ABSTRACT

TONG, QUANSONG. Measurement, Modeling, and Analysis of Ozone and its Key Precursors in the Southeast United States National Parks (Under the direction of Dr. Viney P. Aneja).

Lower tropospheric ozone (O₃) continues to be a major air pollution problem in the southeast United States due to its adverse effects on humans and the environment. This study presents measurements, modeling, and interpretation of ozone (O₃) and its key precursors based on measurements collected from three Southeast US National Parks: Shenandoah National Park (SHEN), VA, Great Smoky Mountains National Park (GRSM), TN/NC, and Mammoth Cave National Park (MACA), KY. Our analysis shows that whereas O₃ concentration at low-elevation rural site rises sharply to a short-lived afternoon maximum and drops to near zero at night similar to most urban or suburban areas, O₃ at high-elevation rural sites does not display a significant drop during nighttime. As a result, longer-time averaged O₃ levels at high-elevation sites are significantly higher than those at nearby low-elevation sites and high-elevation sites are more likely to exceed the new O₃ National Ambient Air Quality Standard (NAAQS) as the standard changes to a smaller concentration averaged over a longer time period. We introduced an indicator, the (NOₓ-NO)/NOₓ ratio, to represent air mass age. O₃ increases with the increase of photochemical age represented by higher (NOₓ-NO)/NOₓ ratio at both high and low elevation locations. The current study also presents a turnover point (0.9 for value of (NOₓ-NO)/NOₓ) that separates the NOₓ-limited and non-NOₓ-limited ozone production regimes. The regional background O₃ concentrations that are not directly influenced by anthropogenic emissions are estimated to be ~35 ppbv at GRSM, and ~43 ppbv at MACA inferred from the linear regression of O₃ on (NOₓ – NO).
Under the 1-hour NAAQS, both GRSM and SHEN site were at the edge of O₃ exceedance and MACA did not exceed the 1-hour NAAQS for O₃. Under the new 8-hour NAAQS, however, all three national parks are in serious nonattainment of O₃ NAAQS.

The second section of this study focuses on elucidating source attribution, influence area, and process budget of reactive nitrogen oxides in the Southeast national parks, since nitrogen oxides are considered as the limiting factor to ozone production in these areas characterized with strong reactive biogenic VOCs emission. Multiple linear regression analysis provides that point sources contribute a minimum of 23% and 27% of total NOₓ at GRSM and MACA, respectively, during the whole measurement period. Another technique, emission inventory analysis based EPA Emission Inventory, provides a similar estimate that a minimum of 26% and 45% of total NOₓ can be attributed to point source emission at GRSM and MACA sites, respectively. Trajectory-cluster analysis shows that air masses from western (20% out of all air masses) and southwest (17%) sweep over GRSM site most frequently, while pollutants transported from eastern half (i.e., East, Northeast, and Southeast) has limited influence (< 10%) on air quality in the Great Smoky Mountain National Park. Further examination of pollutants associated with these air masses reveals that the highest O₃ concentrations are associated with trajectories from the North and Southwest directions, which can be tracked back to Ohio Valley region and coastal region along Gulf of Mexico. Process budget analysis using Multiscale Air Quality Simulation Platform (MAQSIP) model reveals that chemistry contributions of 32% and 84% to NOₓ correspond to 26% and 80% to O₃ at GRSM and MACA, respectively. The similarity between NOₓ and O₃ process budgets serves as further evidences of close association between nitrogen oxides and effective O₃ production at these rural locations.
In the last part of this study we examined annual, seasonal, and diurnal distributions, as well as case studies of high ozone episodes observed during a multiple-year enhanced monitoring campaign at the Southeast national parks, namely. Though there are no continuous increases in either annual exceedances or the 4th highest ozone concentration at these sites, a long-term increase trend can be identified from measured data. Most frequent exceedances occur in August and September for GRSM site while the maximum exceedances are found in June or August at MACA site. Maximum exceedances at low-elevation site are seen in the midday, and extend into a few hours after sunset. High ozone episodes can be observed, however, in any hour at high elevation site during all photochemically active seasons, most frequently around sunset, and least frequently in early morning. While the air masses associated with ozone exceedances at GRSM site originated in all directions, those with high O₃ at MACA, however, reveal dominant transport originated from southwest with very few exceptions from north. Examining two early September cases shows that high nitrogen oxides concentration is the main driver to elevate ozone concentration to exceedance level at MACA site while ozone transport from polluted area works to form exceedances at GRSM, a mountain top site. Almost all high ozone episodes at MACA site are found developed with clear sky, high temperature, low relative humidity, as well as weak anticyclones traveling in a uniform anti-cyclonal pathway surrounding a high-pressure area. High ozone episodes observed at mountain site, however, are not necessary to be associated with these factors.
Measurement, Modeling, and Analysis of Ozone and Its Key Precursors in the Southeast United States National Parks

by

Quansong Tong

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

Department of Marine, Earth, and Atmospheric Sciences

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2003

Approved By:

S. Pal Arya

Rohit Mathur

Larry Benninger

Viney P. Aneja
(Chair of Advisory Committee)
DEDICATION

To my parents, Dunhao Tong and Dingzhen Xiang, and my wife, Binyu Wang, who love me so much;

To my son, Bill W. Tong, because of whom I learnt how to love.
Quansong Tong was born as the first son to the family on September 6th, 1975 in Yichang, China. Yichang is famous as the hometown to the father of Chinese Literature, Yan Qu and for the biggest National Park in China, Three Gorges. Quansong enjoyed his colorful childhood in Yichang with his younger brother and sister in an environment rich in both natural and cultural beautifulness.

Quansong has been interested in chemistry since middle school. He is the winner of International Olympic Chemistry Prize for high school students in 1993. In 1994, Quansong was admitted to Ocean University of China (OUC), majoring in Chemistry. He received Excellent Undergraduate Award three times and Outstanding Leadership Award twice during his four-year college in OUC. In recognition of his academic credits and community service, Quansong was selected as one of the winners of Statewide Excellent Undergraduate Award in 1997. Quansong obtained his B.S. of Chemistry from the department of Chemistry and a secondary Bachelor degree from the College of Trade and Economics in Ocean University of China in 1998.

In 1999, Quansong moved to Beijing and joined Prof. Chen’s group in College of Chemistry and Molecular Engineering, Beijing University. His research in Beijing University focused on the study of molecular relaxation time at the interface between solid and liquid phases. Quansong started his Ph.D. Study in North Carolina State University in 2000, carrying on his interest in chemistry, with emphasis on the interaction between atmospheric chemistry and environment. After dedicating three years to air quality research, Quansong is the author or co-author of seven published or to-be-submitted journal papers, and seven scientific presentations. Besides his
academic work, Quansong is also active in community service in Raleigh area. He worked as a volunteer to NC Ocean Science Bowl, Service Raleigh, and many other community services. He is a group leader in NC State Office of International Student and Scholar Service, and Department Ambassador for International Program in MEAS department since 2001. Quansong also served as the secretary and treasurer to AWMA Student Chapter in NC State since 2001, and as the President of Chinese Student & Scholar Friendship Association in NC State during 2001 and 2002.

After three productive and happy years in NC State University, Quansong is going to join Princeton University, Woodrow Wilson School as a research scientist. His long-term goal is to become a mighty warrior, fighting for our environment, to keep the air fresh, clean, and enjoyable.
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While approaching the end of my 22-year training in school, I am in huge debt to so many people who mentored and guided me to the way I am walking in and close to the goal I am dreaming of. My deepest appreciation goes to my respectable parents who blessed me with life and wisdom to grow. I thank Binyu my lovely wife for all her support to my research and for taking good care of our family. My sincere thanks to the chair of my graduate committee, Dr. Viney P. Aneja, who has been tremendously helpful to me both professionally and personally. Dr. Rohit Mathur and his colleagues in MCNC are invaluable resources for me to set up computational facilities and to obtain critical information. I am very grateful to Dr. S. Pal Arya and Dr. Larry K. Benninger for their technical reviews and guidance throughout my PhD program. Thanks also to Dr. John D. Ray of US National Park Service for his constructive suggestions on my research over these years.

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Chapter 1. INTRODUCTION

1.1 Background

The topic of ozone has been the focus of atmospheric science for decades, if not longer. Ozone was discovered by Schönben in 1840 as a byproduct of electric discharge in air [Warneck, 2000]. Since then, ozone was warmly welcomed by the people in central Europe with a widespread belief that ozone-rich air is beneficial, as a disinfectant, to human health. Recent research reveals that ozone does benefit human beings by providing a protective layer in the stratosphere. However, the presence of ozone at the ground level has a variety of adverse impacts on human and environmental health (National Research Council (NRC), 1991; US Environmental Protection Agency (EPA), 1997). Ozone in the troposphere is also important since it governs oxidation processes in the Earth’s atmosphere through the formation of hydroxyl (OH) radicals (Thompson, 1992; Lelieveld, 2000).

Traditionally, tropospheric ozone was assumed to be injected from stratosphere-troposphere exchange (STE) across the extratropical tropopause (Regener, 1957). The belief came from the observed O$_3$ gradient with altitude, which suggests a source at the tropopause and a sink near the surface. In the 1960s, Haagen-Smitt et al. (1961) revealed photochemical formation mechanism of ozone in the troposphere. For many years, photochemical air pollution was considered as a problem of mainly local and regional significance, somewhat affecting clean air sites by advection of polluted air. Crutzen (1973, 1974) and Chameides et al. (1973, 1976) suggested that photochemistry could be of more importance on much larger scale. Recent records of long-lasting ozone
measurement series show that ozone concentration has increased not only at the surface, but also in free atmosphere [Feister and Warmbt, 1987]. This result has been taken as evidence for an increase in the photochemical production of ozone in the atmosphere due to the growing emissions of ozone precursors [Warneck, 2000; references therein].

The photochemical ozone problem remains a ubiquitous problem; and it continues to plague human society and ecology in the United States. Moreover, the rising concentrations of ozone in the United States appear to be part of a larger pattern of ozone increases throughout much of the northern hemisphere which may be a significant contributor to the global warming due to the greenhouse effect (Ramanathan et al., 1985; Logan, 1985; NRC, 1991; Fehsenfeld et al., 1994; EPA, 1997). Unlike some other air pollutants of concern such as CO and SO₂, which are directly emitted into the atmosphere, ozone is a secondary pollutant formed in the ambient air though a complex set of sunlight-initiated reactions among its precursors. It has been well established that emissions of VOCs and NOx (NO + NO₂) from both anthropogenic and biogenic sources are the precursors of tropospheric ozone. More details of these precursors and their reaction products will be addressed in next chapter.

Regulation of ozone precursor emissions under the U.S. 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 episodes of high ambient ozone levels [NRC, 1991]. Medical and epidemiologic studies indicate that prolonged exposure to moderately high ozone (O₃) concentrations can have deleterious health and environmental effects [Lippmann, 1992; National Research Council (NRC), 1991]. The U.S. Environmental Protection Agency (EPA) has therefore proposed a new National Ambient
Air Quality Standard (NAAQS) for O\textsubscript{3} [Wolff, 1996; EPA, 1997]. Earlier analysis of ground-level O\textsubscript{3} data suggests that this new standard will transform our perceptions of air pollution in the rural United States and the policies used to manage this pollution [EPA, 1996; Chameides et al., 1998].

The southeast region is one of the fastest growing areas in the United States. As a result of this rapid growth, major population and industrial centers in the southeast have experienced air quality degradation similar to that of the urban areas in the northern and western United States. But the air pollution problem in southeast is not limited to urban and industrial centers. In the rural southeastern US, summertime mid-day concentrations of 50-70 ppb are common (Chameides et al., 1998; Fehsenfeld et al., 1994; Aneja et al., 1991). In many ways the south, and the southeast US in particular, represent a natural laboratory for the study of oxidant formation. The spatial homogeneity of sunlight, moisture, and high temperatures that make the southern forest and agriculture highly productive also contribute to high oxidant formation [Fehsenfeld et al., 1993]. Moreover, the relatively low population density and level of industrialization in the region may make natural sources of ozone precursors potentially important. Vegetation, including crops, forests, and ornamental plants, is known to produce VOCs as part of natural respiratory, photosynthetic, and stress defense mechanism. Emission rates of these VOCs typically increase with temperature and photosynthetic activity that are, on average, higher in the south than in north regions in US. These emissions rates, as well as the land cover, characterize the southern US as region rich in biogenic VOC sources [Fehsenfeld et al., 1994; Kang, 2001].
In order to understand the complexity of processes involved in tropospheric ozone, several intensive research campaigns have been conducted in addition to the existing long-term monitoring networks. The Southern Oxidant Study (SOS) was initiated in response to the problem of photochemical oxidant formation, especially for understanding the formation, accumulation, fate, and effects of ozone and other photochemical oxidants in the southeast United States [Fehsenfeld et al., 1994; Cowling and Furiness, 2001]. Some interesting findings of that study are as follows,

1. Models can give right $O_3$ for wrong reasons. The traditional method using regulatory models is to duplicate within some tolerance limits, the observed pattern for $O_3$. This, however, is no guarantee that a model can accurately predict effects of emission controls.

2. State Implementation Plans for meeting $O_3$ standards can use methods other than the traditional emission based modeling approach. Indicator species methods and observation based models are complementary approaches to emission based models.

3. Biogenic hydrocarbons are ubiquitous in southeast United States. Significant daytime concentrations of isoprene from biogenic sources are found in both urban and rural areas that degrade the efficiency of anthropogenic hydrocarbon reductions in controlling ozone levels.

These findings suggest that attempts to decrease ozone pollution in the southeast United States have been confounded by a number of factors, particularly, the lack of comprehensive chemical and meteorological datasets to test numerical and conceptual models of urban- and regional-scale photochemical smog formation, as well as develop
more observational based methods that are well-grounded in theory and bypass many of the difficulties associated with conventional modeling approaches.

In the wake of the SOS project, US National Park Service (NPS) initialized an enhanced measurement campaign to acquire ambient data that include intermittent hydrocarbon samples and continuous measurements of O₃, NOₓ, NO, SO₂, and CO in its three southeast United States Class I National Parks, namely, the Great Smoky Mountain (GRSM) National Park site, TN, Shenandoah (SHEN) National Park site, VA, and Mammoth Cave (MACA) National Park site, KY, from late 1995 to 1998. The NPS effort, which includes monitoring O₃ and its key precursors, has provided ideal opportunities to understand the tropospheric ozone issues in rural areas.

Chameides et al. (1998) reported that implementation of the new NAAQS will bring large parts of the rural eastern United States into non-attainment. While this conclusion was drawn on the basis of data collected up to 1996, more measurements in rural areas after 1996 are needed to verify this trend. This study presents multiple-year, continuous measurements of O₃ and other trace gases at three southeast US, pristine, rural sites. While O₃ levels at these rural areas are probably affected by emissions from multiple urban areas as well as from local and remote rural sources, resolving air quality problem of rural nonattainment may necessitate control strategies to target region-scale emission sources that can exert influence on O₃ levels in these areas.

1.2 Objectives

The primary objective of this research is to perform a comprehensive investigation of O₃, its precursors and other trace gases; their analysis, modeling and interpretation of
measurement data collected from three enhanced ambient air monitoring stations in the Shenandoah, Mammoth Cave, and Great Smoky Mountains National Parks. The research utilizes regression analysis, emission inventory analysis and trajectory-cluster analysis to ascertain pollutant sources affecting the parks. In addition, attempts will be made to evaluate the impact of the new NAAQS [EPA, 1997] on the nonattainment of O₃ in rural Southeast areas.

Particularly, this study attempts to find answers to the following questions:

1. What is the correlation between O₃ and nitrogen oxides, which is widely believed to be the limiting factor to ozone production in rural Southeast United States.

2. What is the relative importance of local and transported pollution to air quality in the national parks?

3. What is the relative importance of natural and anthropogenic emissions to air quality in the national parks?

4. How well do current air quality models represent pollution sources and atmospheric processes that shape air quality in the national parks?

5. What are the seasonal and diurnal distributions of ozone concentration during high ozone episodes in the rural southeast United States and what are their implications to ozone control strategy?

6. What are the long-term trends of ozone exceedances and effectiveness of current ozone abatement strategies applied to rural southeast United States?
1.3 Architecture of This Dissertation

This thesis is composed of the following sections,

Chapter 1 provides a brief introduction to the tropospheric ozone problem, background studies in the southeast US, and objectives of this study.

Chapter 2 gives a review of literature on ozone and its precursors, particularly nitrogen oxidants that are regarded as the limiting factor to summertime ozone production in Southeast United States. Several observational based methods to investigate the source attribution, influencing areas, and other source-receptor relationships of nitrogen oxides are reviewed. The current understanding of ozone production mechanism and the status of air quality modeling are also addressed in the ending part of Chapter 2.

Chapter 3 addresses reactive nitrogen oxides and their relation to O$_3$ production in rural southeast United States and assesses the impact of new O$_3$ NAAQS on regional attainment. The diurnal profiles of O$_3$, NO, NO$_y$, and other trance gases such as CO and SO$_2$ at both low-elevation and high-elevation sites are also explored. Correlation between O$_3$ and photochemical age of air masses are examined to investigate the ozone formation in different regimes of photochemical age. Finally, the impact of the new 8-hour 80 ppbv NAAQS on rural nonattainment is evaluated by extrapolation of data from these sites.

Chapter 4 focuses on both observational based analysis and modeling in elucidating source attribution, influence area, and process budget of reactive nitrogen oxides at two rural southeast national parks. Multiple linear regression analysis and emission inventory analysis are employed to quantify the relative contribution of mobile and point sources to total nitrogen oxides emission. The influence area, or origin of nitrogen oxides, is further investigated using trajectory-cluster analysis. The processes, as
well as their magnitude, responsible for the formation and removal of reactive nitrogen oxides are examined using a comprehensive 3-D air quality model.

Chapter examines the annual, seasonal, and diurnal distributions of ozone, as well as some case studies of the high ozone episodes observed during the multiple-year enhanced monitoring campaign at two class I southeast national parks. Back trajectory analysis is used to study the possible origins of air masses associated with ozone exceedances at these sites. Case studies of typical ozone episodes, mainly in seasons other than summer, are performed to examine both inter-site and inter-season differences that contribute to shape high ozone formation.

An overall summary of this research, major conclusions and suggestions for future research are discussed in Chapter 6.
Reference:


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Chapter 2. Literature Review

2.1 Ozone and its Key Precursors in the Lower Troposphere

2.1.1 Rural O₃ Pollution and the New NAAQS

Medical and epidemiologic studies indicate that prolonged exposure to moderately high ozone (O₃) concentrations can have deleterious health and environmental effects [Lippmann, 1992; National Research Council (NRC), 1991]. The U.S. Environmental Protection Agency (EPA) has thus proposed a new National Ambient Air Quality Standard (NAAQS) for O₃ [EPA, 1997]. Under the old NAAQS, an area was considered in nonattainment and was required to control pollutant emissions if the daily, maximum, 1-hour averaged O₃ concentration exceeded 120 part per billion by volume (ppbv) more than three times in 3 years. The new National Ambient Air Quality Standard (NAAQS) proposed by EPA in 1997 requires that the fourth highest, 8-hour averaged O₃ concentration (averaged over 3 years) not exceed 80 ppbv. Earlier analysis of ground-level O₃ data suggests that this new standard will transform our perceptions of air pollution in the rural United States and the policies used to manage this pollution [EPA, 1996; Chameides et al., 1998].

