Temporal variability and case study of high O_3 episodes in two southeastern US national parks

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Abstract: Despite a decreasing trend nationwide, eight-hour O_3 concentrations in 25 of US national parks have increased by 8% during last decade. This study presents a 13-year observation of high O_3 at the Great Smoky Mountains (GRSM) and Mammoth Cave (MACA) national parks, both among the 25 impacted parks. Although there is no monotonic increase, the later half witnessed three-fold exceedances than the former. O_3 exceedances occurred most frequently in June at MACA, and in August or September at GRSM. High O_3 episodes at MACA occurred during daytime or early evening, but exceedances at GRSM can be found in any hour. Air masses with high O_3 at GRSM came from all directions, whereas those at MACA are predominantly from the southwest. Case studies show that high O_3 episodes at MACA are developed under clear sky, high temperature, low humidity, and weak winds traveling in a uniform anti-cyclonal pathway.

Keywords: air quality; high O_3 episodes; national parks; O_3 exceedances; temporal variability.

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1 Introduction

High ozone (O_3) episodes in the ambient air are associated with a variety of adverse health and environmental effects (National Research Council (NRC), 1991; US EPA, 2000). Regulation of O_3 precursors emissions under the US Clean Air Act of 1970 and its subsequent amendments has been partially successful in reducing human exposure, but many areas of the country are still subject to high ambient O_3 episodes (i.e. non-attainment areas) (Cowling and Furiness, 2001; US EPA, 2000). Over 40% of the O_3 non-attainment areas are in the southeast region (Fehsenfeld et al., 1994). Many more counties, in addition to those already exceeding the one-hour average O_3 standard, are estimated to be unable to attain the new eight-hour average O_3 standard effective in 1999 (Chameides et al., 1997). This paper shows that the new O_3 standard is more stringent than previous one-hour standard, by examining high O_3 episodes observed during a 13-year monitoring campaign at two class I southeast US national parks, namely, the Great Smoky Mountain (GRSM) and Mammoth Cave (MACA) national parks.

Despite a nationwide decreasing trend, eight-hour average O_3 concentrations in 25 of the US national parks have increased, on the average, about 8% from 1989 to 1998 (US EPA, 2000). Among them, GRSM has experienced the most rapid increase in the frequency of O_3 exceedances during this period (US EPA, 2000). The Great Smoky Mountains national park encompasses nearly 2100 km^2 (800 square miles) of mountain ridges and deep-cleft valleys in the states of Tennessee and North Carolina. As one of the most heavily visited Class-I national parks, the rapid increase of high O_3 episodes in GRSM is demanding substantial attention due to the resultant adverse effects on public

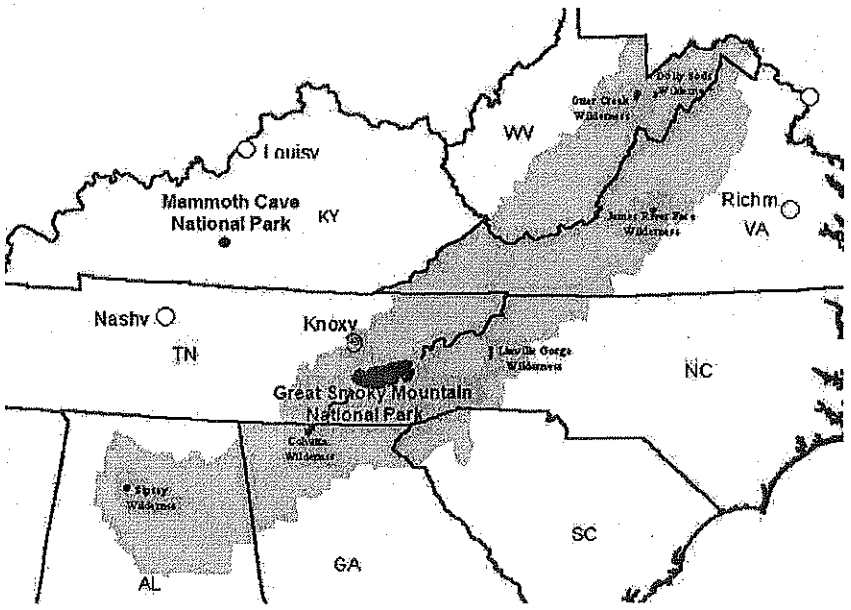
health and natural resources from increasing O_3 exposure. The Mammoth Cave national park in Kentucky is also located in the southeast United States and is one of the 25 national parks with increasing O_3 trends. Both sites are surrounded by forest or agricultural areas, with large isolated industrial point sources whose emissions can be transported to the measurement sites under certain meteorological conditions (Fehsenfeld et al., 1994).

Starting with a brief description of measurement data used in this analysis, we examine the inter-annual variability of O_3 exceedances observed at these sites from 1990 to 2002. Next, we investigate the seasonal and diurnal distributions of high O_3 episodes based on data obtained from an enhanced monitoring campaign conducted from 1996 to 2001. Finally, a case study is presented to address the influence of chemical precursors and meteorology on the formation of high O_3 episodes. Since the two measurement sites represent the typical rural setting throughout much of the southeast US, measurement-based analysis presented in this paper is expected to improve our understanding of the regional characteristics of high O_3 episodes in the southeast US.

