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NOTE-BOOK

Exceedances of the National Ambient Air Quality Standard for Ozone Occurring at a "Pristine" Area Site

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The term "photochemical oxidant" refers to ozone and other secondary oxidants (e.g., H_2O_2 and peroxyacetyl nitrate) formed in photochemical smog. There is an increasing body of literature suggesting that photochemical air pollutants affect human health, vegetation and welfare. Ozone, the most prevalent photochemical oxidant, has been the most studied and its effects are best understood.

Ozone affects vegetation and is thought to be the most important toxic air pollutant affecting American forests[1] and crops.[2] High ozone levels observed in rural areas are of special significance to forestry and agriculture, and have been implicated in decline of high elevation forests in North America and Europe.[3] During the recent International Conference, "Assessment of Crop Loss from Air Pollutants," Raleigh, North Carolina (1987), ozone was identified as the primary air pollutant causing crop loss in the United States totaling $1 to 5 billion. The Office of Technology Assessment of the U.S. Congress has estimated that the loss in crop yield in the Southeast due to ozone alone could exceed $900 million per year.

Ozone inhibits photosynthesis and alters partitioning of photosynthate. In various plant species, photosynthesis was significantly decreased by ozone at concentrations of 0.05 ppm for 4 hours, 0.1 ppm for 1 hour, or 0.2 ppm for 1 hour.[4] An inhibition of photosynthesis decreases the production of the primary components needed for plant growth.[5] Reductions in photosynthesis occurred at ozone levels and exposure durations that occur in the ambient air of the southeastern United States.

Early findings of ozone injury to grape vines[6] and to tobacco[7] were observed primarily in the oxidant-polluted urban atmosphere of Los Angeles and its environs. Although generally thought of as occurring downwind of significant urban or industrial pollution sources, it is becoming increasingly evident that high levels of ozone can and do occur in remote areas.[8] It is now recognized that vegetation at rural sites may be injured by ozone as well, due to the transport and transformation of these species from anthropogenic sources.[9-13]

We present ozone measurements for high elevation "pristine" area sites in the Mt. Mitchell, North Carolina State Park located in the southeastern United States. These data have been collected as part of an on-going project, one of the goals of which is to assess rural ozone exposure. They may also provide insight into those processes which affect rural ozone levels, and perhaps might guide policy makers in developing strategies for rural ozone control.

Monitoring Ozone at the Mt. Mitchell, NC Observatory

Continuous, gas-phase ozone measurements were taken at Mt. Mitchell, North Carolina, which is thought to be a "pristine" area site, during the growing season (May through September) of 1986 and 1988, and May through October 1987, as part of the U.S. Environmental Protection Agency (EPA)-sponsored Mountain Cloud Chemistry Project (MCCP). This program was set up in 1986 for monitoring the physical and chemical climatology at five high-elevation rural locations in the eastern United States, the southernmost site being Mt. Mitchell. As well as being the site with the highest elevation in the MCCP network, Mt. Mitchell also has the distinction of being the highest point east of the Mississippi River in the United States. The Mt. Mitchell research site actually consists of three subsites: one is located at Mt. Gibbs (Site 1), on the same ridge as Mt. Mitchell, at an elevation of approximately 2006 meters (MSL); the second is located approximately 2.5 miles away on Commissary Ridge (the southeast shoulder of Mt. Mitchell) (Site 2) at an elevation of approximately 1760 meters (MSL) (Figure 1); and the third is located near Black Mountain, North Carolina in the Asheville watershed, at an elevation of approximately 850 meters (MSL). We discuss the data only from sites 1 and 2 (high elevation locales) in this paper.

Meteorological, cloud microphysics, cloudwater and gas phase chemical parameters were measured at these sites.[14,15] Ozone measurements were made with a Thermo Electron Co. (TECO) analyzer, model 49, based on ultraviolet absorption. Oxides of nitrogen were monitored with a Monitor Lab model 8440 analyzer, based on chemiluminescence.