Ozone has historically been regarded as the principal urban/suburban air quality problem in the United States [NRC, 1991]. The current control strategies have justifiably focused on emission controls within the nonattainment area [NRC, 1991; EPA, 1997; Chameides et al., 1998]. Continuous ground-level O₃ monitoring, however, shows the national parks in the rural eastern United States are experiencing periodic high ozone episodes during summertime [EPA, 1997]. An analysis of data from the Aerometric
Information Retrieval System (AIRS) monitoring network showed that the new NAAQS would almost triple the number of non-attainment counties in the United States [EPA, 1996]. Chameides et al (1998) reported that implementation of the new NAAQS will bring large parts of the rural eastern United States into non-attainment. While this conclusion was drawn on the basis of data collected up to 1996, more measurements in rural areas after 1996 are needed to verify this trend. This study presents multiple-year, continuous measurements of O₃ and other trace gases at three southeast US rural sites, namely, the Great Smoky Mountain (GRSM) national park site, TN, Shenandoah (SHEN) National Park site, VA, and Mammoth Cave (MACA) National Park site, KY, from late 1995 to 1998. While O₃ levels at these rural areas are probably affected by emissions from multiple urban areas as well as from local and remote rural sources, resolving air quality problem of rural nonattainment may necessitate control strategies to target region-scale emission sources that can exert influence on O₃ levels of these areas.

2.1.2 Budget of Tropospheric Ozone

Ozone in the troposphere has both natural and anthropogenic sources (Table 2.1 [World Meteorological Organization (WMO), 1999]). Downward transport of ozone from the stratosphere as the result of stratosphere/troposphere exchange (STE) processes is the only known natural source of ozone in the troposphere [Junge, 1962]. Much of the O₃ in the troposphere is produced photochemically by reactions involving oxides of nitrogen and volatile organic compounds (VOCs) of both anthropogenic and biogenic origins. Ozone is lost by dry deposition and by photochemical reactions with other trace species.
There is substantial evidence for an increase in tropospheric O$_3$ since industrialization [Warneck, 2000]. Volz and Kley (1988) suggest tropospheric O$_3$ over Europe has increased by at least a factor of two since 1876. Ozone observations during the past 30 years indicate a 1-2% per year increase over Europe [Janach, 1989]. There is some speculation that globally averaged OH may be increasing as well. Krol et al. [1998] estimate a 0.46% yr$^{-1}$ increase in global OH abundance from 1978 to 1993, although a similar study by Prinn et al. [1995] found no change in global OH. The increase in tropospheric O$_3$ since the nineteenth century has been attributed to enhanced photochemical O$_3$ produced in a troposphere that has become increasingly polluted by the activities of man. The mechanism of O$_3$ production in the lower troposphere will be discussed in the following section.

\[ \text{Table 2.1 Estimated Ozone Budget for the Northern Hemisphere} \]

<table>
<thead>
<tr>
<th>Source</th>
<th>Flux (Tg N yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transport from the stratosphere</td>
<td>320-510</td>
</tr>
<tr>
<td>Photochemical Production</td>
<td>1200-2000</td>
</tr>
</tbody>
</table>

\[ \text{Sinks} \]

<table>
<thead>
<tr>
<th>Source</th>
<th>Flux (Tg N yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Deposition</td>
<td>450-960</td>
</tr>
<tr>
<td>Photochemical Destruction</td>
<td>1200-1400</td>
</tr>
</tbody>
</table>

2.1.3 O$_3$ Photochemistry in the Lower Troposphere

O$_3$ is formed photochemically from the photolysis of NO$_2$,

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}^3(P) \quad (2-1) \]

\[ \text{O}^3(P) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (M = \text{air}) \quad (2-2) \]
and the produced NO and O\textsubscript{3} can react rapidly with each other

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  \hspace{1cm} (2-3)

Reactions (2-1), (2-2) and (2-3) result in a photostationary cycle among NO, NO\textsubscript{2} and O\textsubscript{3} with no net formation or loss of O\textsubscript{3}, as shown in Figure 2.1A [Atkinson, 2000]. For net O\textsubscript{3} accumulation to occur, NO has to be oxidized by some species other than O\textsubscript{3} itself.

![Figure 2.1.A, Photostationary process of ozone formation](image)

In the presence of VOCs (including methane and non-methane hydrocarbons (NMHCs)), the degradation reactions of VOCs lead to the formation of RO\textsubscript{2} and HO\textsubscript{2} radicals, which are of strong oxidizing potential. RO\textsubscript{2} and HO\textsubscript{2} radicals can compete with O\textsubscript{3} to convert NO to NO\textsubscript{2},

\[ \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \]  \hspace{1cm} (2-4)

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  \hspace{1cm} (2-5)

which then photolyzes to form O\textsubscript{3} (Figure 2.1.B). This process is called O\textsubscript{3} accumulation and results in net formation of O\textsubscript{3}.
Figure 2.1.B Ozone accumulation process in troposphere

Much of the importance of $O_3$ to atmospheric chemistry lies in the fact that $O_3$ is the key precursor to hydroxyl radical (OH) [Thompson, 1992], which governs the lifetime of most pollutants emitted into the atmosphere. Photolysis of $O_3$ at wavelength $\geq 290$ nm forms excited oxygen, $O(^1D)$, atom [DeMore et al., 1997],

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (\lambda \leq 335 \text{ nm}) \quad (2-6)$$

$O(^1D)$ atoms are either deactivated to ground-state oxygen, $O(^3P)$ atoms,

$$O(^1D) + M \rightarrow O(^3P) + M \quad (M = N_2, O_2) \quad (2-7)$$

or react with water vapor to generate OH radicals [DeMore et al., 1997; Atkinson et al., 2000],

$$O(^1D) + H_2O \rightarrow 2OH \quad (2-9)$$

Note that whereas deactivation of $O(^1D)$ reproduces $O_3$ (reactions (2-7)-(2-8)), formation of OH radical (reaction (2-9)) represents a net loss of tropospheric $O_3$. In the absence of NO or at sufficiently low NO concentrations, reactions of $O_3$ with OH and HO$_2$ radicals,

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (2-10)$$
are additional loss processes of tropospheric O₃ [Atkinson, 2000].

Whether photochemistry leads to net O₃ formation or destruction depends on NO level presented in the atmosphere. The rate of reaction of HO₂ radical with NO is critical to determine the net influence on O₃ budget. In NO-rich environment, HO₂ and RO₂ radicals oxidize NO to NO₂ (reactions (2-4)-(2-5)), which subsequently leads to O₃ formation. In NO-limited environment, self-reactions of peroxides radicals occur,

\[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (2-12)
\]

\[
\text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2 \quad (2-13)
\]

Based on the rate constants for these reactions of HO₂ and RO₂ radicals and atmospheric concentrations of HO₂ and NO, Logan (1985) estimated that net photochemical O₃ formation occurs when NO mixing ratio \( \geq (10-30) \times 10^{-12} \) while net photochemical O₃ loss occurs when NO mixing ratio less than that.

### 2.1.4 NOₓ-Limited vs VOCs-Limited Conditions of O₃ Photochemistry

As a secondary pollutant, the abatement of O₃ pollution can only be effective by controlling emission sources of its key precursors, i.e., NOₓ and VOCs. Early O₃ control strategies emphasized reductions of anthropogenic emissions of VOCs, particularly those emitted in automobile exhaust. These strategies prove successful in reducing peak O₃ concentration over time in cities where anthropogenic emissions are dominant [Fiore et al., 1998]. For the eastern United States, however, it has been well established by both observations and modeling that O₃ production in summer is limited primarily by the
availability of NO\textsubscript{x} since this area is characterized with large emissions of very reactive VOCs from biogenic sources [Trainer et al., 1987, 1993; Chameides et al., 1988, 1992; Jacob et al., 1993]. Controls on anthropogenic NO\textsubscript{x} in addition to anthropogenic VOCs are now thought to be necessary to reduce ozone in regions such as rural eastern US [NRC, 1991].

Ozone abatement issue is further complicated by the possible seasonal transition between NO\textsubscript{x}- and VOCs-limited conditions for O\textsubscript{3} production in rural eastern US. Kleinman (1991) has argued from theoretical considerations that a seasonal transition from NO\textsubscript{x}- to VOCs-limited conditions should take place in the region between summer and winter. The argument is based on the titration of odd hydrogen (OH, HO\textsubscript{2} and RO\textsubscript{2}) by NO\textsubscript{x} in the continental boundary layer as discussed in preceding section. The major sources of odd hydrogen are the photolysis of O\textsubscript{3} to O(\textsuperscript{1}D) followed by reaction of O(\textsuperscript{1}D) with water vapor (reactions 2-6, 2-9, 2-10, and 2-11). The formed odd H then converts NO to NO\textsubscript{2} and subsequently leads to net O\textsubscript{3} production in the lower troposphere.

Whether O\textsubscript{3} production is NO\textsubscript{x}- or VOCs-limited can be identified by the pathway of odd-H loss [Sillman et al, 1990; Kleinman, 1991; Jacob et al., 1995]. Under NO\textsubscript{x}-limited O\textsubscript{3} production, the loss of odd-H is principally by self-reactions of peroxy radicals, producing peroxides (reactions (2-12)–(2-13)). Under VOCs-limited condition, the loss is dominated by reaction of NO\textsubscript{2} with OH to produce HNO\textsubscript{3},

\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \]  

(2-14)

It has been pointed out that the odd-H production rate over the eastern US decreases by an order of magnitude from summer to winter because of declining solar radiation and humidity, crossing the turnover point where odd-H radicals can be titrated
in the boundary layer by NOx emissions, resulting in a seasonal transition from NOx- to VOCs-limited conditions. Though the seasonal transition is theoretically possible, whether it actually occurs depends on the VOCs/NOx ratio and on the mechanism for NOx oxidation [Jacob et al., 1995; references therein].

A seasonal transition in photochemical regime would be of little interest if it occurred in late fall when O$_3$ production is low. If such a transition takes place during period associated with frequent O$_3$ episodes, it will bear important implications for the design of air pollution control strategies. The emission control strategy designed to reduce O$_3$ levels in summer may not be effective for period after or before the transitions [Jacob et al., 1995]. This study will analyze the seasonal distribution of high ozone episodes, and examine if there are considerable ozone exceedance during periods such as fall and spring, during which season the seasonal transition of O$_3$ sensitivity may necessitate different control strategies other than the current summer-oriented management policies.

2.2 Data Acquisition and Quality Assurance

2.2.1 Sampling Site Description

The Great Smoky Mountains (GRSM) site (35°41′48″N, 83°36′35″W), at an elevation of 1243 m above sea level, is located at the summit of Cove Mountain which is in Sevier County, Tennessee, on a ridge in the Great Smoky Mountains National Park. The Great Smoky Mountains (GRSM) National Park encompasses 2100 km$^2$ (800 square miles) of mountain ridges and deep-cleft valleys in the states of Tennessee and North Carolina. Among all monitored parks, the Great Smoky Mountain national park is marked with most rapid increase in numbers of days exceeding the National Ambient Air
Quality Standard (NAAQS) for ozone [EPA, 2000]. The measurement station is constructed within the tower frame of an inactive fire tower at an elevation of 6 m above the ground. Continuous gas samples lines extend from the station to an elevation of 22 m aboveground. The meteorological equipment is also located at this level on the fire tower.

The Mammoth Cave (MACA) site (37°13’04”N, 86°04’25”W), at an elevation of 230 m above sea level, is located in Mammoth Cave National Park approximately 5 miles from Cave City, Kentucky, in a clearing about 30 m from the surrounding forest area. Both GRSM and MACA sites were operated by a partnership between the National Park Service (NPS) and Tennessee Valley Authority (TVA). The monitoring stations consist of environmentally controlled shelters. The local meteorological measurements were made at the same elevation as the air sampling inlets, except as noted, at 10 m above ground level.

Ambient data was also collected at Shenandoah National Park – Big Meadows (SHEN) site (38.50° N, 78.45° W), which is located on the top of a mountain plateau (1100 m above mean sea level) in the center of Shenandoah National Park in Virginia. Big Meadows is near the western boundary of the park and is higher in elevation than the surrounding area for several kilometers, favoring exposure to regional flow patterns with minimal disturbance by the local orography. The SHEN site lies within the Chesapeake Bay Watershed and is mostly removed from anthropogenic sources of air pollution [Poulida et al., 1991]. Further details of the site, instruments, experimental techniques used, and chemical data/results are given separately [Doddridge et al., 1991, 1992; Poulida et al., 1991; Moy et al., 1994; Hallock-Waters, 2000].
2.2.2 Experiment

Air samples for O$_3$, SO$_2$, and CO were collected through a common 3/8” inch OD Teflon tube running from the sampling inlet head to a manifold located in the rear of the instrument cabinet. Individual ¼” inch OD Teflon sampling line, equipped with 5 micron Teflon particulate filters, were used to deliver air samples to their respective monitors. Samples of O$_3$, SO$_2$, and CO were analyzed 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 ¼” inch OD Teflon sampling lines. The NO/NO$_y$ measurement system used a TEII Model 42S as a time sharing analyzer to measure NO and NO$_y$ from the two independent sampling lines. The NO$_y$ air sampling inlet system also contained the molybdenum converter, which was located external to the TEII Model 42S, for NO$_y$ reduction to NO. Because of the long transfer line from the gas sampling inlet system, an auxiliary control box and associated pump was required to maintain constant flow through both independent sampling lines as the Models 42S alternated between the NO and NO$_y$ sampling modes.

The calibration gases, as well as the gases used for daily Quality Assurance/Quality Control Procedure (QA/QC) activities, were EPA Protocol SO$_2$, CO, NO, and NO$_2$ gas cylinders provided by Scott Specialty Gases. The n-propyl nitrate (NPN) gas cylinder was obtained from Environmental Science & Engineering, Inc (ESE), Florida. For the routine QA/QC activities, a Campbell CR10 data logger was programmed to automatically control the gas selection and concentration, the sampling line selection, and the execution of the gas addition or gas substitution procedure. The sites are equipped with a TEII 111 Zero Air generating system and a TEII 146 Dynamic Gas Calibrator. The
CO catalytic reactor from the TEII Model 111 provided CO-free ambient air for the CO monitor. More details of the measurements can be obtained from Olszyna et al. (1998).

### 2.2.3 Data Quality Assurance and Quality Control (QA/QC)

The goal to explore the chemistry between O$_3$ and its key precursors in rural region requires a high degree of data comparability between the measurement sites. This goal is partially achieved by adopting the same QA plan and by using the same protocols, measurement techniques, and equipment. Both measurement operations followed the Quality Assurance/Quality Control (QA/QC) established for the ground-based air monitoring stations that participated in the SOS/Nashville 1995 Intensive.

A full description of the QA/QC has been given by TVA (1995). Shortly, the QA/QC procedure consisted of zero, span, and precision checks using gas substitution and gas addition techniques. The gas addition technique determined matrix effects in the sampling system. Gas additions of NO at the midday median NO$_y$ concentration level were conducted to both the NO$_y$ and NO sampling lines three times a day. The NPN is used as a surrogate for gaseous HNO$_3$, which is the more difficult of the nitrogen oxides to reduce NO. The NO addition to the NO sampling line was a system check for losses due to chemical reactions of NO with O$_3$ and other oxidants in the NO sampling line. Measurements for O$_3$ were conducted according to SLAMS protocol, modified to operate the O$_3$ instrument on the 200 ppbv full scale range. The O$_3$ concentrations for the daily span and precision checks for the sites are 160 ppbv and 40 ppbv which are 80% and 20% of the 200 ppbv instrument range. The internal ozonator in the TEII 146 was used to provide standard concentrations for the ozone precision and span checks.
2.3 Methodologies

2.3.1 O$_3$ Production Potential of Nitrogen oxides (OPPN)

It has been established that the production of ozone in rural areas with NO$_x$ levels of less than a few ppbv is limited by the availability of nitrogen oxides [Fishman et al, 1979; Logan, 1985; Liu et al., 1987]. The ozone production potential, dO$_3$ / dNO$_x$, is defined as the number of ozone molecules produced by each NO$_x$ molecule before it is oxidized to more stable products such as HNO$_3$ and peroxyacetyl nitrate (PAN). Knowledge of this production potential allows an estimate of the amount of ozone formed from the total NOx emitted E$_{NOx}$ [Liu et al, 1987]:

\[
P(O_3) = \frac{dO_3}{dNO_x} E_{NOx}
\]  

(2-15)

Model studies have indicated that the amount of ozone produced per NO$_x$ oxidized depends on the nonlinearity of O$_3$ and its precursors, with the ozone production potential decreasing with increasing NO$_x$ levels [Liu et al., 1987; Trainer et al., 1993].

Trainer et al. (1993) reported a correlation of O$_3$ with NO$_y$ concentrations based on measurements in eastern North America. These correlations are expected since the NO$_y$ concentration in an air parcel is at least a rough measure of the concentration of NO$_x$ that was emitted into the air parcel [Trainer et al., 1993]. A seasonal trend has also been discussed since the seasonal dependences of OPPN are expected from decreases in temperature, water vapor, solar flux intensity, and biogenic VOCs emission as the annual cycle advances.
2.3.2 Cluster-Trajectory Analysis

Origin of air masses approaching the measurement site can be investigated by the combination of cluster analysis [Dorling, et al., 1992] of hybrid single-particle Lagrangian integrated trajectories (HY-SPLIT) model results [Draxler, 1997] and emission sources categorization based on EPA emission inventory [EPA, 2000]. Cluster analysis is frequently employed in air pollution studies to address pollutant source origin, e.g., Slanina et al. (1983) and Pio et al. (1991) identified continental, maritime, and anthropogenic sources regimes of pollutants. This method aims to maximize inter-group variance and to minimize within-group variance. Numerous algorithms have been developed for cluster analysis [Anderberg, 1973]. The approach chosen in this study is the one proposed by Dorling et al. (1992). Briefly, end points of each trajectory are taken as input to clustering algorithm. The first step chooses a large number of seed trajectories and all other trajectories are assigned to the seeds that can achieve minimum Root Mean Square Deviation (RMSD). The seed or average trajectory of each cluster is then recalculated from its members continuously until all trajectories are correctly assigned. After that, the number of clusters is decreased by merging two closest clusters. Sudden drop in the total RMSD as the number of clusters is reduced is interpreted as the merging of clusters of trajectories that are significantly different in terms of the wind directions and speeds associated with them. HYSPLIT-4 [Draxler, 1997] model was chosen to calculate air mass trajectories for cluster analysis. The actual operation routines are explained by Draxler (1997) and will not be discussed here. An optimum cluster number can be obtained by plotting the percentage change in the total RMSD with respect to decreasing cluster numbers. As in any other clustering methodology, some decisions have
to be made by the user. The user can define a percentage change in RMSD which, when exceeded at some stage in the reduction of the number of clusters, signifies an optimum number of clusters to be retained in the analysis.