2 Measurements

We analyse in this study continuous measurements of surface O_3 at two southeastern US national parks from 1990 to 2002. The Great Smoky Mountains (GRSM) site (35° 41' 48" N, 83° 36' 35" W), 1243 m above sea level, is located at the summit of Cove Mountain in the Great Smoky Mountains national park in Tennessee. The Mammoth Cave (MACA) site (37° 13' 04" N, 86° 04' 25" W), 230 m above sea level, is located in the Mammoth Cave national park approximately five miles from Cave City, Kentucky, in a clearing about 30 m from the surrounding forest area (Figure 1). Recognising the rapid increase in the frequency of exceedance days (days when any eight-hour average O_3 concentration exceeding 85 ppbv) observed during the first half of the 13-year measurement period, the US National Park Service (NPS) launched an enhanced monitoring campaign to better understand the controlling factors affecting O_3 exceedances at these southeast national parks (Kang et al., 2001; Olszyna et al. 1998; Tong et al., 2005). Ambient data including intermittent hydrocarbon samples and continuous measurements of ozone (O_3), total reactive oxides of nitrogen (NO_y), nitric oxide (NO), sulphur dioxide (SO_2), and carbon monoxide (CO), were collected at two the national parks from 1996 to 2001 (TVA, 1995). Ambient air samples for O_3, SO_2, and CO were collected using a Teflon tube equipped with five-micron Teflon particulate filters. These samples were analysed using O_3 Model 49, SO_2 Model 43S, and CO Model 48S monitors from Thermo Environmental Instruments, Incorporated (TEII). Air samples for NO and NO_y were each collected separately through 1/4" OD Teflon sampling lines. NO and NO_y were analysed using a TEII Model 42S with an external Mo converter operated in a time-sharing mode to measure the two trace gases separately. Gases used for calibration and daily quality assurance/quality control (QA/QC) activities were EPA Protocol SO_2, CO, NO, and NO_2 gas cylinders provided by Scott-Marin. For routine QA/QC activities, a Campbell CR10 data logger was configured to automatically control gas influx, sampling switches, gas addition and gas substitution. A TEII 111 Zero Air generating system and a TEII 146 Dynamic Gas Calibrator were also used. A CO catalytic reactor in the TEII Model 111 provided CO-free ambient air for zero checks and correction of instrument drift.

Figure 1 Location of measurement sites (in circles) in two Southeastern US national parks



Measurement operations followed the QA/QC procedures established for the Level II ground-based air monitoring stations that participated in the SOS/Nashville 1995 Intensive (TVA, 1995; Tong et al., 2005). The procedure consists of zero, span and precision checks using gas-substitution/gas-addition techniques that determined matrix effects in the sampling system. Additions of NO at the midday median NO_y concentration were conducted to both NO_y and NO sampling lines three times a day. Measurements for O_3 were conducted according to SLAMS protocol, modified to operate the O_3 instrument in the range from 0 to 200 ppbv. More detailed information on instruments, experimental techniques and data QA/QC procedures can be found from Olszyna et al. (1998) and in the TVA AQ/QC manual.

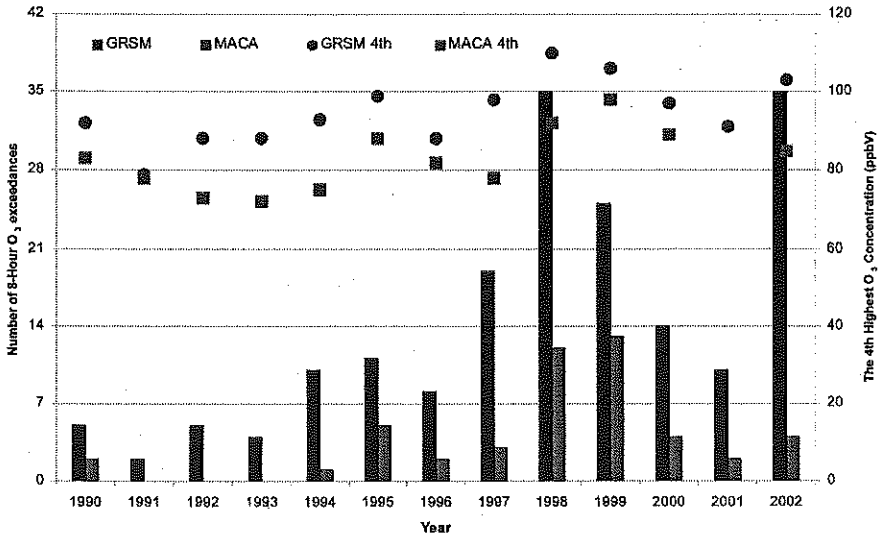
3 Results and discussion

3.1 Inter-annual variability of O_3 exceedances

Long-term O_3 measurements from the two southeast national parks show a significant increase in the frequency of exceedances. Figure 2 illustrates the numbers of eight-hour O_3 exceedances from 1990 to 2002 at GRSM and MACA. Although the levels of nitrogen oxides and CO measured at MACA are considerably higher than that at GRSM (Tong, 2005), the number of O_3 exceedances is consistently larger at GRSM than at MACA during the whole measurement period. Results from both measurements and computer modelling (Kang et al., 2001, 2003) suggest that O_3 production efficiency at MACA is probably limited by the availability of hydrocarbons. Photochemical O_3 production alone is not expected to account for the significantly larger number in O_3 exceedances at GRSM,

a remote site absent of major emission sources. We attribute it to an increased O_3 background concentration, frequent input of free atmosphere and the absence of night time scavenging processes which is typical at an elevated rural location (Aneja et al., 1991).