The quality assurance protocols both for ozone and oxides of nitrogen measurement, in general, include zero and span checks weekly and multipoint calibration two times during the measurement season. The calibrations were based on a National Bureau of Standards (NBS) traceable reference standard.

Results and Discussion

Data were stored as 15-minute and hourly averages in a Campbell Scientific Model 21XL datalogger. 1-hour averages are included for comparison to the National Ambient Air Quality Standard (NAAQS) for ozone, while the 15-minute averaged values are valuable as an indication of extreme, short-term levels of exposure. Oxides of nitrogen were continuously monitored, however levels were seldom observed above the limit of detection for the instrument, which is 2 ppbv.

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Ozone was monitored continuously, and the minimum, maximum, and arithmetic mean monthly levels for 1986, 1987 and 1988 are summarized in Tables I (15-minute average) and II (1-hour average) for the two high elevation sites. Maximum 1-hour average levels of the season at Site 2 were noted during the month of October in 1986 (~80 ppbv), and during July in 1987 (111 ppbv) and 1988 (134 ppbv). At Site 1, maximum values were observed during June of 1986 (111 ppbv), August of 1987 (103 ppbv) and during July of 1988 (151 (ppbv).

At the earth's surface, maxima in ozone concentration tend to follow maxima in solar radiation by a few hours, so that highest levels are observed in the late afternoon.[16] Preliminary results from Mt. Mitchell show that the ozone concentration remains fairly constant, and sometimes a nocturnal maximum is observed. The average daytime value for the entire growing season was 49 ppbv in 1987 compared to the average nighttime value of 53 ppbv. Similarly, in 1988 the average daytime value was 65 ppbv, compared to 68 ppbv for the average nighttime value. Statistical analysis (t-statistic) shows there is a significant difference between the daytime and nighttime concentrations at confidence levels above 95 percent and 90 percent in 1988 and 1987 respectively at Site 1, suggesting a reverse diurnal variation. Other investigators have also noted a reverse diurnal variation (with the nighttime concentrations being slightly higher than the daytime).[16,17] This inverse diurnal pattern may be due to depletion of ozone in the mixing layer or due to depositon processes during the day and the lowering of the mixed layer below the mountaintop during the evening.

Table I Summary of minimum, maximum, and (mean) values for ozone levels at Mt. Mitchell, Sites 1 (~2006m MSL) and 2 (~1760m MSL) for growing seasons of 1986, 1987, and 1988. Concentrations are in ppbv, and values are for 15-minute averaged data. (Note: data were collected in October during 1986 and 1987 only).

Year	Site	May	June	July	Aug	Sept	Oct
1986	MM1						
1987	MM1	22.5/74.9 (50.3)	23.3/93.8 (57.6)	11.3/107 (50.2)	20.0/108 (54.1)	14.3/84.2 (46.4)	10.2/76.8 (45.8)
1988	MM1	22.8/118 (72.0)	33.8/158 (82.8)	20.7/158 (68.7)	15.5/112 (57.4)	10.7/90.7 (46.6)	
1986	MM2				26.9/100 (53.4)	18.5/67.7 (40.5)	
1987	MM2	15.2/99.3 (49.6)	15.4/100 (49.4)	10.9/148 (49.3)	12.8/102 (53.8)	15.9/124 (43.9)	
1988	MM2	31.7/106 (59.5)	17.4/114 (67.6)	15.7/138 (55.1)	13.9/94.7 (41.9)	8.3/98.7 (35.2)	

During the 1986 and 1987 monitoring periods, there were no exceedances of the National Ambient Air Quality Standard (NAAQS) of 0.12 ppm (124 ppbv) for ozone at Mt. Mitchell Sites 1 and 2, however the NAAQS was exceeded in 1988 at both sites, as can be seen in Table III and in the cumulative frequency of ozone concentrations for each year for both sites, in Figures 2 and 3. In 1988, the standard was exceeded at Site 1 for 1.2 percent of the time (~35 total hours), and at Site 2 for 0.17 percent of the time (~5 hours). The higher ozone levels at Mt. Mitchell during the 1988 monitoring season were due in part to several occurrences of multiday high concentration ozone episodes over the eastern United States.