2.3.3 Multiple Linear Regression Analysis

According to the US EPA, more than 90% of the anthropogenic NO\textsubscript{x} emissions in the United States are by either mobile sources or point sources [EPA, 1997; Stehr et al. 2000]. Mobile sources emit high levels of CO, but relatively low levels of SO\textsubscript{2}, while the reverse is true for point sources [EPA, 1997]. Therefore, NO\textsubscript{x} emissions may be well correlated with either SO\textsubscript{2} or CO, leaving relatively little NO\textsubscript{x} uncounted for [Stehr et al. 2000]. In actual calculations, NO\textsubscript{x} is replaced by NO\textsubscript{y}, since some fraction of the pollutants is oxidized before arriving at the receptor site.

Relative emission source strength can be evaluated at a surface receptor site using observed pollutant data and the techniques of regression analysis. NO\textsubscript{y} is taken as the response variable in a multiple linear regression analysis of the combination of CO and SO\textsubscript{2} as factors. The mathematical expression of the fitted model is:

\[ [\text{NO}_y] = \alpha[\text{SO}_2] + \beta[\text{CO}] + \delta \] (2-16)

where \( \alpha \) and \( \beta \) are the linear coefficients between \([\text{NO}_y]\) and \([\text{SO}_2]\) and \([\text{CO}]\) while \( \delta \) represents the intercept. With the estimated values of coefficients, the parameterized model can be used to evaluate the contributions of emission sources (mobile and point) using the measured CO and SO\textsubscript{2} concentrations.

Once parameterized, the simulation model can be used to evaluate the relative importance of mobile and point sources by incorporating the measured concentrations of
CO and SO\textsubscript{2} into Eq. (2-16). Contribution from point sources is evaluated by setting CO term and \( \delta \) to zero since the intercept is only attributed to natural CO background. Contribution from mobile sources is determined by taking off SO\textsubscript{2} term, i.e., by CO term plus intercept.

2.3.4 Emission Inventory Analysis

Emission inventory analysis has been used in earlier work [e.g., Parrish et al., 1991; Goldan et al., 1995; Stehr et al. 2000] to examine the relationships between NO\textsubscript{y}, CO, and SO\textsubscript{2}. Briefly, the ratio (indicated by \( x \)) of NO\textsubscript{y} from point sources (NO\textsubscript{y}\textsubscript{p}) to mobile sources (NO\textsubscript{y}\textsubscript{m}) can be obtained from the division of two factors:

\[
\frac{\text{NOy}_p}{\text{NOy}_m} = \left\{ \frac{\text{NSR}_p}{\text{NCR}_m} \left[ \frac{\mu_{[SO_2]}}{[CO]-[CO]_{bg}} \right] \right\} \tag{2-17}
\]

Where NSR\textsubscript{p} and NCR\textsubscript{m} represent the molar ratios of NO\textsubscript{y} to SO\textsubscript{2} from point sources and NO\textsubscript{y} to CO from mobile sources, respectively. [SO\textsubscript{2}] and [CO] are the concentration of SO\textsubscript{2} and CO measured at the site; [CO]\textsubscript{bg} is the background CO concentration that is independent of local photochemical processes. An adjusting parameter, \( \mu \), is introduced to account for the fraction of SO\textsubscript{2} that has been oxidized into sulfate before arriving at the receptor site. Therefore,

\[
\text{Fraction of NOy attributed to mobile sources} = \frac{1}{1+x} \tag{2-18a}
\]

\[
\text{Fraction of NOy attributed to point sources} = \frac{x}{1+x} \tag{2-18b}
\]

The molar ratios for emission analysis are calculated on the basis of EPA emissions inventories [EPA, 1999]. The ratio of NO\textsubscript{y} to SO\textsubscript{2} (i.e., NSR\textsubscript{p} in Eq. (2-17)) for point sources and the ratio of NO\textsubscript{y} to CO (i.e., NCR\textsubscript{m} in Eq. (2-17)) for mobile sources are
derived from anthropogenic state-level emission data. The extent of these sets of states was determined by back trajectory analysis.

2.3.5 Air Quality Modeling

As a powerful and sometimes unique measure, numerous air quality models have been developed to address regional air quality problem. Those can be broadly categorized as mesoscale and synoptic models by horizontal scale, episodic and long-term models by time scale; and Eulerian and Lagrangian model according to their mathematic framework [Arya, 1999]. Regardless of their diversity in term of dimensions and scales, all comprehensive urban airshed and regional air quality models share a list of essential components [Seinfeld, 1986; Arya, 1999]. These components include anthropogenic and natural emission sources, advection, horizontal and vertical diffusion, homogeneous and heterogeneous chemistry, and removal processes. Different models can be distinguished in the manner and complexity of how they deal with each component.

Among numerous regional air quality models available to the scientific community, US EPA Models-3 / Community Multiscale Air Quality (CMAQ) modeling system and its prototype – Multiscale Air Quality Simulation Platform (MAQSIP) are chosen for this study due to several privileges they bear. Among these are their multi-scale, multi-pollutant capabilities, complete documentation, state-of-the-art physical and chemical parameterizations, and a modular structure allowing flexibility of choice from alternative meteorological, chemical, and physical modules. Models-3 is an advanced air quality modeling system that addressed air quality from the “One Atmosphere”
perspective. Whereas the modeling systems have been elucidated elsewhere [EPA, 1999], only a brief introduction will be given in the remaining of this section as follows,

1. Meteorological Driver. Meteorological model is essential to provide necessary information such as transport wind, PBL height, temperature, humidity and solar radiation. With only limited meteorological data available from observations, a suitable mesoscale meteorology model can be adopted to provide spatially varying meteorological data over the whole domain. The meteorology model that has been adopted and evaluated with CMAQ is the fifth-generation Pennsylvania State University / National Center for Atmospheric Research (NCAR) Mesoscale Model (MM5), although other meteorology models are being considered for compatibility with CMAQ. The raw output of MM5 simulation, however, is not always suitable to be used in the subsequent emission and chemistry models. The conversion of MM5 output to useful fields for the other Models-3 programs is accomplished in the Meteorology Chemistry Interface Processor (MCIP), which computes required variables and creates an output file a compatible format (nominally, netCDF in Models-3 system).

2. Emission Driver. Temporally and spatially specified emission data, as input to the chemistry and transport model, is created by emission models based on available emission inventory database. These emission models include GEMAP (EMS-95), EPS, FREDS and SMOKE. The Sparse Matrix Operator Kernel Emission System (SMOKE) is the emission-processing model we used in this study to provide emission data. Hourly biogenic emission rate of isoprenes, monoterpenes, and soil NO for each grid cell are estimated using the Biogenic
Emission Inventory System, version2 (BEIS-2). Anthropogenic sources, such as point sources and area sources are estimated on the basis of extrapolation of limited direct measurements for point sources, and application of limited measurements or estimates to spatial surrogate data for area sources. Mobile source emissions are modeled to generate either portions of emission inventories or hourly data for direct use in chemistry and transport model. The output of emission model provides either individual species or ‘lumped’ species. The actually lumping of discrete compounds to form mechanism species is carried out using the split factors and mapping table associated with the chemical mechanisms to be used in chemistry and transport model.

3. Transport. The transport process principally consists of advection and diffusion that cause the movement and dispersion of pollutants in space and time, although transport by the parameterized subgrid-scale cloud can be of significance occasionally. To provide CMAQ with multiscale capability, the transport processes are formulated in conservation forms for a generalized coordinate system. This enables CMAQ to function under a wide variety of dynamic situations and concentration distribution characteristics.

4. Chemistry. The representation of chemical interactions among atmospheric constituents is an essential element of air quality model. For computational efficiency, chemical interactions in the gas, liquid, and solid phases are modeled separately in Models-3/CMAQ: (1) Gas-phase chemistry. CMAQ currently includes three base chemical mechanisms—CB4 (Gery et al., 1989), RADM2 (Stockwell et al., 1990), and SAPRC-97 (Carter, 1997). (2) Aerosol formation. An
aerosol extension is needed to address gas and aerosol interactions. (3) Aqueous chemistry. Another extension is attached to original chemistry mechanism to simulate aqueous phase chemical interactions.

Models-3/CMAQ and MAQSIP are equipped with several advanced capabilities to achieve the objectives of this study. Among these capabilities, process analysis and sensitivity analysis are particularly of my interest. Process analysis can calculate the contribution of emission, chemistry and transport to the presence of pollutants of interest, while sensitivity analysis can investigate the influence of varying emissions associated with seasonality and anthropogenic activities.
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Chapter 3

Trace Gases and Ozone Nonattainments in Three Southeast United States National Parks
3.1 Abstract

Continuous measurements of ozone (O\textsubscript{3}), total reactive nitrogen oxides (NO\textsubscript{y}), and other trace gases were made at three enhanced rural monitoring sites located in the southeast United States national parks from 1995 to 1998. Our analysis shows that whereas O\textsubscript{3} at low-elevation rural site rise sharply to a short-lived afternoon maximum and drop to near zero at night as that in most urban or suburban areas, O\textsubscript{3} at high-elevation rural sites does not display a significant drop during nighttime. As a result, high-elevation site is more likely to violate the new O\textsubscript{3} NAAQS as the standard changes to a smaller concentration averaged over a longer time period. The diurnal variation of NO\textsubscript{y} and NO at MACA peaks in the early morning while SO\textsubscript{2} reaches a maximum about two hours later than NO and NO\textsubscript{y}. This time difference suggests the possible contributions of biogenic emissions to NO\textsubscript{x} from soil. Similar to O\textsubscript{3}, NO\textsubscript{y}, NO, and SO\textsubscript{2} don’t show significant diurnal variations at high elevation locations. The ratio of (NO\textsubscript{y} - NO)/NO\textsubscript{y}, a new indicator of air mass age, is introduced in this study due to several advantages it bears. The current study also presents a turnover point (0.9 for (NO\textsubscript{y} - NO)/NO\textsubscript{y}) that separates NO\textsubscript{x}-limited and non-NO\textsubscript{x}-limited O\textsubscript{3} production regimes. The regional background O\textsubscript{3} concentrations that are not directly influenced by anthropogenic emissions are estimated at ~35 ppbv at GRSM, and ~43 ppbv at MACA. Impact of the new 8-hour-80-ppbv NAAQS on rural nonattainment is addressed by extrapolation of data from these sites from January 1996 through December 1998. Our analysis also shows that under the 1-hour NAAQS, both GRSM and SHEN site were at the edge of O\textsubscript{3} violation and MACA did not violate the 1-hour NAAQS for O\textsubscript{3}. Under the new 8-hour
NAAQS, however, all three national parks are in serious nonattainment of O₃ NAAQS. Further investigation is in need to screen the influencing areas and identify the seasonal characteristics of O₃ episodes to provide critical information of shaping a successful O₃ control strategies in the areas of concern.
3.2. Introduction

Tropospheric ozone (O$_3$) continues to be a major air pollution problem in the southeast United States due to its adverse effects on human and environment [National Research Council (NRC), 1991; Lippmann, 1992; US Environment Protection Agency (EPA), 1997]. Ozone may govern oxidization processes in the atmosphere by acting as the key precursor to hydroxyl radical (OH) [Thompson, 1992]. According to US EPA, an area is in nonattainment and is required to control pollutant emissions if the fourth maximum 1-hour averaged O$_3$ concentration exceeds 120 part per billion by volume (ppbv) in 3 years. Despite that significant controls on ozone have been implemented, the national parks in the eastern United States are experiencing periodic high ozone episodes during summertime (EPA, 1997; Kang et al., 2001, 2003, Tong et al., 2003). The new National Ambient Air Quality Standard (NAAQS) proposed by EPA in 1997 requires that the fourth highest, 8-hour averaged O$_3$ concentration (averaged over 3 years) not exceed 80 ppbv. Chameides et al (1998) reported that implementation of the new NAAQS will bring large parts of the rural eastern United States into nonattainment. Analysis of rural O$_3$ data suggests that this new standard will transform our perceptions of air pollution in the rural United States and the policies used to manage this pollution. While this conclusion was drawn on the basis of 1-year (1995) data collected at rural sites, more measurements in rural areas are needed to verify this opinion. This study presents multiple-year, continuous measurements of O$_3$ and other trace gases at three southeast US rural sites, namely, the Great Smoky Mountain (GRSM) National Park site, TN, Shenandoah (SHEN) National Park site, VA, and Mammoth Cave (MACA) National Park site, KY, from late 1995 to 1998.
Ozone is formed in the lower troposphere through photochemical processes with the presence of nitrogen oxides \((\text{NO}_x = \text{NO} + \text{NO}_2)\) and volatile organic compounds (VOCs). Characteristics and \(O_3\) production of VOCs at these locations have been discussed by Kang et al. (2001, 2003). This paper focuses on observation-based analysis of nitrogen oxides and its influence on local ozone production. Locations such as the southeast US national parks are classified as \(\text{NO}_x\) limited for local ozone production during photochemically active period (Kang et al., 2001, 2003; Li et al., 1999; Aneja et al., 1996). Therefore, better understanding of the availability and variation of nitrogen oxides is critical to shape more successful ozone control strategies in the southeast US. \(\text{NO}_x\) emissions have complicated effects on \(O_3\) by first depleting \(O_3\) and then catalyzing its production. For locations with large \(\text{NO}_x\) sources, \(O_3\) levels can reach a high afternoon peak and drop to near zero during nighttime titration by freshly emitted \(\text{NO}_x\), resulting in a strong diurnal variation. At rural site, which is remote from large \(\text{NO}_x\) sources, \(O_3\) does not display such a regular diurnal trend. The afternoon maximum is smaller but the minimum in the morning and at night is larger because of lack of fresh \(\text{NO}_x\) titration. Therefore, while nonattainment of the 1-hour-120-ppbv NAAQS occurs mostly in urban and suburban areas, rural nonattainment becomes more likely as the standard has changed to a smaller concentration averaged over a longer time period, i.e., 8-hour-80-ppbv average [Chameides et al., 1998]. This will be particularly the case for high elevation site, where \(O_3\) displays almost no diurnal variation [Jacob et al., 1995; Aneja et al., 1991; references therein]. Both the three nonurban sites covered in this study are not associated with immediate \(\text{NO}_x\) emission, and one site, MACA, is at low-
elevation (200m above sea level) while the others, GRSM and SHEN, are mountaintop sites with more than 1000m above sea level. It is expected that these sites are indicative of the typical rural setting throughout much of the southeast US.

To explore influence of emitted and transported pollutants on local air quality in rural areas, the National Park Service (NPS) has been acquiring ambient data that includes continuous measurements of \( \text{O}_3 \), \( \text{NO}_y \), NO, \( \text{SO}_2 \), CO (carbon monoxide), and meteorological data at GRSM, SHEN, and MACA sites since 1995. The observational results are important because the regional distribution of oxides of nitrogen within rural southeast US is relatively unknown [SOS Report, 1994]. In this paper, observation based analyses are performed on (1) the temporal profiles of \( \text{O}_3 \), \( \text{NO}_y \), NO, and \( \text{SO}_2 \), and compared to those reported from other measurements sites; (2) the ozone production efficiency of nitrogen oxides; and (3) photochemical aging of air masses approaching the measurement sites.

### 3.3. Measurements

Ozone (\( \text{O}_3 \)), total reactive oxides of nitrogen (\( \text{NO}_y \)), nitric oxide (NO), sulfur dioxide (\( \text{SO}_2 \)), and carbon monoxide (CO), and other meteorological parameters were measured at three enhanced monitoring sites (Figure 1) in the Southeast United States. The Great Smoky Mountains (GRSM) site (35°41’48”N, 83°36’35”W), at an elevation of 1243 m above sea level, is located at the summit of Cove Mountain which is in Sevier County, Tennessee, on a ridge in the Great Smoky Mountains National Park. The Great Smoky Mountains National Park encompasses 2100 km\(^2\) (800 square miles) of mountain ridges and deep-cleft valleys in the states of Tennessee and North Carolina. Among all
monitored National Parks, the Great Smoky Mountain National Park is marked with most rapid increase in numbers of days exceeding the National Ambient Air Quality Standard (NAAQS) for ozone [EPA, 1997]. The measurement station is constructed within the tower frame of an inactive fire tower at an elevation of 6 m above the ground. Continuous gas samples lines extend from the station to an elevation of 22 m aboveground. The meteorological equipment is also located at this level on the fire tower.

The Mammoth Cave (MACA) site (37°13’04” N, 86°04’25” W), at an elevation of 230 m above sea level, is located in Mammoth Cave National Park approximately 5 miles from Cave City, Kentucky, in a clearing about 30 m from the surrounding forest area. Both GRSM and MACA sites were operated by a partnership between the National Park Service (NPS) and Tennessee Valley Authority (TVA). Instruments at both monitoring stations were kept in climate-controlled shelters. The local meteorological measurements were made at the same elevation as the air sampling inlets, except as noted, at 10 m above ground level.

Ambient air samples for O$_3$, SO$_2$, and CO were collected through a common 3/8” inch OD Teflon tube running from the sampling inlet head extended outside the instrument cabinet. Individual ¼” inch OD Teflon sampling line, equipped with 5 micron Teflon particulate filters, were used to deliver air samples to their respective monitors [Olszyna et al. 1998]. Samples of O$_3$, SO$_2$, and CO were analyzed 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 ¼” inch OD Teflon sampling lines. The NO/NO$_y$ measurement system used a TEII Model 42S as a time-sharing analyzer to measure NO and NO$_y$ from the two independent
sampling lines. The NO$_y$ air sampling inlet system also contained the molybdenum converter, which was located external to the TEII Model 42S, for NO$_y$ reduction to NO. Because of the long transfer line from the gas sampling inlet system, an auxiliary control box and associated pump was required to maintain constant flow through both independent sampling lines as the Models 42S alternated between the NO and NO$_y$ sampling modes.

The calibration gases, as well as the gases used for daily Quality Assurance/Quality Control Procedure (QA/QC) activities, were EPA Protocol SO$_2$, CO, NO, and NO$_2$ gas cylinders provided by Scott Specialty Gases. For the routine QA/QC activities, a Campbell CR10 data logger was configured to automatically control the gas influx, the sampling switches, and the execution of the gas addition or gas substitution. The sites are equipped with a TEII 111 Zero Air generating system and a TEII 146 Dynamic Gas Calibrator. The CO catalytic reactor from the TEII Model 111 provided CO-free ambient air for the CO monitor.