Figure 2 Inter-annual variability of 8-hr O_3 exceedances and the fourth highest O_3 concentrations (ppbv) at GRSM and MACA from 1990 to 2002



The fourth highest O_3 levels at GRSM are higher than at MACA during the same period (Figure 2). The fourth highest hourly O_3 is a statistical measure frequently used to represent long-term O_3 trends, since it is considered less sensitive to extreme values that are well above the natural background level (US EPA, 2000). Differences between the fourth highest O_3 levels at GRSM and MACA range from 1 to 20 ppbv, with values at GRSM consistently higher than at MACA. Trends at both sites are similar to those of eight-hour O_3 exceedances. Generally, there are few or no O_3 exceedances in a year when the fourth highest concentration is lower than 80 ppbv. When the fourth highest concentration is greater than 110 ppbv, which is lower than the previous one-hour O_3 standard, that year was marked with a large number of eight-hour O_3 exceedences. This is in accord with an earlier work by Yang and Miller (2002) who reported that the number of exceedances of the 8-hour standard, given a typical distribution of surface O_3 measurements, were about two to three times greater than those of the 1one-hour standard.

Although there are no monotonic increases in either eight-hour O_3 exceedances or the fourth highest O_3 concentrations at both sites, a long-term increasing trend is observed in the eight-hour O_3 exceedances. During the first half of the measurement period (1990–1995), the number of eight-hour exceedances was 6.2 per year at GRSM, and 1.3 per year at MACA. The later half of the period (1996–2001) experienced three times more exceedances per year at each site. The 13-year averaged number of O_3 exceedances is 20.9 per year at GRSM and 5.7 per year at MACA. A long-term increasing trend is also illustrated in Figure 2 in the fourth highest O_3 concentration. From the first to later half,

averaged fourth highest concentrations increase from 89.8 to 99.0 ppbv at GRSM, and from 78.2 to 87.3 ppbv at MACA. These results suggest a deterioration of air quality in the studied national parks during the 13-year period, although further observations are needed to confirm the long-term tendency.

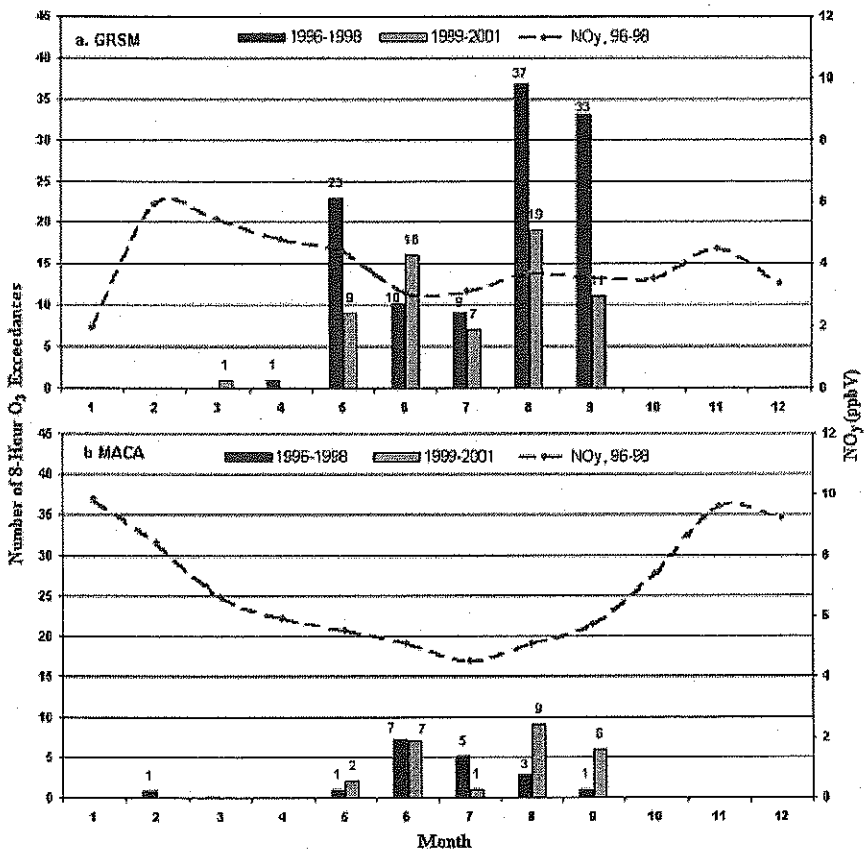
3.2 Seasonal distribution of high O_3 episodes