Table II. Summary of minimum, maximum, and (mean) values for ozone levels at Mt. Mitchell, Sites 1 (~2006m MSL) and 2 (~1760 MSL) for growing seasons of 1986, 1987, and 1988. Concentrations are in ppbv, and values are for hourly averaged data. (Note: data were collected in October during 1986 and 1987 only.

Year	Site	May	June	July	Aug	Sept	Oct
1986	MM1		54/111 (74.3)		23/94 (45.0)	27/75 (47.6)	18/71 (39.6)
1987	MM1	24.5/73.4 (50.2)	23.7/93.1 (57.5)	11.3/96.4 (50.1)	23.4/103 (54.1)	15.3/77.1 (46.4)	10.9/74.3 (45.8)
1988	MM1	42.5/116 (72.0)	36.1/123 (82.8)	30.0/151 (68.7)	22.8/114 (57.4)	11.5/84.3 (46.7)	
1986	MM2				28/69 (46.0)	22/67 (45.7)	24/80 (44.3)
1987	MM2	18.0/94.4 (49.5)	17.2/91.5 (49.5)	17.9/111 (49.3)	22.2/96.9 (53.8)	17.0/77.6 (43.9)	
1988	MM2	36.7/105 (59.6)	24.3/108 (67.6)	18.7/134 (55.1)	14.3/92.1 (50.0)	9.3/64.2 (35.2)	

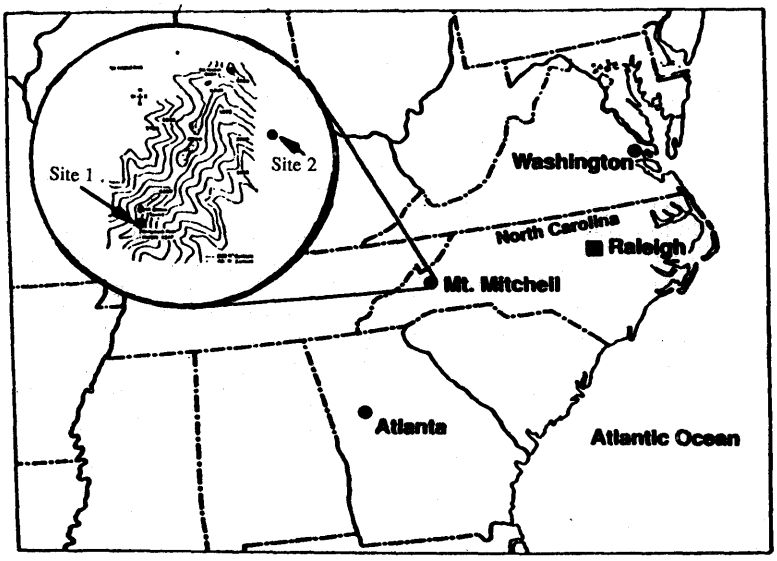

Figure 1. Location of Mt. Mitchell, Black Mountains Range, North Carolina, USA.

Perhaps even more interesting, though, is the frequency of levels sufficient to cause damage to vegetation. Reich and Amundson[5] and Mohnen and Cowling[18] have reported that ozone exposure to 50 ppbv or more is sufficient to cause damage to certain species of vegetation. Ozone levels were at least this high for a significant portion of the time during the growing season. In 1986, at Site 2, the 15-minute averaged ozone concentration was greater than 50 ppbv for 41 percent of the time (~1064 hours) during the growing season, and the frequency of occurrence of this level increased with each year since 1986 (Table III). A similar trend was observed at Site 1. Dur-

ing the growing seasons of 1987 and 1988, ozone levels remained at or above 50 ppbv ~53 percent and ~77 percent of the time, respectively (~1824 and ~2269 hours) (Table III). Similarly, at Site 2, the frequency of occurrence of ozone levels greater than 100 ppbv was 0.04 percent, 0.06 percent, and 2.5 percent in 1986, 1987, and 1988, respectively (~1,2, and ~75 total hours).