The measurement operations followed the Quality Assurance/Quality Control (QA/QC) established for the ground-based air monitoring stations that participated in the SOS/Nashville 1995 Intensive. A full description of the QA/QC has been given by TVA (1995) and by Olszyna et al. (1998). Briefly, the QA/QC procedure consisted of zero, span, and precision checks using gas substitution / addition techniques which determined matrix effects in the sampling system. Gas additions of NO at the midday median NO$_y$ concentration level were conducted to both the NO$_y$ and NO sampling lines three times a day. The NO addition to the NO sampling line was a system check for losses due to chemical reactions of NO with O$_3$ and other oxidants in the NO sampling line.
Measurements for O₃ were conducted according to SLAMS protocol, modified to operate the O₃ instrument on the scale range between 0 and 200 ppbv. The O₃ concentrations for the daily span and precision checks for the sites are 160 ppbv and 40 ppbv which are 80% and 20% of the full instrument range. The internal ozonator in the TEII 146 was used to provide standard concentrations for the ozone precision and span checks.

Ambient data was also collected at Shenandoah National Park – Big Meadows (SHEN) site (38.50° N, 78.45° W), which is located on the top of a mountain plateau (1100 m above mean sea level) in the center of Shenandoah National Park in Virginia. Big Meadows is near the western boundary of the park and is higher in elevation than the surrounding area for several kilometers, favoring exposure to regional flow patterns with minimal disturbance by the local orography. The SHEN site lies within the Chesapeake Bay Watershed and is mostly removed from anthropogenic sources of air pollution [Poulida et al., 1991]. Further details of the site description, instruments, and experimental techniques can be found elsewhere from [Hallock, 2002; Reference therein].

3.4 Temporal Profile of O₃, NOₓ, NO, and SO₂

Figure 3.2, 3.3, and 3.4 show the diurnal profile of O₃, NOₓ, NO, and SO₂ averaged for each season at GRSM, MACA, and SHEN, respectively, during the entire measurement period. CO data is also collected (not presented in this plot); no significant diurnal variation is found in all seasons at all sites. All the species were simultaneously measured at a time quantum of five minutes, except that missing measurements of NO, CO and SO₂ during spring, summer and part of fall at SHEN site (Figure 3.4). Hourly
averaged data, instead of original five-minute measured data, is used in this study since spectral analysis of respective species showed that more than 91% of the variance in each specie occurs in timescale longer than 1 hour. Measurements of O₃ at MACA display regular variation trend for all four seasons, with maximum in the afternoon (1400-1500 EST) and minimum before sunrise (0600EST). This is the typical diurnal shape for ozone variation at low elevation locations  [Warneck, 2000]. O₃ at GRSM and SHEN, however, doesn’t display significant diurnal variation as those at MACA, although slightly higher ozone concentrations can be observed in late afternoon or right after sunset for all seasons except winter. Generally, when increased solar insolation triggers the breakup of the nocturnal boundary layer (NBL) above the measurement site, air masses with undepleted O₃ begins to mix down to the surface [Li, et al, 1999]. At the same time, local photochemical production also contributes to increased ozone level. Combination of transport and photochemistry can explain the daytime maximum of O₃ and its regularity at MACA. After sunset, the formation of stable NBL prevents air mass with higher level of O₃ from reaching the surface; furthermore lack of photochemistry and other depletion mechanisms such as titration by fresh nitrogen oxides will further lower ozone level to its minimum before sunrise. Similar observations of the absence of daytime maximum ozone levels at GRSM and SHEN have been reported by other investigators [Aneja et al., 1991; references therein] for high-elevation locations. O₃ is relatively stable in the upper atmosphere, and its lifetime is thought to be approximately 10 days [Liu et al., 1980] and even longer (50 or 60 days, Hough and Derwent, 1990) [Aneja et al., 1991]. Since both GRSM and SHEN are more than 1000m above the sea level, it is almost always above the planetary boundary layer [Poulida et al., 1991; Doddridge et al., 1992] except in the
late afternoon, when the boundary layer is well mixed with air masses from upper troposphere. Depletion mechanisms working at MACA may not effectively lower O$_3$ level at high elevation locations such as GRSM and SHEN, resulting in the lack of regular diurnal variation.

The diurnal profiles of NO$_y$ and NO at MACA consistently display maximum in the early morning between 0700-0900 EST, while SO$_2$ reach a maximum about two hours later than NO and NO$_y$. Trainer et al. (1993) suggested that regional transport of polluted air masses above the NBL is responsible for the morning peaks of NO$_y$ and NO. Kim et al. (1994) and Aneja et al. (1996) revealed the possibility of enhanced biogenic emissions of NO$_x$ from the soils during the morning as contributing to morning NO$_y$ and NO. Our observations of temporal difference between peaks of SO$_2$ and nitrogen oxides support the later mechanism. SO$_2$ is mainly a pollutant attributed to anthropogenic sources, while NO and NO$_y$ is from both natural and anthropogenic sources. The fact that nitrogen oxides peak two hours prior to maximum anthropogenic emission or transport (indicated by SO$_2$ peak) implies considerable contribution from emission sources other than regional transport and anthropogenic emissions at MACA. Similar to O$_3$, NO$_y$, NO and SO$_2$ show lack of significant and/or regular diurnal variation during all seasons at GRSM and the available seasons at SHEN. Again, influence of boundary layer dynamics and mixing are expected to account for the phenomena.

An alternative hypothesis [Fehsenfeld et al., 1983] for the lack of diurnal variation of O$_3$ is that there is no apparent diurnal trend for low levels of NO$_x$ (0.1-0.3 ppbv). Earlier measurements at remote mountain locations [e.g., Mt. Mitchell site by Aneja et al. (1996); Canadian Rockies site by Peake and Fong (1990)] reported evidences supporting
this explanation. Since ozone production in southeast US is limited by available nitrogen oxides during most photochemically active period, nitrogen oxides has been widely used as indicators to ozone sensitivity [Vogel et al., 1999; Milford et al., 1994; Sillman et al., 1990]. Table 3.1 summarized the seasonal average of O$_3$, SO$_2$, CO, NO, and NO$_y$ measured at GRSM, MACA, and SHEN. NO concentration at GRSM varies between 0.06 and 0.22 ppbv, and that at MACA site between 0.29 and 1.05 ppbv. The available measurement at SHEN suggests a NO level between the two. Direct measurements of NO$_2$ are not available due to lack of qualified data, but an estimate can be made for daytime conditions (with solar angle < 70°) by assuming photochemical steady state among reactions of NO$_2$, NO, O$_3$ and peroxyl radicals [Brunner et al., 1998; Jacob et al., 1995]. The calculated ratio of NO to NO$_x$ is in satisfactory agreement to direct field measurements [e.g., Aneja et al., 1996; Kim et al., 1994]. Significantly low NO$_x$ may severely constrain in-situ photochemical production of ozone at the remote mountain location, and, therefore, leads to the lack of diurnal variation. Milford et al. (1994) also proposed using NO$_y$ to evaluate ozone production sensitivity. A threshold value falling in the range of 10 to 25 ppbv is adopted as standard to define NO$_x$-limited or non-NO$_x$-limited condition for O$_3$ formation. Although the exact boarders of this threshold are under argument, it is well accepted that for air mass with NO$_y$ concentration far lower than 10 ppbv O$_3$ photochemistry can be largely limited by available nitrogen oxides. The measured NO$_y$ for all three sites (Table 3.1) are lower than 10 ppbv, indicating that O$_3$ formation may be controlled by nitrogen oxides for all sites. In a model study [Kang et al., 2003] for these locations, the average daytime VOC/NO$_x$ ratios for the base case are: 118/1 (GRSM), 18/1 (MACA), and 58/1 (SHEN). If the VOC/NO$_x$ ratio > 15/1 is
considered to be in the NO\textsubscript{x}-limited O\textsubscript{3} production regime [Dodge, 1977], then O\textsubscript{3} production at all three locations is in the NO\textsubscript{x}-limited regime, but the ratio at MACA is just beyond this threshold value on average.

### 3.5 Correlation of O\textsubscript{3} with NO\textsubscript{y}

Figure 3.5 summarized the monthly variation of O\textsubscript{3} production potential of NO\textsubscript{y} (OPPN) based on the simultaneous measurements of O\textsubscript{3} and NO\textsubscript{y} at the three sites. OPPN is defined as the ratio of ozone produced to NO\textsubscript{y} consumed (-d[O\textsubscript{3}]/d[NO\textsubscript{y}]) or correlation of O\textsubscript{3} with NO\textsubscript{y}. The correlations (i.e., positive OPPN values) are observed for each site between June to September, when local photochemical production of O\textsubscript{3} is most active. These correlations are expected since the NO\textsubscript{y} concentration in an air mass is at least a rough measure of the concentration of NO\textsubscript{x} (which catalyzes the photochemical process) that are emitted into the air mass [Trainer et al., 1993]. The correlations are further enhanced by the facts that biogenic VOCs emissions are active and solar radiation reaches its maximum during this period. For seasons other than summer and early fall, a smaller or even negative OPPN values are seen. This seasonal trend may be explained by decreases of temperature, water vapor, solar influx intensity, and biogenic NMHC emissions [Fahey et al., 1986]. Generally, higher OPPN values also come with higher R square (r\textsuperscript{2}) values, which is another measure of strength of the correlations.

Figure 3.5 also reflects the difference between locations. Data from MACA indicates shorter period (only four months of positive OPPN values) of apparent correlations and the OPPN value is generally smaller than those at other sites. At the GRSM and SHEN, there are six or seven months during which the correlations exist. The
difference is unlikely attributed to the variation of temperature, water vapor, or solar influx content in the air masses due to different longitude and latitude. Otherwise, GRSM and SHEN sites would show significant difference to each other. In contrast, these two sites present consistent trends for almost all months in which measurements conducted except in April. Instead, emissions of reactive VOCs and nitrogen oxides are expected as part of reason responsible for the difference. Kang et al. (2003) reported that VOCs at MACA site has an O$_3$ production efficiency of 3 to 6 times higher than those at GRSM and SHEN sites. This implies a stronger control of O$_3$ formation in Mammoth Cave national park by VOCs. There are also considerable higher emissions of fresh nitrogen oxides at MACA site (Table 3.1). As discussed earlier, the concentrations of fresh nitrogen oxides are generally 1.2-4.8 times higher than those presented at other sites. These factors may cause a smaller ratio of VOCs to NO$_x$ and thereby lead O$_3$ production at MACA into different regime than others. Furthermore, regional transport by boundary layer dynamics is expected to play role in the different behaviors of OPPN at different sites. Once again, GRSM and SHEN are high elevation sites that mostly lie above the nocturnal inversion. Species at MACA, in contrast, are subject to the influence of NBL. During nighttime, trace gases such as O$_3$ and nitric acid (HNO$_3$) are strongly depleted due to surface removal and suppressed vertical mixing. Simultaneously, concentrations of species with surface emission sources such as NO$_x$ can accumulate to high levels [Trainer et. al. 1993] and thereby change the ratio of O$_3$ to NO$_y$ (OPPN). In other words, photochemical aging of the air masses presented at these sites have sufficient influence on the correlations of O$_3$ with NO$_y$. This issue is to be further explored in next section.
3.6 Photochemical Age of Air Masses

Photochemical aging of air masses plays an important role in the in-situ \( O_3 \) production [Naja et al., 2002; Aneja et al., 1996; Trainer et al., 1993]. Figure 3.6 and 3.7 display the correlation between ozone and air mass age at GRSM and MACA, respectively. Data in August and September are chosen on the basis of seasonal OPPN variations (Figure 3.5), which reveal maximum values during these months. Five minutes measurement data are used in this analysis to reflect the short timescale of \( O_3 \) production from photochemistry. Different from previous studies [Hess et al., 1992; Trainer et al., 1993; Aneja et al., 1996], most of which used the ratio of \( NO_x \) (the oxidized products of \( NO_x \)) to \( NO_y \), the current study employs the ratio of oxidized products of NO (i.e., \( NO_y - NO \)) to total reactive nitrogen oxides (\( NO_y \)) as indicator to air mass age. This indicator is introduced here due to several privileges over that of \( NO_x \) to \( NO_y \). Firstly, NO is the dominant specie (approximately 90%) for \( NO_x \) emissions from both anthropogenic and biogenic sources [Warneck 2000]. All other species in \( NO_y \) can be attributed to the oxidized products of NO. \( NO_2 \) itself is the immediate and direct oxidized products of NO. Secondly, as the oxidized specie of NO, \( NO_2 \), as well as other more inertial \( NO_y \) species, have the potential to produce atomic oxygen that leads to ozone formation. Actually, photolysis of \( NO_2 \) has been widely thought as the predominant processes that produce ozone in the lower troposphere. As a result, some researchers [e.g., Nunnermacker et al., 2000] took the sum of ozone and \( NO_2 \) to evaluate ozone production efficiency (OPEx) in power plant plumes.

Figures 3.6 and 3.7 show that \( O_3 \) increases with the degree of photochemical conversation of NO to its oxidized products at both high and low elevation sites. \( O_3 \)
concentration is expected to be low in young air mass because tropospheric $O_3$ is mainly formed by the same photochemical processes that lead to the conversion of NO into reservoir species [NRC, 1992; Trainer et al., 1993; Aneja et al., 1996]. Increased ratio mirrors the more complete photochemical conversion of fresh air mass into more oxidized one (aging). Unlike results from previous study [Aneja et al., 1996; Trainer et al., 1993], linear regression fitting between $O_3$ and photochemical aging are found unsuitable to the whole regime for both GRSM and MACA. Similar nonlinear relationship trend between ozone and air mass age has been reported by other investigators. Olszyna et al. (1994) and Hess et al. (1992) reported that ozone increases with increasing photochemical age and then remains constant after the age over a specific point, e.g., 0.7 for $(NO_y-NO_x)/NO_y$. The current study (Figure 3.6 and 3.7) also presents a turnover point [Hess et al, 1992] that stands as the watershed for NO$_x$- and non-NO$_x$-limited ozone production condition. To determine the turnover point, all observed data are grouped into three sections, i.e., young (value of $(NO_y-NO)/NO < 0.88$), aged (that value $> 0.92$), and middle (those between the fresh and aged). For each individual site, the strength of correlations is higher for aged air masses than that for young air masses. Even though varying in slopes and intercepts, both sites share that the two regression lines intercept at a point near 0.9 for value of $(NO_y-NO)/NOy$. Data from GRSM display a weaker correlation (smaller R-square values) for all regimes than that from MACA site. Part of the reason is that the selected data set from GRSM consists mainly of September measurements, while that from MACA site of both September and August measurements. It has been reported that there exists a transition from NO$_x$-limited to VOCs-limited condition for $O_3$ production in September in eastern US [Jacob et al., 1995] and therefore
a weaker correlation is expected between $O_3$ and nitrogen oxides. Moreover, air mass at MACA is also subject to NBL ceiling and local emission sources that perturb the presence of $O_3$ and nitrogen oxides and lead to weakened correlation.

Unlike the results reported by Olszyna et al (1994), $O_3$ concentration does not remain constant after the turnover point at either GRSM or MACA in the current study. Even for air masses whose age are close to 1, $O_3$ concentrations are found varying in a wide range. It is not surprising since photochemical age is only a dimensionless measure which indicates the oxidizing status for unit air mass, while $O_3$ concentration results from the absolute amount of nitrogen oxides involved in the photochemical production and transport. The variation of $O_3$ concentration within aged regime reflected the variance of nitrogen oxides contained in the air masses. The dependence of $O_3$ production on the amount of nitrogen oxides is illustrated in Figure 3.8 and 3.9 for GRSM and MACA, respectively. Only measurements for those air masses whose age (value of $([NO_y]-[NO])/[NO]$)) is larger than 0.9 are selected and plotted in the figures. For MACA site, a further time limit (1000-1500 local time) is applied to filter the influence of NBL. Linear regression of ozone on $(NO_y - NO)$ yields $[O_3] = 4.69 \times ([NO_y] - [NO]) + 35$ ($R^2 = 0.40$) for GRSM and $[O_3] = 3.32 \times ([NO_y] - [NO]) + 43$ ($R^2 = 0.27$) for MACA, respectively. The ozone production efficiency of oxidized products of NO is higher at GRSM than that at MACA, which implies either surplus of nitrogen oxides or lack of sufficient VOCs presented at MACA site. This can be assured by the statistics tabulated in Table 3.1. Both fresh and total reactive nitrogen oxides at MACA are significantly higher than those at GRSM. The difference in the ratio of VOCs/NOx and the hydrocarbon composition of the air masses may also play a role in shaping the range of slope [Kang et al., 2001, 2003].
The intercepts in the above linear regression represent the background O$_3$ concentrations that are not directly influenced by anthropogenic emissions. This regional background ozone concentration are ~35 ppbv for GRSM, and ~43 ppbv for MACA. Although the estimated regional background at GRSM is lower than that at MACA site, the actually measured summertime O$_3$ concentration (~65 ppbv, Table 3.1) at GRSM site is considerably higher than that at MACA (~40 ppbv). Transport of O$_3$ at GRSM (a mountain top site) and, again, nighttime depletion of O$_3$ at MACA, is expected to account for the discrepancy. Modeling study shows that approximately 80% of ground-level O$_3$ presented at GRSM is transported to the site by horizontal advection, while only 20% of O$_3$ is from transport at MACA, with the rest from in-situ photochemical production [Tong et al., 2003]. Moreover, it is interesting to note that a regional background thereby determined (43 ppbv) is even higher than the seasonal average (40 ppbv) observed at MACA. This phenomenon is attributed to the nighttime depletion of ozone by the titration of freshly emitted nitrogen oxides and other species. The nighttime ozone is also taken into the seasonal average and therefore lowers the average value (Table 3.1). In another word, even though the daytime peak can be high enough to exceed the 1-hour O$_3$ NAAQS, but longer-time averaged O$_3$ may not violate the new 8-hour O$_3$ NAAQS due to the depletion mechanism. Therefore, rural nonattainment becomes more likely as the standard changes to a smaller concentration averaged over a longer time period. This issue, first raised by Chameides et al. in 1998, is to be discussed in the coming section.

3.7 Impact of the New O$_3$ NAAQS on Rural Nonattainment

It has been predicted that the newly proposed 8-hour-80-ppbv O$_3$ NAAQS standard will transform our perceptions of air pollution in the rural United States and the
policies used to manage this pollution [Chameides et al., 1998]. Earlier analysis of data from the Aerometric Information Retrieval System (AIRS) monitoring network showed that the newly proposed 8-hour-80-ppbv NAAQS would almost triple the number of nonattainment counties in the United States [EPA, 1996]. However, the AIRS monitoring sites are mostly urban and suburban, and thus O₃ pollution in rural areas has not been addressed by this analysis. Using data collected by the Southern Oxidants Study Spatial Ozone Network (SON) and EPA’s Clean Air Status and Trends Network (CASTNet), which are designed to characterize rural air quality, Chameides et al. (1998) reported that although only 6 of the 85 sites were in nonattainment under the 1-hour NAAQS, 41 would have been in nonattainment of the proposed 8-hour standard in 1995. While this conclusion comes out of only one-year data, more continuous measurements are needed to verify this trend. O₃ attainment of the three rural sites covered in this study is tabulated in Table 3.2 based on the three-year measurement campaign after 1995 as an attempt to testify the impact of new NAAQS on rural O₃ attainment in Southeast US.