Seasonal distribution of O_3 exceedances is displayed in Figure 3a and b for GRSM and MACA, respectively. We focus in this section on the O_3 data in the later half of the 13-year measurement. The later half experienced a higher number of O_3 exceedences. Concurrent measurements of reactive nitrogen oxides are also available during this period (Tong et al., 2005). Measurements are further divided into two subsets, period I (1996–1998) and period II (1999–2001), because our examination of the interannual variability reveals an increase of high O_3 episodes in the first three years and a decrease in the later years (Figure 2). Monthly averaged NO_y concentration is also plotted in Figure 3 for period I (1996–1998). High O_3 episodes are widely distributed in late spring, summer and early autumn. Occasionally, ambient O_3 concentrations exceeded the eight-hr standard even in April and March (Figure 3a). At GRSM, the largest number of exceedances is found in August (37 times) and the second largest in September (33 times) during period I, and in August (19 times) and June (16 times) during period II. Exceedances in July are the least significant during the photochemically active season (May to September) for both periods at GRSM. The smaller number of O_3 exceedances in July is consistent with a lower level of nitrogen oxides (3.0 ppbv) in summer (Figure 3a). The availability of nitrogen oxides could have limited *in-situ* photochemical O_3 production in July, regardless of strong solar radiation and biogenic VOCs emissions. Another hypothesis, proposed by Kang et al. (2003), is that O_3 concentrations increase with increasing hydrocarbons, but then decrease when hydrocarbons concentrations exceed a certain turnover point. Since the Great Smoky Mountain national park is heavily forested and biogenic hydrocarbon emissions are most substantial in midsummer, it is possible that high levels of hydrocarbons actually prevent O_3 from frequently surpassing the O_3 NAAQS. An earlier modelling study provides evidence for this mechanism in which O_3 is reduced through the direct reactions with biogenic hydrocarbons and the removal of nitrogen oxides to form inert organic nitrogen (Kang et al., 2003).

At MACA, the maximum number of exceedances is found in June (seven times) during period I, and in August (nine times) during period II (Figure 3b). These numbers are smaller than those at GRSM. Simultaneous measurements of O_3 and other trace gases (not shown here) indicate that the formation of nocturnal inversion and titration by fresh nitrogen oxides can deplete O_3 effectively and thereby prevent the build up of persistent high O_3 concentrations overnight. This is typical for low elevation sites, and is responsible for the significantly lower number of exceedances at a low elevation site than at an elevated site such as GRSM. Again, the number of O_3 exceedances is not the largest in July for either period. During period II, the number of O_3 exceedances in July is actually the smallest of all photochemically active months, similar to that at GRSM. Monthly averaged NO_y concentrations at MACA show a strong seasonal variation, with a maximum in January (~ 10 ppbv) and a minimum in July (~ 4.5 ppbv) (Figure 3b). Different from that at GRSM, summer O_3 concentrations at MACA are closely related to the availability of O_3 precursors. Process budget analysis shows that approximately 80%

of total O_3 at MACA is produced by local photochemistry while only 26% of total O_3 is from in-situ chemical production at GRSM (Tong et al., 2005). The limited availability of nitrogen oxides, which are considered as the limiting precursor to summer O_3 production at rural southeast locations (Cowling and Furiness, 2001), may be responsible for the fact that the maximum O_3 exceedances did not appear during mid-summer at MACA.

Figure 3 Seasonal variability of O_3 exceedances and NO_y concentrations at (a) GRSM and (b) MACA from 1996 to 2001

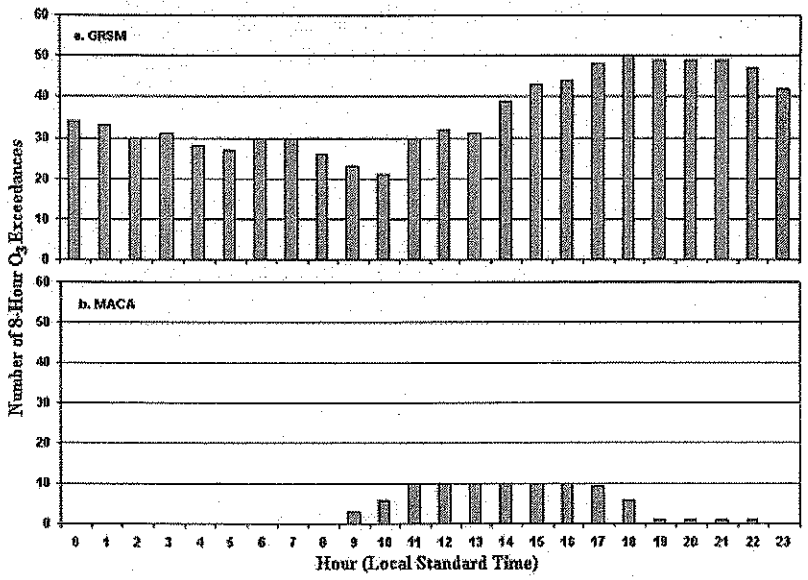


3.3 *Diurnal distribution*

Diurnal distribution of eight-hour O_3 exceedances at GRSM and MACA is displayed in Figure 4a and b. The number of exceedances for a particular hour is calculated from the statistics of eight-hour exceedances observed from 1996 to 1998. Each hour within an eight-hour episode gets one count for its contribution to the exceedance, therefore, the total hourly-based count is eight times as large as the actual number of eight-hour exceedances. At GRSM, high O_3 episodes occur most frequently around sunset, and least