Vertical gradients in ozone, increasing with increasing elevation, have been observed for rural, mountainous areas in the eastern United States. Particularly in 1988, maximum and mean ozone levels at Site 1 (the higher elevation site) were significantly higher than those at Site 2, suggesting that a vertical gradient exists at Mt. Mitchell, as well. This phenomenon is discussed by Wolff et al.[17]

Overall, it appears that ozone levels were higher at Mt. Mitchell during the 1988 monitoring season, compared to that of the previous two seasons. Since the summer of 1988 was unusually warm, the high ozone levels of 1988 would be expected. The mean and maximum values were higher than for the preceding two years, and the percent of concentration levels over 50 ppbv, over 100 ppbv, and over 124 ppbv (the NAAQS) were higher.

It has been suggested that the lack of ozone reduction in some southeastern United States sites may be due, at least in part, to atmospheric processes involving natural hydrocarbons (NMHC).[18] When state implementation plans for achieving the NAAQS for ozone were developed, the potential role that naturally occurring NMHC might play in the formation of ozone was ignored. But natural NMHC tend to be more reactive than anthropogenic hydrocarbons[18] and possibly more prone to participating in photochemical reactions. Major sources of natural NMHC are trees, both deciduous and coniferous, and their emission rates depend on factors affecting photosynthesis (such as solar radiation) or vapor pressures (such as temperature). The southeastern region of the United States may have the right combination of warm, sunny summers and an abundance of forested areas to experience high enough natural hydrocarbon emissions to offset the efforts to reduce ozone levels by reducing anthropogenic hydrocarbon emissions, alone.

Table III. Frequency of occurrence of elevated levels over 50 ppbv, 100 ppbv, and 124 ppbv for 15-minute and hourly averaged data, at Mt. Mitchell Sites 1 and 2, for the growing periods of 1986, 1987, and 1988.

		% over 50 ppb		% over 100 ppb		% over 124 ppb	
Year	Site	15-min	hourly	15-min	hourly	15-min	hourly
1986	MM1		42.6 (1850h)		0.21 (5h)		0.0
1987	MM1	52.7 (1848h)	52.7 (1824h)	0.05 (7h)	0.03 (1h)	0.0	0.0
1988	MM1	76.3 (2291h)	76.5 (2269h)	7.2 (216h)	7.2 (212h)	1.2 (36h)	1.2 (35h)
1986	MM2	41.3 (1064h)	30.4 (522h)	0.04 (1h)	0.0	0.0	0.0
1987	MM2	46.5 (1447h)	46.7 (1437h)	0.06 (2h)	0.06 (2h)	0.02 (1h)	0.0
1988	MM2	51.2 (1538h)	51.5 (1534h)	2.5 (75h)	2.5 (75h)	0.21 (6h)	0.17 (5h)

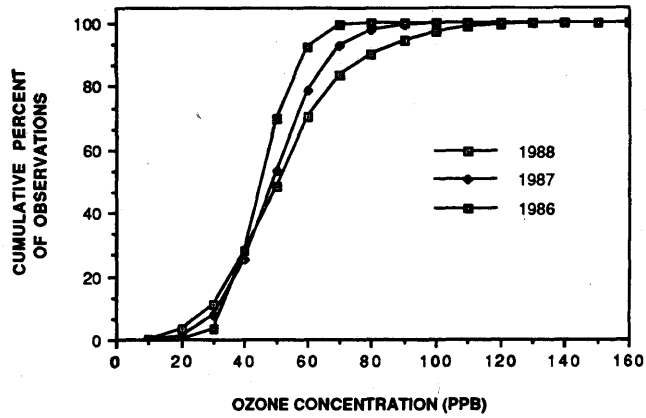

Figure 3. Cumulative frequency distribution of hourly-averaged values for May–October at Mt. Mitchell Site 2 (1760 m) during 1986, 1987, and 1988.