Extrapolation of data from these sites from January 1996 through December 1998 shows that under the 1-hour NAAQS, both GRSM and SHEN site were at the edge of O₃ violation and MACA did not violate the 1-hour NAAQS for O₃. Under the new 8-hour NAAQS, however, all three national parks are in serious nonattainment of O₃ NAAQS, with a total of 62, 17, and 32 exceedances for GRSM, MACA, and SHEN sites for the three-year period. Increased number of exceedances under the new NAAQS not only categorizes these areas as nonattainment of O₃ pollution, but also presents a challenge to design working O₃ control strategy in these areas. It has been required by US EPA that each of the O₃ nonattainment areas needs to develop an implementation plan to mitigate
O3 pollution if NAAQS violation occurs during a 3-year period prior to the design of the plan (St. John et al., 2000). Under the 1-hour NAAQS, it was not urgent to design O3 mitigation strategy since the three national parks of concern are not or just begin to step into nonattainment. With the small violation number and the characteristics of violation episode (e.g., all occurring in August), it is expected to be easier to designate a working control strategy to meet the requirement of 1-hour NAAQS. The new 8-hour NAAQS violations, compared to that of 1-hour NAAQS, are scattered into different seasons, from April to October, during which the control strategies aimed at summertime O3 pollution may not be effective [Jacob et al., 1995]. A further challenge presented in Table 3.2 is that there are more 8-hour exceedances observed at the high-elevation GRSM and SHEN sites than at the low-elevation MACA site. While both GRSM and SHEN sites shows evidences of NOx-limited O3 production regime, they are removed from immediate sources of large NOx emission. Instead, modeling study shows most of O3 is transported to these sites by horizontal advection [Tong et al., 2003; Kang et al., 2003]. O3 levels there are probably affected by emissions from multiple urban areas as well as from local and remote rural sources [Chameides et al., 1998]. Therefore, rural nonattainment is calling control strategies to target region-scale emission sources that can exert influence on O3 levels of these areas, which is different from the current control strategies that have justifiably focused on emission controls within the nonattainment area.

3.8 Conclusions

The objective of this study is to characterize reactive nitrogen oxides and its relation to O3 production at rural Southeast United States in attempt to assess the impact
of new O₃ NAAQS on regional attainment. Our analysis shows that whereas O₃ at low-elevation rural site increases sharply to a short-lived afternoon maximum and drop to near zero at night as that in most urban or suburban areas, O₃ at high-elevation rural sites does not display a significant drop during nighttime. Absence of large diurnal variation of O₃ is general phenomena over eastern US [Jacob et al., 1995; Aneja et al., 1991; References therein]. As a result, longer-time averaged O₃ levels at high-elevation are much higher than those at nearby low-elevation site. We have shown that high-elevation site is more likely to violate the new O₃ NAAQS as the standard changes to a smaller concentration averaged over a longer time period.

We also introduced a new indicator, the (NOᵧ-NO)/NOᵧ ratio, to represent air mass age due to several privileges it bears. O₃ increases with the increase of photochemical age represented by higher (NOᵧ-NO)/NOᵧ ratio at both high and low elevation locations. Different from previous study, linear relationship between O₃ concentration and photochemical age is found unsuitable to the whole regime for both GRSM and MACA. The current study presents a turnover point (0.9 for value of (NOᵧ-NO)/NOᵧ) that separates the NOₓ- and non-NOₓ-limited ozone production regimes. The regional background O₃ concentrations that are not directly influenced by anthropogenic emissions are estimated to be ~35 ppbv at GRSM, and ~43 ppbv at MACA inferred from the linear regression of O₃ on (NOᵧ–NO).

Impact of the new 8-hour-80-ppbv NAAQS on rural nonattainment is addressed by extrapolation of data from these sites from January 1996 through December 1998. Our analysis shows that under the 1-hour NAAQS, both GRSM and SHEN site were at the edge of O₃ violation and MACA did not violate the 1-hour NAAQS for O₃. Under the
new 8-hour NAAQS, however, all three national parks are in serious nonattainment of O$_3$ NAAQS. Increased number of exceedances under the new NAAQS not only categorizes these areas as nonattainment of O$_3$ pollution, but also presents a challenge to design O$_3$ control strategies for these areas. The new 8-hour NAAQS violations, compared to that of 1-hour NAAQS, are scattered into different seasons, from April to October, during which the control strategies aimed at summertime O$_3$ pollution may not be effective [Jacob et al., 1995]. A further challenge is that there are more 8-hour exceedances observed at the high-elevation sites than at the low-elevation site. O$_3$ levels at high elevation site are probably subject to emissions from multiple urban areas as well as from local and remote rural sources [Chameides et al., 1998]. Therefore, this type of nonattainment is calling for control strategies to target region-scale emission sources that can exert influence on O$_3$ levels of these areas, rather than the current control strategies that have justifiably focused on emission controls within the nonattainment area. Further investigation is in need to screen the influencing areas and identify the seasonal characteristics of O$_3$ episodes to provide critical information of shaping a successful O$_3$ control strategies in the areas of concern.

**Acknowledgements.** This research was funded by the National Park Service, Air Resources Division cooperative agreement 4000-7-9003. Thank Scott Berenyi, Jim Renfro, and Ken Olszyna (TVA) for their efforts in collecting the data.
Reference:


Hollock, K.A., Trace gas observations over rural Virginia: photochemistry and transport.


Table 3.1 Seasonal average of ozone, SO$_2$, CO, NO, and NOy at Great Smoky Mountain (GRSM) site, Mammoth Cave (MACA) site, and Shenandoah (SHEN) site during 1996-1998.

<table>
<thead>
<tr>
<th>Season Location</th>
<th>Ozone</th>
<th>SO$_2$</th>
<th>CO</th>
<th>NO</th>
<th>NOy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GRSM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>53.3</td>
<td>2.4</td>
<td>194.7</td>
<td>0.20</td>
<td>5.0</td>
</tr>
<tr>
<td>Summer</td>
<td>64.7</td>
<td>2.1</td>
<td>187.8</td>
<td>0.06</td>
<td>3.2</td>
</tr>
<tr>
<td>Fall</td>
<td>50.5</td>
<td>2.0</td>
<td>166.1</td>
<td>0.18</td>
<td>3.8</td>
</tr>
<tr>
<td>Winter</td>
<td>32.1</td>
<td>2.5</td>
<td>164.2</td>
<td>0.22</td>
<td>3.9</td>
</tr>
<tr>
<td><strong>MACA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>39.0</td>
<td>2.7</td>
<td>210.5</td>
<td>0.49</td>
<td>6.2</td>
</tr>
<tr>
<td>Summer</td>
<td>39.7</td>
<td>1.7</td>
<td>193.8</td>
<td>0.29</td>
<td>5.0</td>
</tr>
<tr>
<td>Fall</td>
<td>31.7</td>
<td>2.9</td>
<td>191.7</td>
<td>0.75</td>
<td>7.0</td>
</tr>
<tr>
<td>Winter</td>
<td>24.0</td>
<td>5.3</td>
<td>225.4</td>
<td>1.05</td>
<td>9.2</td>
</tr>
<tr>
<td><strong>SHEN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>54.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.6</td>
</tr>
<tr>
<td>Summer</td>
<td>63.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.1</td>
</tr>
<tr>
<td>Fall</td>
<td>43.5</td>
<td>2.5</td>
<td>145.2</td>
<td>0.39</td>
<td>7.1</td>
</tr>
<tr>
<td>Winter</td>
<td>30.7</td>
<td>3.1</td>
<td>145.2</td>
<td>0.82</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Table 3.2 Number of violations of O3 standards at the Great Smoky Mountain (GRSM) site, Mammoth Cave (MACA) site, and Shenandoah (SHEN) site under the current NAAQS and the proposed 8-hour NAAQS for ozone (O3) from 1996 to 1998.

<table>
<thead>
<tr>
<th>Location</th>
<th>Period</th>
<th>1996</th>
<th>1997</th>
<th>1998</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-Hr</td>
<td>8-Hr</td>
<td>1-Hr</td>
<td>8-Hr</td>
<td>1-Hr</td>
</tr>
<tr>
<td>Great Smoky Mountain NP</td>
<td>0</td>
<td>8</td>
<td>1</td>
<td>19</td>
<td>3</td>
</tr>
<tr>
<td>Mammoth Cave NP</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Shenandoah NP</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>
Figure 3.1 Locations of the three monitoring sites in national parks are indicated with the red cycles.

- **Mammoth Cave (MACA) site**
  (37°13′04″N, 86°04′25″W, 230m ABS)

- **Shenandoah National Park (SHEN) site**
  (38°50′ N, 78°45′ W, 1100 m above sea level)

- **Great Smoky Mountains (GRSM) site**
  (35°41′48″N, 83°36′35″W, 1243 m above sea level)
Figure 3.2  Diurnal variations of O$_3$, NO$_y$, NO and SO$_2$ at the Great Smoky Mountain (GRSM) national park site for spring, summer, fall and winter in 1995 to 1998.
Figure 3.3  Diurnal variations of O$_3$, NO$_y$, NO and SO$_2$ at the Mammoth Cave (MACA) national park site for spring, summer, fall and winter in 1996 to 1998.
Figure 3.4  Diurnal variations of O$_3$, NO$_y$, NO and SO$_2$ at the Shenandoah (SHEN) National Park site for spring, summer, fall and winter in 1996 to 1998.
Figure 3.5 Monthly Variations of Ozone Production Potential of NOy in three Eastern US National Parks, 1995-1998

- Great Smoky Mountain National Park
- Mammoth Cave National Park
- Shenandoah National Park
Figure 3.6 Correlation between ozone and air mass age at GRSM site

$y = 10.627x + 26.518$

$R^2 = 0.0039$

$y = 228.79x - 170.46$

$R^2 = 0.2084$
Figure 3.7 Corelation between ozone and air mass age at MACA site

- \( y = 485.96x - 400.81 \) with \( R^2 = 0.4218 \)
- \( y = 61.649x - 16.032 \) with \( R^2 = 0.1883 \)
Figure 3.8 Correlation between ozone and (NOy-NO) for aged Air Masses at GRSM site

\[ y = 4.6946x + 35.117 \]

\[ R^2 = 0.3959 \]
Figure 3.9 Correlation of Ozone and (NOy-NO) at MACA for aged air Masses

\[ y = 3.3245x + 43.679 \]

\[ R^2 = 0.2695 \]
Chapter 4

Reactive Nitrogen Oxides in Southeast United States National Parks: Sources Identification, Origin, and Budget Analysis
4.1 Abstract

Understanding of nitrogen oxides is essential to design successful ozone control strategies for areas characterized with strong reactive biogenic VOCs emission. We present in this study both measurement-based analysis and modeling in elucidating source attribution, influence area, and process budget of reactive nitrogen oxides in rural southeast region. Trace gas species were measured continuously at both mountain-top and flatland sites including: ozone (O$_3$), reactive nitrogen oxides (NO, NO$_y$), carbon monoxide (CO), and sulfur dioxide (SO$_2$). Multiple linear regression analysis reveals that the ratios of [CO]/[NO$_y$] are 52.6 and 24.4 for the annual average at the Great Smoky Mountain (GRSM) site and at the Mammoth Cave (MACA) site, respectively, while the ratios of [NO$_y$]/[SO$_2$] are 2.09 and 1.56. Regression analysis suggests that point sources contribute a minimum of 23% and 27% of total NO$_y$ at GRSM and MACA, respectively, during the whole measurement period. Another technique, emission inventory analysis based on EPA Emission Inventory, provides a similar estimate that a minimum of 26% and 45% of total NO$_y$ can be attributed to point source emission at GRSM and MACA sites, respectively. The influence area, or origin of nitrogen oxides, is further investigated using trajectory-cluster analysis. The results show that air masses from western (20% out of all air masses) and southwest (17%) sweep most frequently GRSM site, while pollutants transported from eastern half (i.e., eastern, northeast, or southeast) have limited influence (< 10%) on air quality in the Great Smoky Mountain national park. Further examination of pollutants associated with these air masses reveals that the highest O$_3$ concentrations are associated with trajectories from the north and southwest direction, which can be tracked back to Ohio Valley region and coastal region along Gulf of
Mexico. The processes, as well as their magnitude, responsible for the formation and removal of reactive nitrogen oxides are investigated using a comprehensive 3-D air quality model (Multiscale Air Quality SImulation Platform (MAQSIP)). Chemistry contributions of 32% and 84% to NO\textsubscript{z} correspond to 26% and 80% to O\textsubscript{3} at GRSM and MACA, respectively. The similarity between NO\textsubscript{z} and O\textsubscript{3} process budgets serves as further evidences of close association between nitrogen oxides and effective O\textsubscript{3} production at these rural locations.
4.2 INTRODUCTION

Ambient ozone concentrations found in the lower troposphere continue to be a major air pollution problem in urban areas of the United States [National Research Council (NRC), 1991; Lippmann, 1992]. Despite the fact that significant controls on ozone precursors have been implemented, rural areas in the eastern and southern US have periodic high ozone episodes during the summertime [NRC, 1991; US Environmental Protection Agency (EPA), 1999]. Over 40% of the ozone non-attainment areas of the United States are in the southeast region. Several eastern national parks, where monitoring is conducted, have high ozone concentrations [Table A-20, EPA, 1998], among which, the Great Smoky Mountains National Park, TN has experienced most rapid increase in the frequency of exceedance days (which are days when any 8-hour period has an average ozone concentration exceeding 85 ppbv) during last decade. The increasing trend in the number of high ozone days is unexpected since the park is a predominantly rural area and a mandatory Class I area under the Clean Air Act Amendments of 1990. In 1997, the U.S. EPA has proposed a new National Ambient Air Quality Standard (NAAQS) for Ozone and other crucial pollutants. Previous analysis of measurements from the Aerometric Information Retrieval System (AIRS) monitoring network reported that the new NAAQS would almost triple the number of nonattainment counties in the United States [EPA, 1996].

Since ozone is produced in the lower troposphere photochemically from hydrocarbons in the presence of NO\(_x\) (NO\(_x\) = NO + NO\(_2\)), efforts at reducing ozone concentrations have generally emphasized control of the organic anthropogenic precursors. These strategies prove efficient for the abatement of ozone concentrations in
cities where anthropogenic emissions dominate the ambient mixing ratio (e.g., Los Angeles) [Fiore et al., 1998]. In the rural regions of the Southeast United States, however, considerable amounts of very reactive VOCs emitted from biogenic sources [e.g., isoprene from oak tree] can contribute substantially to ozone production (Trainer, et al., 1987; Chamiedes, et al., 1988; Kasibhatla et al., 1998; Roberts et al., 1998; Li et al., 1999). Controls on anthropogenic NOx in addition to anthropogenic VOCs are now thought necessary to reduce ozone in regions characterized by strong biogenic VOCs emissions such as in the southeast National Parks and their adjunct areas [NRC, 1991; Ryerson, et al., 2001].

Previous modeling study (Kang et al, 2003) indicates that there are differences in the ozone production potential and VOC reactivity between the three National Park Service (NPS) enhanced-monitoring sites at Shenandoah, Mammoth Cave, and Great Smoky Mountains. In prior articles (Kang et al., 2001; Kang et al., 2003) we reported VOC measurements that indicated that greater than 90% of the reactivity at Great Smoky Mountains National Park is from isoprene. Budget analysis from MAQSIP modeling has indicated that more than half the local ozone is transported from other areas; 26 to 43% of ozone is from local photochemical reactions. Yet, 67 to 95% of the VOC could be attributed to local emissions. Thus, understanding the contribution of nitrogen oxides to ozone formation during transport and for local photochemistry is key to predicting what effect planned reductions in NOx emissions from large point sources might have on observed ozone concentrations at the southeast National Parks.

In order to further explore the influence of emitted and transported pollutants on local air quality in rural areas, ambient data was acquired that includes intermittent
hydrocarbon samples and continuous measurements of O$_3$, NO$_y$, NO, SO$_2$, and CO. This study deals with data analysis and modeling on the measurements collected from 1995 to 1998. Most earlier studies of nitrogen oxides in eastern United States have been constrained to just a few months. The current study examines both the diurnal and seasonal variations NO$_y$ over several years in source contributions of NO$_y$, the probable source regions, and the transport budget terms.

4.3 Measurements and Methodology

4.3.1 Measurements

Ozone (O$_3$), total reactive oxides of nitrogen (NO$_y$), nitric oxide (NO), sulfur dioxide (SO$_2$), and carbon monoxide (CO), and other meteorological parameters were measured at three enhanced monitoring sites (Figure 1) in the Southeast United States. The Great Smoky Mountains (GRSM) site (35°41’48”N, 83°36’35”W), at an elevation of 1243 m above sea level, is located at the summit of Cove Mountain which is in Sevier County, Tennessee, on a ridge in the Great Smoky Mountains National Park. The Great Smoky Mountains National Park encompasses 2100 km$^2$ (800 square miles) of mountain ridges and deep-cleft valleys in the states of Tennessee and North Carolina. The Mammoth Cave (MACA) site (37°13’04”N, 86°04’25”W), at an elevation of 230 m above sea level, is located in Mammoth Cave National Park approximately 5 miles from Cave City, Kentucky, in a clearing about 30 m from the surrounding forest area. Both sites were operated by a partnership between the National Park Service (NPS) and Tennessee Valley Authority (TVA). Detailed information of the site description, instruments, experimental techniques, and data Quality Assurance and Quality Control
(QA/QC) procedures has been given by Olszyna et al. (1998). Briefly, ambient air samples for O₃, SO₂, and CO were collected through a Teflon tube equipped with 5 micron Teflon particulate filters. Samples of O₃, SO₂, and CO were analyzed using O₃ Model 49, SO₂ Model 43S, and CO Model 48S monitors from Thermo Environmental Instruments, Incorporated (TEII). Air samples for NO and NOₓ were each collected separately through ¼” inch OD Teflon sampling lines. The NO/NOₓ measurement system used a TEII Model 42S as a time-sharing analyzer to measure NO and NOₓ from the two independent sampling lines. The calibration gases, as well as the gases used for daily Quality Assurance/Quality Control Procedure (QA/QC) activities, were EPA Protocol SO₂, CO, NO, and NO₂ gas cylinders provided by Scott Specialty Gases. For the routine QA/QC activities, a Campbell CR10 data logger was configured to automatically control the gas influx, the sampling switches, and the execution of the gas addition or gas substitution. The sites are equipped with a TEII 111 Zero Air generating system and a TEII 146 Dynamic Gas Calibrator. The CO catalytic reactor from the TEII Model 111 provided CO-free ambient air for the CO monitor.

The measurement operations followed the Quality Assurance/Quality Control (QA/QC) established for the ground-based air monitoring stations that participated in the SOS/Nashville 1995 Intensive [TVA, 1995]. The QA/QC procedure consisted of zero, span, and precision checks using gas substitution / addition techniques which determined matrix effects in the sampling system. Gas additions of NO at the midday median NOₓ concentration level were conducted to both the NOₓ and NO sampling lines three times a day. The NO addition to the NO sampling line was a system check for losses due to chemical reactions of NO with O₃ and other oxidants in the NO sampling line.
Measurements for O$_3$ were conducted according to SLAMS protocol, modified to operate the O$_3$ instrument on the scale range between 0 and 200 ppbv. The O$_3$ concentrations for the daily span and precision checks for the sites are 160 ppbv and 40 ppbv which are 80% and 20% of the full instrument range. The internal ozonator in the TEII 146 was used to provide standard concentrations for the ozone precision and span checks.