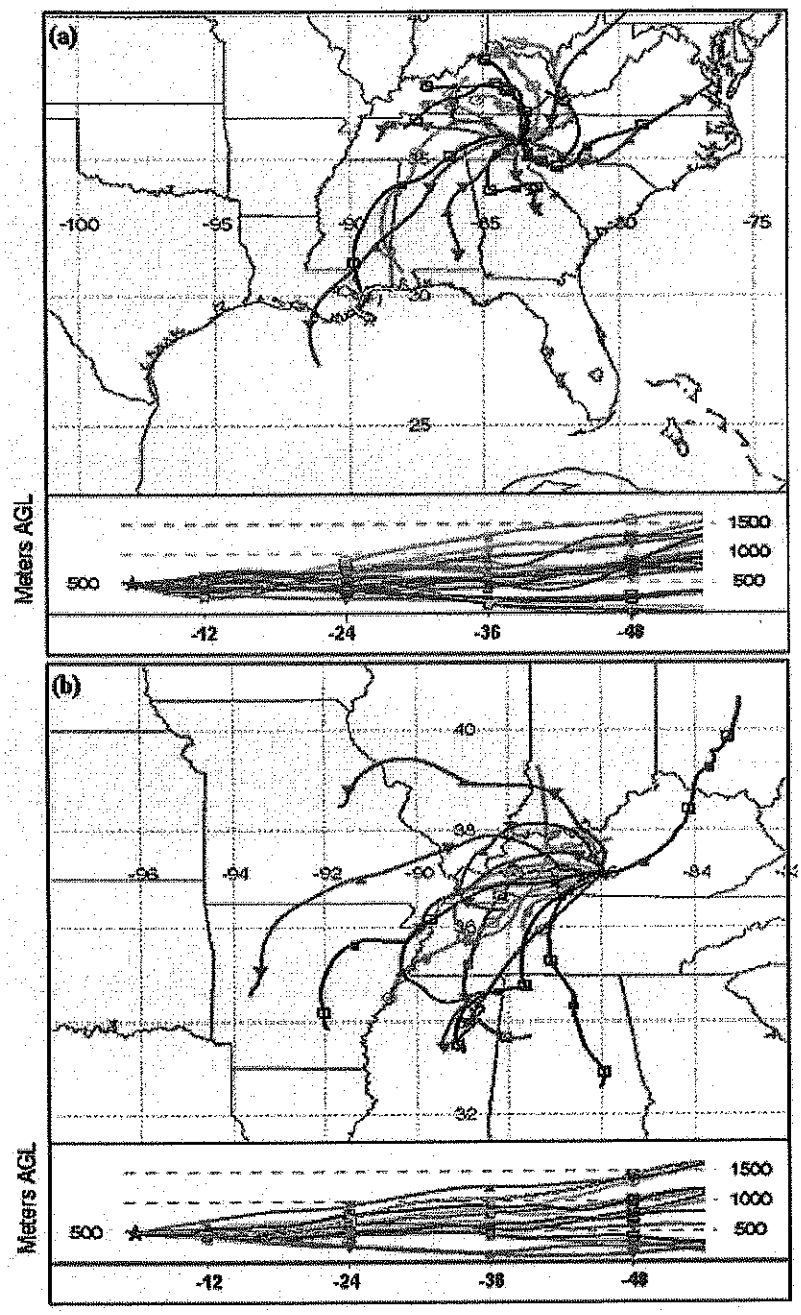
frequently in the early morning (Figure 5a). High O_3 episodes can be observed in any hour at GRSM during the photochemically active season, regardless of the availability of sunlight. High O_3 episodes at MACA occur most frequently during midday, and extend into a few hours after sunset. There are no O_3 exceedances at MACA occurring between midnight and early morning.

Figure 4 Diurnal distribution of O_3 exceedances at (a) GRSM and (b) MACA from 1996 to 1998. O_3 exceedances are defined as the eight-hour averaged concentration exceeding 80 ppbv. Each of the eight hours gets one count for the exceedances taking place in it



The shape of diurnal profiles of exceedances at the two sites mirrors the relative contributions of transport, local production and removal processes to O_3 budget in the national parks. O_3 concentrations at MACA increase when air masses with undepleted O_3 from the residual layer begin to mix down to the surface shortly after the breakup of the nocturnal boundary layer (NBL) (Aneja et al., 2000). At the same time, local photochemical production contributes to raising O_3 levels. The combination of transport and photochemistry can explain a largely daytime distribution of O_3 exceedances observed at MACA. After sunset, the formation of stable NBL prevents air masses containing higher levels of O_3 from reaching the surface. Night time depletion mechanisms such as dry deposition and titration by fresh nitrogen oxides contribute further to lower O_3 to a level under the O_3 standard. Figure 4b shows that such a process can be accomplished before midnight, therefore, it is unlikely that O_3 exceedances will occur after midnight and before the break of NBL triggered by increased solar radiation in the early morning.

Figure 5 Back trajectories of air masses associated with O_3 concentration larger than 90 ppbv at (a) GRSM; (b) MACA



The characteristics of diurnal O_3 variations at GRSM, however, are controlled by different mechanisms. At a low elevation site, the ceiling effect imposed by the formation of NBL hastens O_3 depletion below it and prevents O_3 in the upper layer (residual layer) from deposition, maintaining a higher level of O_3 above NBL. Since the GRSM site is 1220 m above sea level, it is almost always above the shallow NBL over plains during night time (Doddridge et al., 1992; Poulida et al., 1991). In other words, GRSM is more frequently swept by air masses containing higher levels of O_3 and O_3 concentrations at these locations are less subject to the depletion mechanisms described above. Similar diurnal patterns of O_3 concentrations at high-elevation sites have been found in other research campaigns (Aneja et al., 1991, and references therein; Jacob et al., 1995).

