an example).

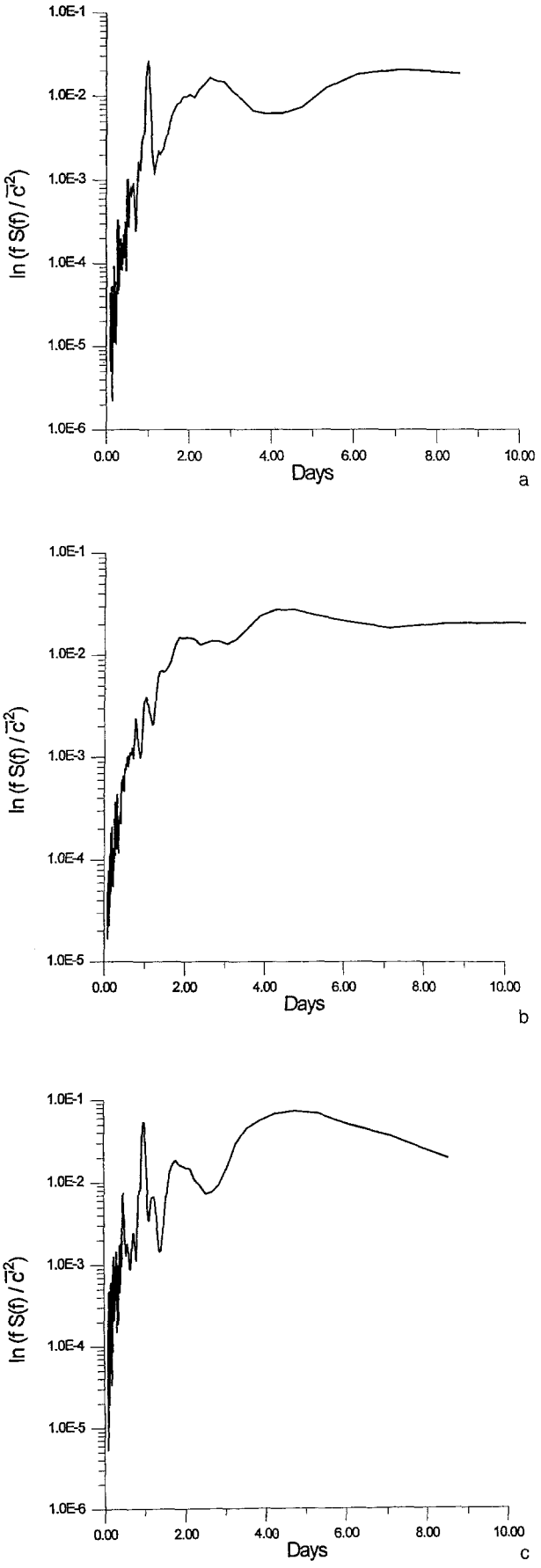

Fig. 9. Spectral representations of combined months of (a) winter, (b), spring, and (c), summer hourly ozone concentrations data for 1994 at the Brooklyn NDDN site

2.11.3 Summer Season Ozone Spectra

A diel peak and a lesser, broad peak at about two- to four-day periodicities are indicated (Fig. 9c). These characteristics are presumed to be consistent with suppressed-enhanced photochemical production of ozone during the generally weaker weather patterns of the summer season in the Rocky Mountain region. No stratospheric-tropospheric events were indicated for these months.

3. Discussion and Conclusions

The diel amplitudes of the mean hourly ozone concentrations at the Centennial NDDN site and the 3-m Brooklyn tower height change between winter and spring; the Brooklyn NDDN and 23-m and 30-m Brooklyn tower height concentrations show less seasonal change. During winter, when there is snow cover at both locations, the diel amplitudes of the hourly values are quite small. Even though there is a difference of 500 m in elevation between the Centennial and Brooklyn sites, there is little difference in mean concentrations. By March, daytime ozone values at the lower-elevation site are higher by 1.3 ppb, and nighttime values are lower by 0.4 ppb. By May, these differences are even greater; daytime ozone values at Centennial are higher by 4 ppb, and nighttime values are lower by 1.8 ppb. The lower nighttime values at Centennial reconcile with earlier snowmelt there and increased deposition at the surface. The lower daytime ozone values at the high-elevation Brooklyn site may be due in part to its location immediately downwind of Medicine Bow Peak where there is a higher frequency of cloud cover.

The ozone data taken on the Brooklyn tower above the forest canopy and at a 10-m height downwind of the forest agree well. The data provide evidence that strong turbulence from the higher terrain of the Snowy Range over the top of the sparse forest canopy produces a thoroughly mixed layer over and downwind of the forest. The winter months exhibit diel amplitudes of the hourly mean concentrations of only a

few ppb, increasing slightly in the spring. An examination of summer data indicates that ozone concentrations do not continue to increase during July and August. They suggest a downward transport through the troposphere and turbulent transfer to the underlying surface, and a paucity of ozone precursers such as NO_x or NMHC's.

Turbulent diffusion of an intrusion as it approaches the forest canopy causes a period of several hours when ozone concentrations gradually increase to a maximum value, and again decrease. During a period of frequent intrusion bursts, such as during May, 1994, diffusion causes elevated periods of ozone concentrations which last for several days. These are clearly evident in data recorded above and below the coniferous forest canopy, and contribute from 5 to 18 per cent of the monthly mean ozone concentrations during April and May.

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Authors' address: G. Wooldridge, K. Zeller and R. Musselman, USDA Rocky Mountain Forest and Range Experiment Station, 240 West Prospect Road, Fort Collins, CO 80526, U.S.A.