4.3.2 Emission Source Identifications: Point vs. Mobile Sources

According to the EPA, more than 90% of the anthropogenic NO$_x$ emissions in the United States are by either mobile sources or point sources [EPA, 1997; Stehr et al. 2000]. Mobile sources emit high levels of CO, but relatively low levels of SO$_2$, while the reverse is true for point sources [EPA, 1999]. Therefore, NO$_x$ emissions may be well correlated with either SO$_2$ or CO, leaving relatively little NO$_x$ uncounted for [Stehr et al. 2000]. In actual calculations, NO$_x$ is replaced by NO$_y$, since some fraction of the pollutants is oxidized before arriving at the receptor site.

Relative emission source strength can be evaluated at a surface receptor site using observed pollutant data and the techniques of regression analysis and of emission inventory analysis ratioed to actual concentrations. Emission inventory analysis uses the molar ratios of NO$_x$ to CO and NO$_x$ to SO$_2$ reported by EPA emission inventories (1997) while regression analysis obtains these ratios by fitting a multivariate regression model to measured data. Both techniques use measured CO and SO$_2$ concentrations as input to estimate the relative contributions from point and mobile sources.
Regression analysis

$\text{NO}_y$ is taken as the response variable in a multiple linear regression analysis of the combination of CO and SO$_2$ as factors. The mathematical expression of the fitted model is:

$$[\text{NO}_y] = \alpha[\text{SO}_2] + \beta[\text{CO}] + \delta$$

where $\alpha$ and $\beta$ represent the linear coefficients between $[\text{NO}_y]$ and $[\text{SO}_2]$ and $[\text{CO}]$; $\delta$ represents the intercept. With the $\alpha$ and $\beta$ coefficients, the parameterized model can be used to evaluate the contributions of emission sources (mobile and point) using the measured CO and SO$_2$ concentrations.

Since the pollutant emissions and the atmospheric reactions have some seasonal component, the analysis was repeated by season. The entire data set is divided into four seasons, i.e., spring, summer, fall, and winter to explore the seasonal variations. Each group is further classified into two sub-sets (mid-day (1000 - 1500 EST, corresponding to the period of maximum photochemical activity) and night-time (2300 - 0500 EST) to examine the day/night differences. After initially fitting the parameterized models to each time period group, studentized residuals were used to remove outliers from each data set. Observations with an absolute studentized residual >2 were removed. In order to validate the assumptions of the linear regression model in each time period, the Durbin-Watson test was used to test the first order autocorrelation. A Q-Q plot was employed to test the normality of the predicted residuals which suggest a normal distribution of residuals.

SAS statistical analysis software was used to estimate the $\alpha$, $\beta$, and $\delta$ terms of the regression equation (1) using the validated measurement data from MACA (Mammoth Cave National Park) and GRSM sites. Table 4.1 and 4.2 present the results of multiple
linear regression analysis at each season at GRSM and MACA sites, respectively. The coefficients of $[SO_2]$ (i.e., $\alpha$) for all dataset are 0.49 for daytime, 0.50 for nighttime, and 0.49 for overall at GRSM site, and 0.74 for daytime, 0.54 for nighttime, and 0.64 for overall at MACA site. These values are in good agreement with the nationwide average emission inventory ratio of $[NO_x]/[SO_2]$ (0.64, EPA, 1997). The deviation from national average value can be explained by the influence of local point sources and the removal of nitrogen oxides during the transformation process from NO$_x$ to more oxidized species. Seasonal analysis shows the ratios are 0.51, 0.30, 0.41, and 0.68 for spring, summer, fall, and winter, respectively at GRSM site, and 0.56, 0.61, 0.71, and 0.57 at MACA site. Stehr et al. (2000) also reported similar values (0.75 ~ 0.88, September-December) at the high elevation Shenandoah site, VA (1100m above sea level). However, two other low elevation sites examined by Stehr et al. (2000) gave lower ratios 0.36~0.41 at Arendtsville, PA for June-September, and 0.18~0.48 at Wye site on the eastern shore of the Chesapeake Bay, MD for September-December. Higher oxidizing potential of the atmosphere is thought to account for the lower values in summer and fall, especially when the higher levels of hydroxyl radical and ozone may be present. This trend can be identified from the remote GRSM site, which is located at high elevation without immediate local emission sources. However, this may not be the case for low elevation sites. Air masses approaching these sites are generally more subject to the polluted air in which characteristics of emission sources may have significant influence. For example, the lower values at Wye and Arendtsville sites reflected the fact that the emissions are characterized by a high sulfur content [Stehr et al, 2000]. The higher values in summer and fall at MACA site can be attributed to characteristics of local emissions that
determined the content of air masses reaching the site. Day/night differences are negligible in fall and summer, but are significant in winter and spring for both low and high elevations. Larger diurnal differences in winter and spring are attributed to the combined influence of activities of the planetary boundary layer [Doddridge et al., 1992] and seasonal variations of dominating emission characteristics.

The coefficients of $[CO]$ (i.e., $\beta$) for all data are 0.037 for midday, 0.041 for midnight, and 0.041 for all periods at MACA site, compared to 0.021 for midday, 0.015 for midnight, and 0.019 for all period at GRSM site [Tong et al., 2003]. Seasonally, the values are around 0.034, 0.025, 0.049, and 0.061 for spring, summer, fall, and winter, respectively at MACA site, and 0.018, 0.015, 0.027, and 0.013 at GRSM site. Again, day/night differences of values are significant in winter for both low and high elevations. The values are much lower than the EPA emission ratio of $[NO_x]/[CO] = 0.084$ [EPA, 1997]. These ratios are also considerably lower than the values reported by earlier works (0.041~0.091, Stehr., et al., 2000; 0.069, Goldan et al., 1995; 0.075±0.027, Buhr et al., 1992; 0.12, National Acid Precipitation Assessment Program (NAPAP), Saeger et al., 1989). Since the ratio of $[NO_y]$ to $[CO]$ is controlled by background NO$_y$ concentration and CO concentration, the low value of $\beta$ can be caused by either lower background NO$_y$ concentration, or higher CO background concentration, or combination of both. Previous analysis [Tong et al., 2003] reveals that the CO background level is found to be not significantly higher than the averaged value in clean air region of the northern hemisphere. Thereby, the low value of $\beta$ implies the lower background nitrogen oxides level, which, as a result, may lay a limitation on the in-situ ozone production at the site [Tong et al., 2003].
Once parameterized, the simulation model can be used to evaluate the relative importance of mobile and point sources by incorporating the measured concentrations of CO and SO\(_2\) into Eq. (1), with corresponding parameters provided in tables 4.1 and 4.2. Contribution from point sources is evaluated by setting CO term and \(\delta\) to zero since the intercept is only attributed to natural CO background [Tong et al., 2003; Stehr, et al., 2000]. Contribution from mobile sources is determined by taking off SO\(_2\) term, i.e., by CO term plus intercept.

**Emission inventory analysis**

Emission inventory analysis has been used in earlier work [e.g., Parrish et al., 1991; Goldan et al., 1995; Stehr et al. 2000] to examine the relationships between NO\(_y\), CO, and SO\(_2\). Briefly, the ratio (indicated by x) of NO\(_y\) from point sources (NO\(_y\)\(_p\)) to mobile sources (NO\(_y\)\(_m\)) can be obtained from the division of two factors:

\[
\frac{\text{NO}_y}{\text{NO}_y} = \left(\frac{\text{NSR}_p}{\text{NCR}_m}\right) \left(\frac{\mu\text{[SO}_2\text{]}}{[\text{CO}][\text{CO}]_{bg}}\right)
\]

Where NSR\(_p\) and NCR\(_m\) represent the molar ratios of NO\(_y\) to SO\(_2\) from point sources and NO\(_y\) to CO from mobile sources, respectively. [SO\(_2\)] and [CO] are the concentration of SO\(_2\) and CO measured at the site; [CO]\(_{bg}\) is the background CO concentration that is independent of local photochemical processes. An adjusting parameter, \(\mu\), is introduced to account for the fraction of SO\(_2\) that has been oxidized into sulfate before arriving at the receptor site. Therefore,

\[
\begin{align*}
\text{Fraction of NO}_y \text{ attributed to mobile sources} & \quad \frac{1}{1+x} \\
\text{Fraction of NO}_y \text{ attributed to point sources} & \quad \frac{x}{1+x}
\end{align*}
\]
The molar ratios for emission analysis are calculated on the basis of EPA emissions inventories [EPA, 1999]. The ratio of NO\textsubscript{y} to SO\textsubscript{2} (i.e., NSR\textsubscript{p} in Eq. (2)) for point sources and the ratio of NO\textsubscript{y} to CO (i.e., NCR\textsubscript{m} in Eq. (2)) for mobile sources are derived from anthropogenic state-level emission data. Emission data of 18 states (Alabama, Arkansas, Georgia, Illinois, Indiana, Kentucky, Louisiana, Maryland, Michigan, Mississippi, North Carolina, South Carolina, Tennessee, Virginia, Washington, D.C., West Virginia, and Wisconsin) are used to calculate the ratios for GRSM site, and another 29 states for MACA sites. The extent of these sets of states was determined by back trajectory analysis, which will be described in details in the following section. Values of NSR\textsubscript{p} and NCR\textsubscript{m} are found as 1.70 and 0.19 for GRSM site, and 2.09 and 0.20 for MACA site, respectively. These ratios are approximately twice higher than those obtained by Stehr et al. (2000), which are mostly for northeast United States.

Theoretically, the CO background concentration, [CO]\textsubscript{bg}, can be obtained by dividing the interception with negative CO coefficient (-\(\beta\) as above) in Eq. (1) from regression analysis, since the zero-[NOy] is believed mostly governed by CO background concentration [Stehr et al., 2000]. The results of CO background concentration calculated by this means were found heavily deviated from the expected range [Warneck, 2000; Parrish et al., 1991; Doddridge et al., 1992]. This reflects both statistical uncertainties in regression analysis and the combined influences of SO\textsubscript{2} and NO\textsubscript{y} emissions. Instead, Parrish et al. [1991] and Doddridge et al. [1992] express the ratio of CO to NO\textsubscript{y} as

\[
[\text{CO}] = \rho [\text{NO}_y] + [\text{CO}]_{\text{bg}}
\]

where \(\rho\) is the molar emission ratio of CO to NO\textsubscript{y}. The application of such a simplified scatter plot may alleviate the influence of SO\textsubscript{2} and give better CO background. The value
of the coefficient (i.e., \( \rho \)) may be different from the coefficient of \([\text{CO}]/[\text{NO}_y]\) (i.e., \(1/\beta\) in Eq. (1)) in the multiple regression analysis since the other factor, \([\text{SO}_2]\), is excluded in this fitting model. The results of the CO background concentration calculation were consistent with the expected range (122 ppb, Warneck, 2000; 84-127 ppb, Parrish et al., 1991; 110 ppb, Goldan et al., 1995; 120 ppb, Buhr et al., 1995; Doddridge et al., 1992).

Several factors including season, elevation, latitude, and distance from sources over the continental areas appear to influence the calculated CO from observational data. Much lower background values have been reported for Pacific (70-80 ppb, Seiler et al, 1976) and Atlantic (90±12 ppb, Doddridge et al, 1992) ocean air masses. Surface background CO concentrations are most likely composed of a base oceanic air, production of CO not associated with NOy emission, and CO transport far enough from the emitting combustion process that the NOy has been removed.

An adjusting parameter is applied to \(\text{NSR}|_p\) responding to the oxidized fraction of \(\text{SO}_2\) before arriving at the receptor site. The adjusting parameter is obtained by examining the sulfate and sulfur dioxide data from the nearby Look Rock site (GRS420) of the Clean Air Status and Trends Network (CASTNET) jointly operated by the US EPA and NPS (http://www.epa.gov/castnet/data.html). The adjusting parameter for sulfur dioxide is found to be 1.07, 1.14, 1.05, 1.03, and 1.07 for spring, summer, fall, winter, and overall data, respectively, at GRSM site. It should be pointed out that the value might be underestimated since a certain portion of sulfate has been removed by dry and/or wet deposition processes before arriving at the site. Similar adjusting parameter is not available for MACA site due to the lack of sulfur measurements at or close to the
monitoring site. The parameter is set to a default value (1.0) assuming that the oxidization process does not induce significant difference to final results.

4.3.3 Influence Areas Based on Trajectory-Clustering Correlation

Origin of air masses approaching the measurement site was investigated by the combination of cluster analysis [Dorling, et al., 1992] of hybrid single-particle Lagrangian integrated trajectories (HY-SPLIT) model results [Draxler, 1997] and emission sources categorization based on EPA emission inventory [Saxana et al., 1997; EPA, 2000]. Cluster analysis is frequently employed in air pollution study to address pollutant source origin, e.g., Slanina et al. (1983) and Pio et al. (1991) have succeeded in identifying continental, maritime, and anthropogenic sources regimes of pollutants. This method aims to maximize inter-group variance and to minimize within-group variance. Numerous algorithms have been developed for cluster analysis [Anderberg, 1973]. This approach chosen in this study is the one proposed by Dorling (1992a, b). Briefly, end points of each trajectory are taken as input to clustering algorithm. The first step chooses a large number of seed trajectories and all other trajectories are assigned to the seeds that can achieve minimum Root Mean Square Deviation (RMSD). The seed or average trajectory of each cluster is then recalculated from its members continuously until all trajectories are correctly assigned. After that, the number of clusters is decreased by merging two closest clusters. Sudden drop in the total RMSD as the number of clusters is reduced are interpreted as the merging of clusters of trajectories that are significantly different in terms of the wind directions and speeds associated with them.
HYSPLIT-4 [Draxler, 1997] model was chosen to calculate air mass trajectories for cluster analysis. The actual operation routines are explained by Draxler (1992, 1997) and will not be discussed here. Back trajectories were initialized at 1:00pm of local time and elevations of 500m above the ground level of the measurements site. Decision of initial elevation in the back trajectory analysis has been associated with considerable debates, which are particularly the case for mountain top site such as GRSM site. However, the uncertainty tends to be small when a large number of trajectories are taken into average [Brankov, et al., 1998]. The three-dimensional motion is obtained using the 180-km grid size, 2-hourly output from the output wind fields of the National Meteorology Center’s Nested Grid Model (NGM) (http://www.arl.noaa.gov/ready-bin/ngm.pl) for both horizontal and vertical air mass streams before April 1997. Results of data sets after April 1997 were obtained using 3-hourly output from the Eta Data Assimilation System (EDAS) (http://www.arl.noaa.gov/ready-bin/edas.pl). Both data sets were archived and processed by NOAA/ARL covering the United States continent and its immediate coastal waters. End points of the trajectories were subsequently used as input to cluster analysis according to the algorithm described in the preceding paragraph.

An optimum cluster number can be obtained by plotting the percentage change in the total TRMSD with respect to decreasing cluster numbers. As in any other clustering methodology, some decisions have to be made by the user [Romesburg, 1984]. The user can define a percentage change in RMSD which, when exceeded at some stage in the reduction of the number of clusters, signifies an optimum number of clusters to be retained in the analysis. For all trajectories covered in this study, it turns out that a “break” or significant percentage change in reducing the distinct number of clusters from
8 to 7 (the figure is not shown here for the sake of brevity). Seven clusters were therefore retained as best describing significantly different forms of air flow to GRSM site in the period. Once these distinct (optimum number of) clusters of trajectories have been identified, the average back-trajectories for the 7 clusters at GRSM site will be plotted. For further reference, clusters are named according to their general direction: N, NE, S, etc. The cluster that stays relatively closer to the reception site is named C (close) because speed of air parcel has influence on the level of pollutants.

4.4 Process Budget Analysis using MAQSIP Model

A nonhydrostatic version of Multiscale Air Quality SImulation Platform (MAQSIP) model was used to perform budget analysis of nitrogen oxides above the sites. MAQSIP is a comprehensive 3-Dimentional Eulerian grid model [Mathur et al., 2001]. One of MAQSIP’s major attributes is a truly modular platform where physical/chemical processes are cast into modules following the time-splitting approach. Each process module operates on a common concentration field. This feature makes it possible to analyze budgets of modeled species by examining contribution from each modeled process [Kang et. al., 2002]. In this study, model budgets are analyzed in terms of the various physical/ processes such as chemical reactions or chemistry, horizontal advection, vertical advection, horizontal diffusion, vertical diffusion, dry deposition, and emissions [Odman et al., 1996]. Not all the processes could be of equal importanance in the budgets of nitrogen oxides. The vertical budget of each process (Bi) is the weighted contribution from each layer and calculated as follows:
\[
Bi = \frac{\sum_{j=1}^{N} (\sigma_{j-1} - \sigma_j) C_j}{\sum_{j=1}^{N} (\sigma_{j-1} - \sigma_j)}
\]  

(4-5)

where \( \sigma \) represents the vertical co-ordinate system, \( \sigma_j \) is the boundary \( \sigma \) value of the \( j^{th} \) layer, \( C_j \) is the contribution of the process (ppbv/hr) at \( j^{th} \) layer, and \( N \) is the number of vertical layers.

Emissions of CO, VOCs, and NOx are specified temporally and spatially in MAQSIP. The anthropogenic emissions inventory used is the Ozone Transport Assessment (OTAG) inventory for 1995. Biogenic emissions are calculated using the US EPA Biogenic Emission Inventory System 2 (BEIS2) [Geron et al., 1994]. The modeling domain was chosen so as to adequately represent conditions at the sampling site based on the results of back trajectory analysis. Modeling domain (Figure 4.1) was chosen based on the results of back trajectory analysis. The domain reflected a balance of sufficient representation to emission sources and precise description of the local processes. As Figure 4.1 shows, the subdomain of this modeling system consists of 34×42 cells using 36-km horizontal resolution. The vertical domain varying from the surface to 100 mb is discretized using 22 layers of variable resolutions. Our period of MAQSIP model study is extended from July 14 to July 29, 1995. The year of 1995 is selected because of the availability of VOCs measurements during the summer time of 1995. Only daytime data (10:00am to 5:00pm) is taken into considerations due to the characteristics of photochemical process. Temporally varying lateral boundary conditions for various model species were derived from previous model simulations conducted over the southeastern U.S. for the study period. Application of MAQSIP to the data analysis for
the southeastern national parks has been evaluated and validated in earlier work [Mathur, et al., 2001; Kang, et al., 2003].