3.4 Back trajectory analysis

Origins of air masses carrying high levels of O_3 are investigated by back trajectory analysis using the hybrid single-particle Lagrangian integrated trajectories (HY-SPLIT) model (Draxler, 1997). This technique and its actual operation routines of the model have been described elsewhere (Draxler, 1997). The 3D motion of air masses is calculated using the National Meteorology Center's Nested Grid Model (NGM) for both horizontal and vertical air mass streams before April 1997. The results of data sets after April 1997 were obtained using three-hourly output from the Eta Data Assimilation System (EDAS). Back trajectories were initialised at 1:00 pm local time and 500 m above ground level, although the choice of an initial elevation is under considerable debate (Brankov et al., 1999). All trajectories are tracked back to two days (48 hours); our previous work (Tong et al., 2005) suggests that a running time of two to three days can provide reasonable information of O_3 regarding influencing areas.

Figure 5a shows all individual trajectories for each day with at least one hour of O_3 concentration greater than 90 ppbv at GRSM. Although the trajectories indicate that high O_3 air masses arrive in all directions, the majority are from the northwest and southwest, consistent with previous results from a cluster analysis of three-year trajectories calculated for air masses approaching the GRSM site (Tong et al., 2005). Trajectories with high O_3 at MACA (Figure 5b), however, display a dominant transport pattern from the southwest, with very few exceptions from the polluted northeast and Ohio River Valley (US EPA, 2000). At both sites, these trajectories are associated with low wind speed and anticyclonic motions, suggesting that slow circulation during stagnant high-pressure events favours a regional O_3 event. This is typical of regional-scale pollution episodes in the eastern United States (Logan, 1989; Yang and Miller, 2002).

Since all trajectories are initialised at 1:00 pm local time, no daytime/night time difference can be identified from the above analysis. Our earlier analysis of O_3 data showed no high O_3 events at MACA extended into nighttime (Section 3), but GRSM did experience high levels of O_3 during night time. Trajectories for GRSM, initialised at 23:00 local time, were also calculated and compared to the daytime results to examine the effects of the night time boundary layer. These trajectories rarely show any significant daytime/night time difference (not shown here), consistent with an earlier work for a mountain top site in the northeast United States (Hollock, 2002). Hollock (2002) also reported that there is a nearly equal number of trajectories associated with high O_3 during daytime and night time and the night time O_3 loss, due to dry deposition at the surface is not significant at an elevated site.

3.5 Case studies

In this section we present two case studies of high O_3 episodes based on simultaneous measurements of trace gases and meteorological parameters during the enhanced field campaign. Summertime high O_3 episodes have frequently been observed and extensively investigated. In this study, we observed a significant number of high O_3 episodes occurring in seasons other than summer. We, therefore, focus on two typical episodes observed in May and September at MACA where, unlike at GRSM, both local photochemistry and meteorology play a role in determining the levels of surface O_3. A variety of trace gases, O_3, NO_y, NO, CO and SO_2, and meteorological parameters such as ambient air temperature, relative humidity, wind speed and direction, solar radiation and precipitation, were monitored every five minutes during the two episodes, one in late spring (May 22–24, 1997) (Figure 6) and the other in early autumn (September 18–20, 1997) (Figure 7), to examine the effect of seasonality on high O_3 episodes.

The episode-averaged concentration of O_3 was 45.7 ppbv in the May episode, and 40.3 ppbv in the September episode. These values are 6 ~ 9 ppbv higher than the corresponding seasonal averaged O_3 concentrations at MACA (Table 1). Episode-averaged CO, SO_2, NO_y and NO concentrations are 189, 2.5, 5.7, and 0.37 ppbv in May, and 171, 2.4, 6.5, and 0.38 ppbv in September. Concentrations of all these species lie between seasonal averaged values for the two closest seasons (Table 1). Both episodes are developed in conditions associated with clear sky (i.e. strong solar radiation), high temperature, low relative humidity (Figures 6b and 7b), as well as weak anticyclones (Figures 6c and 7c). While similarities are found in meteorological and chemical characteristics of the two episodes, analysis of their back trajectories suggests that air masses came from different regions (Figures 6c and 7c). Air masses on May 23 are mainly from the lower troposphere over the industrialised northern region and then transported to the surface site by downwards motions. In the September case, air masses originate from the coastal region along the Gulf of Mexico, where large NO_x emission sources exist (US EPA, 2000). Our previous study based on trajectory-cluster analysis reveals that the group of air masses originating from the coastal area is associated with the highest O_3 level compared to those from other origins (Tong et al., 2005).

Compared to the case in May, O_3 in the September case is less correlated with NO_y. This has been identified as a general trend that the relationships between O_3 and NO_y become weaker from summer to autumn at MACA. Jacob et al. (1995) reported a similar trend based on model simulations and measurements conducted at the Shenandoah national park, Virginia. They interpreted this phenomenon as a seasonal transition from NOx- to VOCs-limited conditions to O_3 production caused by a decline in solar radiation humidity and biogenic hydrocarbons emissions.