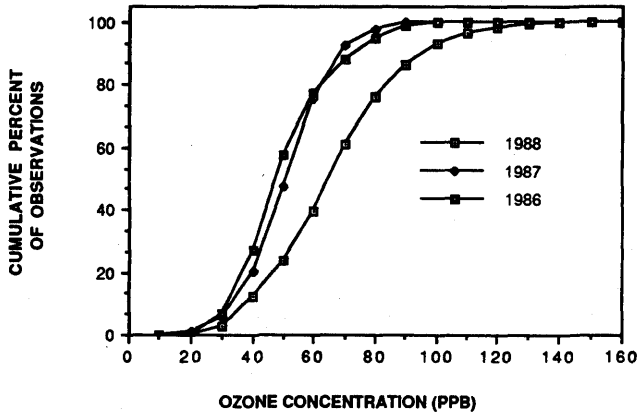

Figure 2. Cumulative frequency distribution of hourly-averaged values for May–October at Mt. Mitchell Site 1 (2006 m) during 1986, 1987, and 1988.

Summary

Despite efforts countrywide to reduce anthropogenic hydrocarbon emissions in order to lower atmospheric ozone in photochemical smog there has been little or no reduction in ozone, and perhaps ozone levels are increasing in some areas.[19] Preliminary results of three years' worth of monitoring of ozone at Mt. Mitchell, North Carolina indicate that it is possible, even at such a remote, rural location as Mt. Mitchell, to observe levels which exceed the NAAQS for ozone. Ozone levels high enough to cause damage to vegetation (greater than 50 ppbv)[20] are commonly observed at Mt. Mitchell.

At Mt. Mitchell, a vertical gradient in ozone with levels increasing with elevation was noted. The common diurnal pattern of high ozone levels late in the afternoon, as observed in many urban areas, was not observed at Mt. Mitchell. In fact a "reverse" diurnal variation has been detected.

Further work is needed in characterizing the oxidants including continued monitoring to establish whether ozone levels are increasing in remote, rural areas of the United States, including

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Mt. Mitchell and other locations in both the Southeast and other regions. Along with that, there is an urgent need to characterize both the hydrocarbons and oxides of nitrogen (both for source and species) present in the atmosphere and evaluate their potential for leading to elevated ozone levels.

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Disclaimer

The contents of this document do not necessarily reflect the view and policies of the Environmental Protection Agency, nor the views of all members of the Mountain Cloud Chemistry consortia, nor does mention of trade names or commercial or non-commercial products constitute endorsement or recommendation for use.

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On a Strategy for Reducing Short-range Daytime Ground Level Concentrations Due to Emissions from Very Tall Stacks

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The daytime atmospheric boundary layer (ABL) depth, h, is an important meteorological parameter in the evaluation of pollutant dispersion from tall stacks. In the case of relatively shallow ABL depths, plumes from tall stacks may be emitted into the capping stable layer aloft, thereby reducing the near field ground-level concentrations. However, plume fumigation, as the ABL deepens, may result in relatively high short-term ground-level concentrations. On the other hand, if the pollutants are emitted directly into the ABL, persistently high ground-level concentrations are likely to occur in the surroundings of the stack (for most tall stacks, peak concentrations will typically occur at distances of 5 to 10 km downwind), with a potential for adverse air quality conditions. Although these characteristics of dispersion from tall stacks are generally well known,[1–4] apparently no attempt has been made to exploit them in order to optimize the ground-level pollutant concentration distribution under very shallow ABL conditions. Under such conditions it may be advantageous to develop a strategy to reduce high *near-stack* pollut-