4.5 RESULTS & DISCUSSION

4.5.1 Source Attribution Comparisons

Both methods discussed in preceding section can be employed to quantify the relative contribution of point sources emission to total nitrogen oxides budget. Figure 4.2 presents the diurnal variations of point source emission contributions to NO\(_y\) at Great Smoky Mountain for each season of 1995-1998. Both analyses reveal regular diurnal trends at GRSM, which display consistent maxima in the early morning between 0500-0800 EST and minima in the late afternoon between 1600-1800 EST. However, irregular or no diurnal trends are observed in winter by either regression analysis or emission inventory analysis. Examining the measurement data indicates that CO and SO\(_2\) do not display significant diurnal variation in winter as in other seasons. For both CO and SO\(_2\), wintertime also shows consistent midday higher and midnight lower concentrations. This can further remove diurnal trend of their relative contributions to total NOy presented at GRSM site. Figure 4.3 illustrates the diurnal variations of point source emission contributions to NO\(_y\) at Mammoth Cave National Park for each season of 1996-1998. Similar to that at GRSM, both techniques reveal consistent maximum and minimum contributions of point sources to total NOy in all seasons except winter, in which there is no strong diurnal trend, and predicted fractions from emission inventory analysis are higher than those from regression analysis. The time when the maxima and minima appear, however, is different from that at GRSM. Maximum fraction from point sources
is found shortly after sunrise (for regression analysis) or during midday (10-15 EST), and minimum before sunrise. Daytime fraction is generally higher than that during nighttime. Such diurnal trends can be largely explained by the activity of planet boundary layer (PBL), in addition to the reasons presented above for GRSM site. Stable nighttime boundary layer (NBL) formed over MACA prevents air mass with higher level of SO$_2$ from reaching the surface site while lower PBL height and higher relative humidity quicken SO$_2$ removal to its minimum level by dry deposition [Finkelstein et al., 2000] and heterogonous chemistry [Jacob et al., 2000]. Breakup of the nocturnal boundary layer above MACA site triggered by sunrise will allow air masses with transported SO$_2$ to mix down to the surface and change the ratio of CO to SO$_2$, consequently, the fraction, over MACA site.

Figures 4.4 and 4.5 present the trends of the fraction of NO$_y$ from point sources with respect to diurnal and seasonal cycles at GRSM and MACA sites, respectively. Contribution of point sources is calculated using the parameters presented in Tables 4.1 and 4.2 for GRSM and MACA, separately. A seasonal difference is observed for both low and high elevation sites, which display a higher portion from point sources during winter and spring season, and lower in summer and fall. Variation of the fraction depends on both mobile and point source emissions and deposition processes. Point sources are predominant in wintertime, and, moreover, SO$_2$ has shorter lifetime in summertime, both of which contributes to lower fraction value from point sources during summer. No strong diurnal variation can be identified for GRSM site (Figure 4.4), while the diurnal trend is significantly stronger at MACA (Figure 4.5). Again, such a difference can be
attributed to the influence of nighttime boundary layer (NBL), which is more frequent and stronger at MACA.

Figures 4.4 and 4.5 also show that the relative contribution from point sources to NO$_y$ at MACA is higher than that at GRSM. Linking it to the higher level of total NO$_y$ presented at MACA [Tong et al., 2003], point sources around the Mammoth Cave National Park may play more important role in the evolution of nitrogen oxides there. Moreover, the diurnal trend at MACA is more regular during photochemically active period, with maximum fraction from point sources at the same time when ozone heads for its peak. Occasionally in the middle of summer, point sources provide up to seventy percent of NO$_y$, which is widely believed to be the limiting factor of photochemical production of ozone in the ambient air.

Summaries of point source contributions to NOy are given in table 4.3 for each season at GRSM and MACA sites as well as results from previous studies [Stehr et al., 2000]. Both analyses show lower fractions of NO$_y$ from point sources in summer and fall, while higher fractions in winter and spring. Point sources contribute 16-22% and 30-38% to total reactive nitrogen oxides in summer and winter, respectively, at GRSM, and 21-40% and 33-47% at MACA. In general, regression analysis provides lower fraction values than the emission inventory analysis. Similar values were reported in other case studies for three other northeast US sites [Stehr et al., 2000]. Both techniques are based on measured SO$_2$ and CO concentrations presented at the site to evaluate point source contribution. However, the calculation of the emission inventory analysis is also dependent on estimated background CO and adjusting parameter for SO$_2$. An overestimate of background CO concentration and/or underestimate of SO$_2$ parameter
may result in a low mobile source emission contribution and, therefore, overestimate of the point source emission contribution to total NO\textsubscript{y}. The ratios adopted in emission inventory analysis represent those from freshly emitted air masses and may not reflect the influence of oxidization, deposition and other removing processes, especially for a site far from emission sources, unless accurate adjusting parameter is available.

### 4.5.2 Influence Areas Based on Trajectory-Clustering Correlation

All the individual trajectories in 1996 are calculated for those days when simultaneous measurements of O\textsubscript{3} and NO\textsubscript{y} are available at GRSM site. The whole trajectory set is then clustered into seven groups using the algorithm stated earlier. One trajectory is selected out of each cluster, which can minimize the average RMSD for all other trajectories within this cluster. Figure 4.6 illustrates the thereby gained seed trajectories from each cluster. Each seed trajectory is labeled with direction best describing the relative position of its origin to the receptor site. The number in the parenthesis shows the percent of the trajectories assigned to a particular cluster. Emission density of NO\textsubscript{y}, taken from EPA county-based emission inventory [EPA, 1998], is also displayed as background in Figure 4.6 to provide regional emission level that might be loaded into those air parcels when traveling through. Figure 4.6 shows that air masses from western (W, 20%) and southwest (SW, 17%) sweep most frequently GRSM site, while pollutants transported from eastern half (i.e., Eastern, Northeast, or Southeast) has limited influence (< 10%) on air quality in the Great Smoky Mountain national park. Air masses originated from or traveling through (i.e., Far North (FN) or Close North (CN)) Ohio valley, which region marked as high level of NO\textsubscript{y} emissions, account for more than
one quart of total trajectory number. Examination of pollutants associated with these individual clusters can provide further information on the magnitude of influence from corresponding source area.

The average O₃ and NOₓ concentrations associated with each cluster are presented in Figure 4.7. The highest O₃ concentrations, as expected, were associated with trajectories from the Close North (CN) (55.4 ppbv) and Far North (FN) (52.6 ppbv) since both CN and FN trajectories originated from Ohio Valley region. Air masses in another cluster, SW, also carry high level of ozone (54.5 ppbv) to GRSM. Trajectories in southwest cluster are generally tracked back to coastal region of Mexico Gulf, where high level of nitrogen oxides emissions are observed. There are two possible mechanisms responsible for high ozone concentration in SW cluster. One is that clean marine air masses load high ozone content when travel through certain region, in which case either C (Close) or W (Western) shall contain higher level of ozone than SW. However, Figure 4.7 reveals no evidence to support this hypothesis. The other one, which is more feasible to the authors, would be that air masses load high ozone content from polluted coastal region, and conserve its ozone level till reaching GRSM site. Of course, other arguments may arise since ozone presence is a mixture of remote transport and local production, as well as removing processes. A comprehensive investigation by means of three-dimensional chemistry and transport model will be discussed in next section to entail such a process budget analysis. At this point, the information delivered here is that (1) polluted coastal region along Mexico Gulf may be linked to air quality at GRSM hundreds of miles away; (2) 48-hour running period can well address emission origin, in another word, air masses of concern shall have a photochemical age in the magnitude of
2-3 days. Further longer back trajectory will extend the original area into marine environment, and will significantly weaken the power of this technique in term of identifying influence area.

Figure 4.7 also displays inconsistence between concentrations of NO\textsubscript{y} and O\textsubscript{3} associated with individual clusters. While ozone in NW, W, and C clusters is low, NO\textsubscript{y} in those clusters is high. This discrepancy can be attributed to either VOCs-limited ozone production or that nitrogen oxides have not fulfilled its potential to produce more ozone [Ryerson et al., 2001; Jacob et al., 1995; Kim et al., 1994]. An alternative to these explanations, proposed by Kang et al. (2003), argued that ozone concentration could be lowered if VOCs concentration exceeds a particular turnover point by converting reactive nitrogen oxides into inertial organic nitrogen. This situation may also be applicable to these clusters, especially for C cluster that travels in area rich in VOCs emissions from both anthropogenic and biogenic sources. Otherwise, stagnant meteorology, high NO\textsubscript{y} and VOCs (Kang et al., 2001) will favor ozone production and thereby present a higher ozone concentration.

4.5.3 Nitrogen Oxides Budget Analysis By MAQSIP

Six processes – chemistry (CHEM), horizontal advection (HADV), vertical advection (VADV), Vertical mixing (VDIF), emissions (EMIS), and dry deposition (DDEP) – have significant effect on budgets of nitrogen compounds. Figure 4.8 and Figure 4.9 represent the mean contribution rates over the entire modeling period (10:00 am to 5:00 pm) of each process for NO\textsubscript{x} and NO\textsubscript{Z} (NO\textsubscript{y} – NO\textsubscript{x}), respectively. The reason that NO\textsubscript{z} instead of NO\textsubscript{y} is analyzed is that NO\textsubscript{z} is primarily the end products of NO\textsubscript{x} and
is considered as a good indicator of O$_3$ production (Li et al., 1997; Aneja et al., 1996), and therefore, NO$_z$ may offer more information about the contribution of nitrogen oxides to O$_3$ production. As Figure 4.8 shows, even though the major contributions to NO$_x$ at the two locations come from horizontal advection (58 – 62%) and local emissions (38 – 42%), and the primary removal process for NO$_x$ is local chemistry (92 – 95%), the magnitude of each process at MACA is more than 3 times larger than that at GRSM, which matches the observational results (1.2-4.8 times, Tong et al., 2003a). In the NO$_z$ side, however, 84% of NO$_z$ is the result of local chemistry at MACA, which only accounts for 32% at GRSM; the rest comes from transport. About half of NO$_z$ is removed by dry deposition at GRSM, while the rate at MACA is 87%; the rest is removed through transport. Also noted that unlike NO$_x$, the combined magnitude of process contributions to NO$_z$ is similar across the two locations, and this suggests that more profound transport and thus more aged air mass at GRSM than at MACA.

If we compare the process budgets of NO$_z$ with that of O$_3$ (Figure 4.10, recreated from Kang et al., 2003), the similarity among the locations as well as the contributions of each individual process at each location is apparent, especially at the positive side, i.e. the production or accumulation side. For instance, chemistry contributions of 32% and 84% to NO$_z$ correspond to 26% and 80% to O$_3$ at GRSM and MACA, respectively. The other primary contributions to the accumulation of NO$_z$ and O$_3$ are from horizontal advection at GRSM and vertical advection at MACA. The difference for the transport contributions to NO$_z$ and O$_3$ at MACA is that both horizontal and vertical advection processes contribute to NO$_z$, but only vertical advection process to O$_3$. On the removal side, dry deposition is the primary process to remove NO$_z$ at all three locations, but it is only responsible for 20
to 43% of O\textsubscript{3} removal. Transport processes (either horizontal or vertical) are responsible for the removal of the rest NO\textsubscript{2} and O\textsubscript{3} with only more important role in removing O\textsubscript{3} than removing NO\textsubscript{2}. Nevertheless, the similarity between NO\textsubscript{2} and O\textsubscript{3} process budgets further evidences that NO\textsubscript{2} can be used as evidence of close association between nitrogen oxides and effective O\textsubscript{3} production at these rural locations.

4.6 CONCLUSIONS AND IMPLICATIONS

These preliminary results have focused on both observational based analysis and modeling in elucidating source attribution, influence area, and process budget of reactive nitrogen oxides at two rural southeast national parks. A regression analysis indicates mobile sources are the predominant source of NO\textsubscript{y} presented at both sites. In the multivariate linear equation, the coefficient of [CO], which should reflect the ratio of NO\textsubscript{x} and CO emissions, is 0.019 and 0.041 for the annual average at the Great Smoky Mountain site and at the Mammoth Cave site, respectively. These ratios are significantly lower than the EPA emission ratio for the US of \([\text{NO}\textsubscript{x}]/[\text{CO}]=0.084\). The coefficient of [SO\textsubscript{2}], which should reflect the ratio of NO\textsubscript{x} and CO emissions, is 0.49 and 0.64 for the annual average at the Great Smoky Mountain (GRSM) site and at the Mammoth Cave (MACA) site, respectively. These ratios are in accord with the EPA emission ratio for the US of \([\text{NO}\textsubscript{x}]/[\text{SO}\textsubscript{2}]=0.64\). Results from regression analysis also show that point sources contribute a minimum of 23% and 27% of total NO\textsubscript{y} at GRSM and MACA, separately, during the whole measurement period. Another technique, emission inventory analysis based EPA Emission Inventory, provides that a minimum of 26% and 45% of total NO\textsubscript{y} can be attributed to point source emission on the basis of same multiple-year continuous
measurements of NOy, CO, and SO2 at GRSM and MACA sites. The discrepancy between the two methods is largely caused by statistical uncertainty and determinations of related factors such as background CO, SO2 adjusting parameter, as well as the molar ratios. Nevertheless, we demonstrate that a minimum of one quarter of reactive nitrogen oxides presented at the two southeast national parks are emitted by point sources located in accessible distance surrounding the receptor sites. Given the already high level of ambient ozone at the national parks, the considerable contribution from point sources can significantly affect attainment of the U.S. ozone standard, which is especially expected since this region is characterized by strong biogenic VOCs sources [Ryerson, et al., 2001; Kang, et al., 2001].

The influence area, or origin of nitrogen oxides, is further investigated using trajectory-cluster analysis. The results show that air masses from western (20% out of all air masses) and southwest (17%) sweep most frequently GRSM site, while pollutants transported from eastern half (i.e., Eastern, Northeast, or Southeast) have limited influence (< 10%) on air quality in the Great Smoky Mountain national park. Air masses originated from or traveling through (i.e., Far North (FN) or Close North (CN)) Ohio valley, which region marked as high level of NOy emissions, account for more than 25% of total trajectory number. Examination of pollutants associated with these individual clusters reveals that the highest O3 concentrations are associated with trajectories from the North and Southwest direction, which can be tracked back to Ohio Valley region and coastal region along Gulf of Mexico, respectively.

The processes, as well as their magnitude, responsible for the formation and removal of reactive nitrogen oxides are examined using a comprehensive 3-D air quality
model (MAQSIP). Process budget analysis provides that the major contributions to fresh nitrogen oxides (i.e., NO\textsubscript{x}) at the two locations come from horizontal advection (58 – 62%) and local emissions (38 - 42%), and the primary removal process for NO\textsubscript{x} is local chemistry (92 – 95%). The magnitude of each process at MACA is more than 3 times larger than that at GRSM, which matches the observational results (1.2-4.8 times, Tong et al., 2003). Similar analysis of oxidized nitrogen oxides, i.e., NO\textsubscript{z}, reveals that 84% of NO\textsubscript{z} is the result of local chemistry at MACA, which only accounts for 32% at GRSM; the rest comes from transport. About half of NO\textsubscript{z} is removed by dry deposition at GRSM, while the rate at MACA is 87%; the rest is removed through transport. Further comparison between the process budgets of NO\textsubscript{z} and that of O\textsubscript{3} reveals the similarity among the locations as well as the contributions of each individual process at each location is apparent, especially at the production or accumulation side. Chemistry contributions of 32% and 84% to NO\textsubscript{z} correspond to 26% and 80% to O\textsubscript{3} at GRSM and MACA, respectively. The similarity between NO\textsubscript{z} and O\textsubscript{3} process budgets serves as further evidences of close association between nitrogen oxides and effective O\textsubscript{3} production at these rural locations. One may note that this modeling study is limited in summer time when biogenic emission is most active. High ozone events in southeast national parks, however, have been frequently observed in seasons other than summer, during which the ozone photochemistry may be characterized by non-NO\textsubscript{x}-limiting condition (Kleithman 1991; Jacob et al., 1995; Sillman; 1998). One of the recent findings by the NASTRO suggests that this may be an over simplification that VOC or NO\textsubscript{x} limitation is not uniquely defined by location or emissions (NARSTO, 2002). Further
efforts are needed to address the seasonal characteristics of ozone and its precursors that contribute to shape air quality in the southeast national parks.

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References


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<td>0.28</td>
<td>0.02</td>
<td>0.013</td>
<td>0.0013</td>
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<td>0.54</td>
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<td>0.1456</td>
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<td>0.2099</td>
<td>3.57</td>
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<tr>
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<td>0.013</td>
<td>0.0021</td>
<td>0.37</td>
<td>1.2036</td>
<td>0.3333</td>
<td>4.91</td>
</tr>
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<td>0.006</td>
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<td>0.28</td>
<td>2.5279</td>
<td>0.5553</td>
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<tr>
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<td>0.02</td>
<td>0.015</td>
<td>0.0011</td>
<td>0.37</td>
<td>0.6676</td>
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Table 4.2. Regression analysis on the data measured in the Mammoth Cave National Park (MACA), KY, for 1995-1998.