Figure 6 (a) Time series of O_3, CO, NOy, NO, and SO_2 at MACA from May 22 to May 24, 1997; (b) Time series of O_3 and meteorological parameters at MACA from May 22 to May 24, 1997, 1997; (c) Back trajectories of air masses approaching MACA on September 1, 1997; (d) Vertical motions of the trajectories in (c)

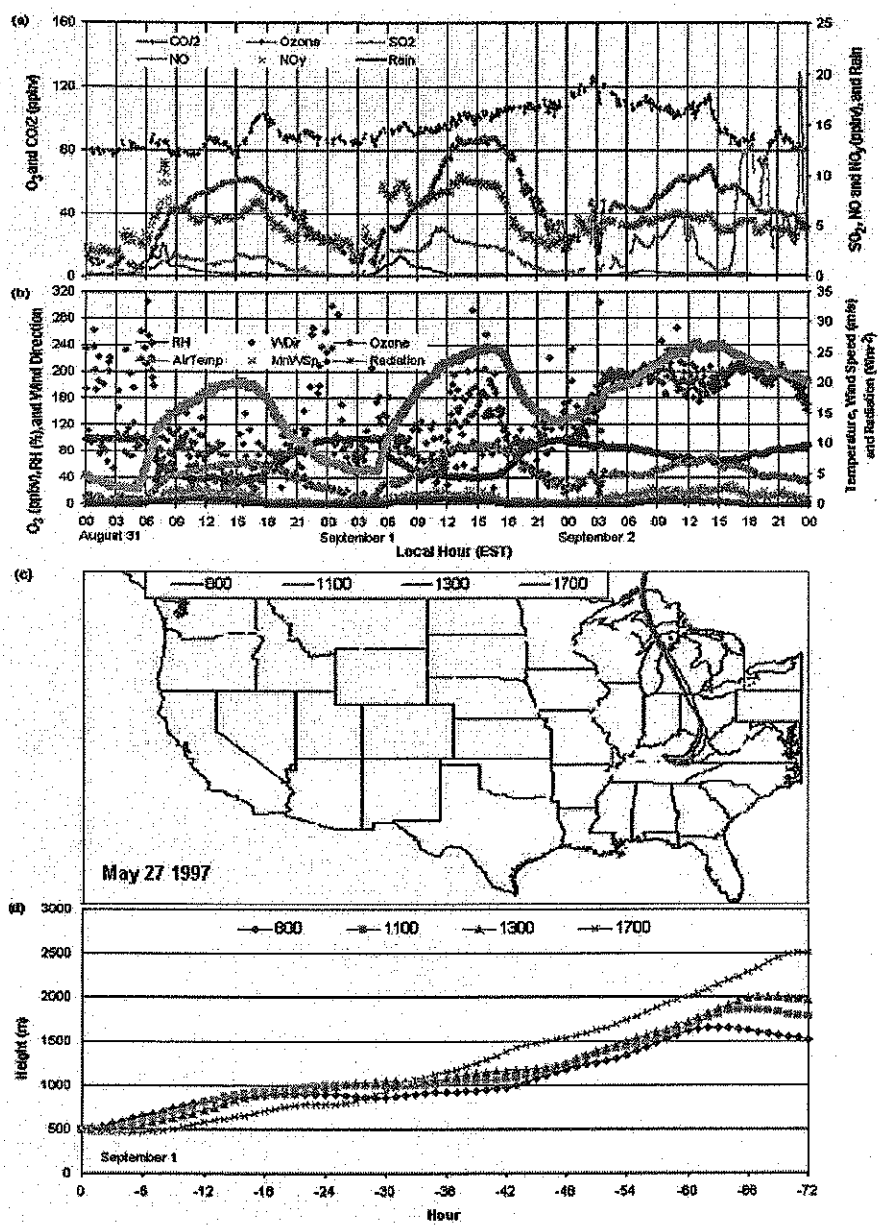


Figure 7 As Figure 6, but using measurements from August 31 to September 2

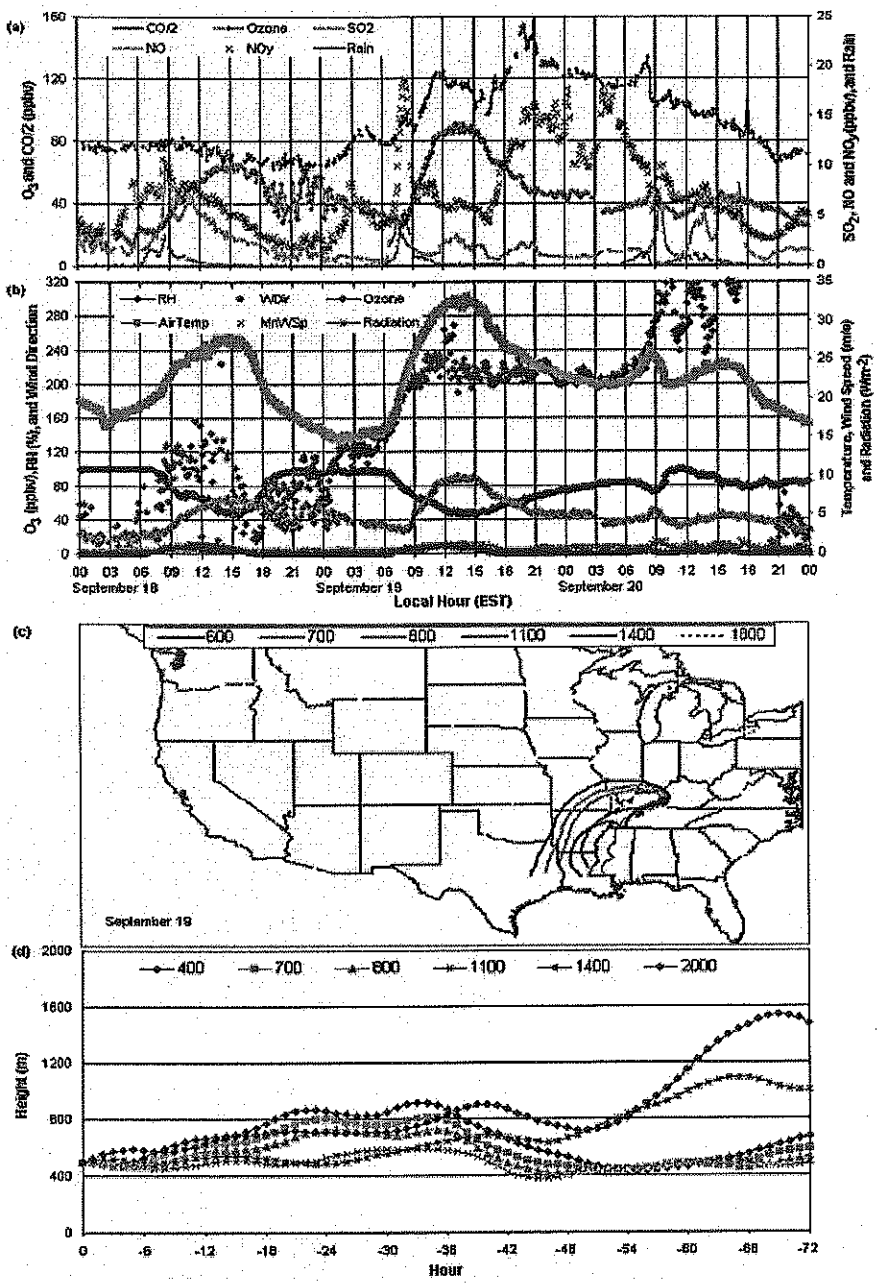


Table 1 Comparison of episodic and seasonal averaged concentrations of O_3, SO_2, CO, NO, and NO_y at the Mammoth Cave (MACA) national park

Location	*Season*	*O_3 (ppbv)*	*SO_2 (ppbv)*	*CO (ppbv)*	*NO (ppbv)*	*NO_y (ppbv)*	*T_a (°C)*	*RH (%)*	*WS (m/s)*
MACA	Spring (1996–1998)	39.0	2.7	210.5	0.49	6.2	–	–	–
	May 22–24, 1997	*45.7*	*2.5*	*189*	*0.37*	*5.7*	*16.7*	*71.4*	*1.14*
	Summer (1996–1998)	39.7	1.7	193.8	0.29	5.0	–	–	–
	September 18–20, 1997	*40.3*	*2.4*	*171*	*0.38*	*6.5*	*20.8*	*79.5*	*0.63*
	Autumn (1996–1998)	31.7	2.9	191.7	0.75	7.0	–	–	–

4 Conclusion and implications

Over the past two decades (1980–1999), ambient O_3 concentration has decreased by 20% based on one-hour surface measurement data, and by 12% based on eight-hour data in the United States (US EPA, 2000). Despite the nationwide decreasing trend, eight-hour O_3 concentrations in 25 of the US national parks, however, have increased by an average of 8% in the last ten years (US EPA, 2000). This study examines the inter-annual, seasonal and diurnal variability, as well as a case study of high O_3 episodes observed from 1990 to 2002 at the Great Smoky Mountain (GRSM) and Mammoth Cave (MACA) national parks. Both are among the 25 national parks characterised by an increase in ambient O_3 concentrations. Among these 25 national parks, the Great Smoky Mountains national park has experienced the most rapid increase in the frequency of O_3 exceedances during this period.

Although there is no monotonic increase in either annual exceedances or the fourth highest O_3 concentration, a long-term increasing trend has been observed from the 13-year measurement data at both sites. The later half period (1996–2002) experiences more than three times more exceedances at both sites than the first (1990–1995). The average fourth highest O_3 concentrations increased from 89.8 to 99.0 ppbv at GRSM, and from 78.2 to 87.3 ppbv at MACA. Most O_3 exceedances are seen in August and September at GRSM and in June at MACA. Neither site shows a maximum number of O_3 exceedences in mid-summer (July). High O_3 episodes at the elevated GRSM site occur most frequently around sunset, and least frequently in the early morning. High O_3 can be observed at any hour at the mountain top site, regardless of the availability of solar radiation. O_3 exceedances at MACA occur only during daytime and shortly after sunset; there is no high O_3 observed between midnight and early morning. Air masses containing high O_3 at GRSM originate from all directions; those at MACA are dominated by transport from the southwest and northwest. Case studies of two typical O_3 episodes, one in May and the other in September, show that almost all high O_3 episodes at MACA are developed with clear sky, high temperature, low relative humidity and weak winds travelling in a uniform anti-cyclonal pathway surrounding a high-pressure area. The results summarised here may

broach further discussion on O_3 control issues in the southeastern United States. Under the one-hour O_3 standard, neither the Great Smoky national park nor the Mammoth Cave national park was categorised as a non-attainment area for O_3. However, both parks are not in compliance with the eight-hour O_3 standard at least since 1995. The fact that O_3 exceedances are widely distributed across spring, summer, and autumn presents a major concern to design efficient O_3 abatement strategies for rural areas in the southeast United States.

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