<table>
<thead>
<tr>
<th>Season</th>
<th>Time</th>
<th>Coeff. of SO2</th>
<th>SD</th>
<th>Coeff of CO</th>
<th>SD</th>
<th>R²</th>
<th>Interception</th>
<th>SD</th>
<th>mean Y</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>All data</td>
<td>0.56</td>
<td>0.01</td>
<td>0.034</td>
<td>0.0011</td>
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<td>-2.57</td>
<td>0.23</td>
<td>5.98</td>
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<td>Midday</td>
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<td>0.02</td>
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<td>Midnight</td>
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<td>0.038</td>
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<td>0.21</td>
<td>-0.79</td>
<td>0.24</td>
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</tr>
<tr>
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<td>Midday</td>
<td>0.69</td>
<td>0.02</td>
<td>0.011</td>
<td>0.0014</td>
<td>0.61</td>
<td>1.20</td>
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<tr>
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<td>Midnight</td>
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<td>0.09</td>
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<td></td>
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<td>0.71</td>
<td>0.02</td>
<td>0.049</td>
<td>0.0002</td>
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<td>-4.35</td>
<td>0.30</td>
<td>6.97</td>
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<tr>
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<td>0.03</td>
<td>0.037</td>
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<tr>
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<td>0.61</td>
<td>-7.58</td>
<td>28</td>
<td>9.20</td>
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<tr>
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<td>0.03</td>
<td>0.067</td>
<td>0.0026</td>
<td>0.69</td>
<td>-8.69</td>
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<td>9.71</td>
</tr>
<tr>
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<td>Midnight</td>
<td>0.48</td>
<td>0.03</td>
<td>0.052</td>
<td>0.0022</td>
<td>0.45</td>
<td>-5.40</td>
<td>0.51</td>
<td>8.77</td>
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<tr>
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<td>0.01</td>
<td>0.041</td>
<td>0.0009</td>
<td>0.44</td>
<td>-3.71</td>
<td>0.13</td>
<td>6.62</td>
</tr>
<tr>
<td>Total</td>
<td>Midday</td>
<td>0.74</td>
<td>0.01</td>
<td>0.037</td>
<td>0.0011</td>
<td>0.62</td>
<td>-3.14</td>
<td>0.22</td>
<td>6.70</td>
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<tr>
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<td>0.57</td>
<td>0.02</td>
<td>0.041</td>
<td>0.0012</td>
<td>0.32</td>
<td>-3.55</td>
<td>0.25</td>
<td>6.36</td>
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Table 4.3. Estimation of contribution of point sources to total NOy emission at Eastern US sites.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Periods</th>
<th>Regression Analysis</th>
<th>Emission Inventory Analysis</th>
<th>Emission Inventory Analysis&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spring (MAM)</td>
<td>23%</td>
<td>33.68%</td>
<td>35.20%</td>
</tr>
<tr>
<td></td>
<td>Summer (JJA)</td>
<td>16%</td>
<td>21.87%</td>
<td>24.19%</td>
</tr>
<tr>
<td>GRSM, TN</td>
<td>Fall (SON)</td>
<td>20%</td>
<td>20.96%</td>
<td>21.78%</td>
</tr>
<tr>
<td></td>
<td>Winter (DSF)</td>
<td>30%</td>
<td>38.07%</td>
<td>38.77%</td>
</tr>
<tr>
<td></td>
<td>All Data</td>
<td>23%</td>
<td>26.24%</td>
<td>27.57%</td>
</tr>
<tr>
<td>SHEN, VA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>September-Dec.</td>
<td>29±5%</td>
<td>30±8%</td>
<td>34±8%</td>
</tr>
<tr>
<td></td>
<td>Spring (MAM)</td>
<td>25%</td>
<td>53%</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Summer (JJA)</td>
<td>21%</td>
<td>40%</td>
<td>-</td>
</tr>
<tr>
<td>MACA, KY</td>
<td>Fall (SON)</td>
<td>29%</td>
<td>42%</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Winter (DSF)</td>
<td>33%</td>
<td>47%</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>All Data</td>
<td>27±3%</td>
<td>45%</td>
<td>-</td>
</tr>
<tr>
<td>Wye, MD&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Sept.-Dec.</td>
<td>11±5%</td>
<td>16±4%</td>
<td>20±5%</td>
</tr>
<tr>
<td>Arendiville, PE&lt;sup&gt;b&lt;/sup&gt;</td>
<td>June-September</td>
<td>21±3%</td>
<td>26±6%</td>
<td>32±8%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Adjusted by sulfur oxidization factor;
<sup>b</sup> Stehr. et al., 2000.
Figure 4.1. Map of the model domain (42x34 in horizontal domain, 36 km grid size)
Figure 4.2. Comparison of results from regression analysis and emission inventory analysis at the Great Smoky Mountain National Park site, TN.
Figure 4.3. Comparison of results from regression analysis and emission inventory analysis at the Mammoth Cave National Park site, TN.
Figure 4.4 Diurnal and Seasonal Variation of Fraction from Point Sources to Total Reactive Nitrogen (NO$_y$) at the Great Smoky Mountain (GRSM) National Park, TN, 1996
Figure 4.5 Diurnal and Seasonal Variation of Fraction from Point Sources to Total Reactive Nitrogen (NO$_y$) at the Mammoth Cave (MACA) National Park, KY, 1996
Figure 4.6. Average trajectory of each cluster of air masses approaching the Great Smoky Mountain (GRSM) National Park, TN. Each average trajectory is labeled with the relative position of its origin to the receptor site. The number in the parenthesis shows the percent of the trajectories assigned to a particular cluster. The background is emission density of NO\textsubscript{x} taken from EPA (1999).
Figure 4.7. Average NO$_y$ and O$_3$ associated with each cluster displayed in Figure 4.6
Figure 4.8. Budget analysis of NO\textsubscript{x} by MAQSIP in the chosen domain during the 1995 summer time
Figure 4.9. Budget analysis of NO\textsubscript{2} by MAQSIP in the chosen domain during the 1995 summer time
Figure 4.10. Budget analysis of O\textsubscript{3} by MAQSIP in the chosen domain during the 1995 summer time (recreated from Kang et al., 2003)
Chapter 5

On the Surface High-Ozone Events in the Rural Southeast United States National Parks: Temporal Distribution, Origin and Case Study
5.1 Abstract

Implementation of the new National Ambient Air Quality Standard (NAAQS) proposed by US EPA in 1996 is estimated to label more Southeast locations as non-attainment areas. This study examined annual, seasonal, and diurnal distributions, as well as case study of high ozone episodes observed during a multiple-year enhanced monitoring campaign at two class I Southeast national parks, namely, the Great Smoky Mountain (GRSM) and Mammoth Cave (MACA) national parks. Though there are no continuous increases in either annual exceedances or the 4th highest ozone concentration at these sites, a long-term increase trend can be identified from measured data. Most frequent exceedances occur in August and September for GRSM site while the maximum exceedances are found in June or August at MACA site. It is interesting to note that neither site shows a mid-summer (July) maximum of ozone exceedence number. Maximum exceedances at low-elevation site are seen in the midday, and extend into a few hours after sunset. High ozone episodes can be observed, however, in any hour at high elevation site during all photochemically active seasons, no matter if sunlight is available or not, most frequently around sunset, and least frequently in early morning. While the air masses associated with ozone exceedances at GRSM site originated in all directions, those with high O₃ at MACA, however, reveal dominant transport originated from southwest with very few exceptions from north. Case study of typical ozone episodes, mainly in seasons other than summer, is performed to examine both inter-site and inter-season difference that contribute to shape high ozone formation. Two early September cases shows that high nitrogen oxides concentration is the main driver to elevate ozone concentration to exceedance level at MACA site while ozone transport
from polluted area works to form exceedances at GRSM, a mountain top site. Almost all high ozone episodes at MACA site are found developed with clear sky, high temperature, low relative humidity, as well as weak anticyclones traveling in a uniform anti-cyclonal pathway surrounding a high-pressure area. High ozone episodes observed at mountain site, however, are not necessary to be associated with these factors. Compared to other cases in late May or even early September, ozone concentration in late September case are much less weakly correlated with NO\textsubscript{y}. This phenomenon has been interpreted as a seasonal transition from NO\textsubscript{x}- to VOCs-limited conditions to ozone caused by declined solar radiation and humidity, as well as biogenic hydrocarbon emissions.
5.2 Introduction

High ozone (O$_3$) episodes in the ambient air are associated with a variety of adverse healthy and environmental effects [Environmental Protection Agency (US EPA), 2001; National Research Council (NRC), 1991]. Regulation of ozone precursor emissions under the U.S. 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 ozone episodes (i.e., non-attainment areas) [US EPA, 2000; Ryerson et al., 2001]. Over 40% of the ozone non-attainment areas of the United States are in the Southeast [Southern Oxidants Study (SOS), Fehsenfeld et al., 1994]. Many more counties, in addition to those already in violation of the 1-hour exceedance standard, are estimated to violate the new National Ambient Air Quality Standard (NAAQS) proposed by US EPA in 1996 [Wolfy, 1996]. This paper shows that the new ozone standard, which is 80 ppbv average over a 8-hour period, proves much more stringent in term of ozone exceedence by examining the high ozone episodes observed during a multiple-year enhanced monitoring campaign at two class I Southeast national parks, namely, the Great Smoky Mountain (GRSM) and Mammoth Cave (MACA) national parks.

The Great Smoky Mountains (GRSM) National Park encompasses 2100 km$^2$ (800 square miles) of mountain ridges and deep-cleft valleys in the states of Tennessee and North Carolina. Among all monitored parks, the Great Smoky Mountain national park is marked with most rapid increase in numbers of days exceeding the National Ambient Air Quality Standard (NAAQS) for ozone [EPA, 2000; Tong et al., 2003a, b]. Given that it is among the most heavily visited national park, the rapid increase of high ozone episodes calls serious attention to human exposure and resource conservation. The Mammoth Cave (MACA) national park, Kentucky, also showed a number of ozone exceeding events
during the measurement campaign. Both sites are dominated by forests and surrounded by forests or agricultural areas, with large isolated industrial point sources whose emissions can be transported to the referred sites under certain meteorological conditions [Fehsenfeld et al., 1994]. Continuous multiple-year measurements of O$_3$, NO$_y$, CO, SO$_2$, and NO at both low and high elevation sites constitute particularly unique set of observations, which may not be comparable elsewhere in the Southeast United States.

This study summarizes the statistical results of ozone exceedance events observed at GRSM and MACA sites for the last decade. Seasonal and diurnal profiles of high ozone episodes are then further explored based on the late 1995-1998 enhanced measurements, which reveal significantly different characteristics between low and high elevation rural sites. Finally, a case study is performed to address the influence of key precursors, meteorology and other factors on the formation of typical high ozone episode. Since the two measurement sites are indicative of the typical rural setting throughout much of the Southeast US, it is hoped that the measurement-based analysis presented in this paper may shed light on the regional characteristics of high ozone episodes in the Southeast US.

5.3 Measurements

Several regional-scale air quality sites in Southeast national parks were operated by US National Park Service (NPS) [Tong, et al., 2003; Kang, et al., 2001]. Continuous measurement data of O$_3$, NO$_y$, CO, SO$_2$, NO, as well as meteorology are collected at Mammoth Cave National Park (MACA), Kentucky, a low elevation (219m) location (37°13’04”N, 86°04’25”W), and the Great Smoky Mountain National Park (GRSM) at
Cove Mountain, Tennessee, a high elevation (1243m) location (35°41’48”N, 83°36’35”W) (Figure 5.1). Each site is located in rural regions and part of the NPS gaseous-pollutant monitoring network. The sampling sites are installed within heavily forested areas with either clean surrounding or a sampling tower above the ground cover. Ambient samples were collected and measured every five minutes.

5.4 Data Analysis, Results, and Discussion

5.4.1 Yearly distribution

One of the measures the US Environmental Protection Agency [2000] employs to monitor ozone trends is the number of the exceedances of the new NAAQS per year. Figure 5.2 shows a plot of the number of exceedances per year for 1990-2002 at GRSM and MACA sites. Although the levels of nitrogen oxides and CO presented at MACA are considerably higher than those at GRSM site over all seasons [Tong et al., 2003b], the number of high ozone episodes is much greater at GRSM than at MACA. Kang et al. [2003] argued that ozone production at MACA is limited by available hydrocarbons while GRSM is rich in this ozone precursor from biogenic emission sources. However, diurnal profiles of ozone mixing ratio at the two sites indicate that while ozone at MACA displays a strong diurnal variation with a peak in the afternoon, ozone at GRSM has no diurnal variation or reaches its maximum only after sunset [Tong 2003b]. Such a lack of daytime maximum in ozone suggests that in-situ photochemical production cannot be the dominant contributor to building up significantly larger number of ozone exceedances at GRSM. Investigation of the diurnal distribution of high ozone occurrences, which can provide further information on the particular hours when high ozone is observed, will be presented in the following section.
Another statistic that can be used to follow the long-term trends of ozone is the $4^{th}$ highest concentration for 1-hour average ozone measured during that year. The $4^{th}$ highest ozone concentration is likely to be less sensitive to extreme values. Figure 5.2 shows that the $4^{th}$ highest at GRSM are higher than those at MACA for all years. The magnitude of difference ranges between 1 and 20 ppbv between the two sites. Generally, the trend of the $4^{th}$ highest concentration is consistent with the trend of ozone exceedances counted using the new NAAQS standard, which is 80 ppbv for 8-hour averaged concentration of ozone. The similarity is especially apparent for the case of GRSM, in which the $4^{th}$ highest concentration approximately follows the trend of 8-hour ozone exceedances. For both sites, there are few or none of ozone exceedances when the $4^{th}$ highest is lower or close to 80 ppbv. When the $4^{th}$ highest went up to 110 ppbv, which is still lower than the earlier 1-hour average ozone NAAQS, that year was associated with the highest ozone episodes. Such an association implies that frequent violations of the 1-hour exceedance standard may represent worse air quality in term of ozone exposure than similar amount of 8-hour violations. This is good agreement with earlier work in Northeast United States, e.g., Yang and Miller (2002) reported that the exceedances of the 8-hour standard were about 2-3 times larger than those of the 1-hour standard.

Though there are no continuous or monotonic increases in either annual exceedances or the $4^{th}$ highest ozone concentration at both sites, a long-term increasing trend can be identified in the number of exceedances, particularly at GRSM. During the first half of measurement period, i.e., 1990-1995, the 8-hour averaged ozone exceedances are 6.2 per year at GRSM site and 1.3 per year at MACA site. The later half, 1996-2001, sees more than 3 times of increase at both sites. The averaged ozone exceedances are
20.9 per year at GRSM site and 5.7 per year at MACA site. Similarly, the averaged 4th highest ozone concentration has increased from 89.8 ppbv to 99.0 ppbv at GRSM site, and from 78.2 ppbv to 87.3 ppbv at MACA site. Yang and Miller (2002) reported a significant decrease in ozone exceedances based on 17 years ground-level observations in Connecticut. Dye et al. (1998) drew similar conclusion for the Northeast region. For the whole United States, a 20% decrease in 1-hour average and 12% decrease in 8-hour average have been reported over last 20 years [1980-1999, US EPA, 2000]. Given the nationwide decreasing trend, the significant increase of high ozone events over last decade are calling further efforts of implementing ozone control related to rural Southeast locations.

5.4.2 Seasonal distribution

Seasonal distribution of ozone exceedances is displayed in Figures 5.3a and 5.3b for GRSM and MACA sites, respectively. Two time slices, period I (1996-1998) and period II (1999-2001), are plotted in figure 5.3 to make inter-annual comparison. Period I saw continuous increase of ozone exceedances, while period II experienced continuous decrease [Figure 5.2]. Monthly averaged NOy simultaneously monitored with O3 is also presented in Figure 5.3 for the period I. As expected, high ozone events are widely distributed in late spring, summer, and early fall. Occasionally, ambient ozone concentration can exceed the 8-hr standard even in April and March (Figure 5.3a). For GRSM site, most frequent exceedances occurred in August (37 times) and September (33 times) during period I, and in August (19 times) and June (16 times) during period II. Exceedances in July are least significant among all photochemically active seasons (May
to September) for both periods. Part of the reason might be that concentration of nitrogen oxides reaches its minimum (3.0 ppbv) in mid-summer (Figure 5.3a), which could have limited photochemical ozone production then. Another hypothesis, proposed by Kang et al. (2003), suggests that ozone concentration increases with increased hydrocarbons within some range, but then decreases when hydrocarbon concentration exceeds a certain turnover point. Since GRSM site is heavily forested and biogenic hydrocarbon emission is most active in the midsummer, it is possible that high level of hydrocarbons keep ozone concentration from frequently surpassing NAAQS standard. Earlier modeling study [Kang et al., 2003] provides evidence to this mechanism of ozone decrease by direct reaction with biogenic hydrocarbons and removal of nitrogen oxides through formation of inert organic nitrogen. Of courses, other factors, like seasonal rainfall or fog formation can also contribute to lower ozone exceedance numbers. Back trajectory analysis over all period [Tong et al, 2003a] shows that air masses originated from Gulf of Mexico, which carry high level of humidity and low level of pollutants, may lead to lower level of ozone at GRSM site.

As to MACA site, the maximum number of exceedances is found in June (7) during period I, and in August (9) during period II. The numbers are relatively smaller than these at GRSM site. Our earlier study based on simultaneous measurements of ozone and other trace gases indicated that the formation of nighttime ceiling and titration by fresh nitrogen oxides can deplete ozone effectively and thereby prevent building up persistent high ozone episodes overnight [Tong et al., 2003b]. This is typical for low elevation sites, and may account for significantly lower number of exceedances at low elevation site than those at high elevation site such as GRSM site. Again, the number of
ozone exceedances in July is not the maximum for both periods. Particularly, the number of exceedances in July during period II is even the least frequent among all photochemically active months. Examining the seasonal trends of NO$_y$ gives that NO$_y$ at MACA demonstrates a strong seasonal variation, with maximum in January (~10 ppbv) and minimum in July (~4.5 ppbv) (Figure 5.3b). Different from the situation at GRSM, summer ozone level at MACA is closely related to the availability of ozone precursors. Process budget analysis shows that approximately 80% of total ozone at MACA is produced by local photochemistry while only 26% of total ozone is from in-situ production at GRSM [Tong et al., 2003a]. Minimum available nitrogen oxides, which are thought as the limiting precursor to summer ozone production at rural Southeast location, may be responsible for the fact the maximum ozone exceedances did not appear during mid-summer at MACA.

5.4.3 Diurnal distribution

Diurnal distribution of exceedance occurrences is displayed in Figures 5.4a and 5.4b for GRSM and MACA sites, respectively. Number of exceedances for a particular hour is calculated from statistics of 8-hour exceedances during 1996 to 1998. Each hour within an eight-hour episode gets one count for its contribution to the exceedance. Therefore, the hourly-based total counts are eight times larger than that of actual 8-hour exceedances. For GRSM site, high ozone episodes occur most frequently around sunset, and least frequently in early morning (Figure 5.4a). This trend is consistent with the diurnal profile of seasonal ozone average at GRSM [Figure 5.2, Tong et al., 2003b]. High ozone episodes can be observed in any hour during all photochemically active seasons,
no matter if sunlight available or not. Maximum exceedances at MACA site, however, are seen in the midday, and extend into a few hours after sunset. There are no ozone exceedances between midnight and early morning.

Shapes of diurnal profiles of exceedances at the two sites can roughly mirror the relative contribution of transport and local production to total ozone level presented at the measurement sites. Ozone concentration at MACA site is elevated when air masses with undepleted ozone begin to mix down to the surface shortly after the breakup of nocturnal boundary layer (NBL) [Tong et al., 2003b]. At the same time, local photochemical production also contributes to increased ozone level. Combination of transport and photochemistry can explain the mainly daytime distribution of ozone exceedances observed at MACA site. After sunset, the formation of stable NBL prevents air masses with higher level of ozone from reaching the surface. Furthermore, lack of photochemistry and other depletion mechanism such as dry deposition and titration by fresh nitrogen oxides can work further to lower ozone to a level under the NAQQS [Tong et al., 2003b]. Figure 5.4b shows that such a process can be accomplished before midnight. Therefore, one can seldom, if ever, observe an ozone exceedance after midnight and before break of NBL triggered by increased solar radiation in the morning.

Characteristics of diurnal ozone variations at GRSM site, however, are shaped by different mechanisms. The ceiling effect caused by NBL fastens ozone depletion below it, and on the other hand, prevents upper layer of ozone from dry deposition and thereby help maintain higher level of ozone above NBL. Such a layer which resides above NBL and contains higher level of ozone is conventionally called ozone residual layer [Aneja et al., 2000]. Since GRSM site is 1220 m above sea level, it is almost always above the
shallow NBL over plains during nighttime [Poulida et al., 1991; Doddridge et al., 1992]. In other words, GRSM site is always swept by air masses containing higher level of ozone and ozone concentration there is not subject to most depletion mechanisms presented at low elevation site such as MACA. The role of residual layer on ozone concentration may explain the higher numbers of exceedances during nighttime at GRSM. Similar trends of ozone variations at elevated sites have been found in other research campaigns (Aneja et al., 1991, and references therein). When increased solar radiation begins to elevate planetary boundary layer (PBL) height, the upward mixing brings cleaner air, after ozone depletion over night, to the measurement site and results in dilution of nighttime air masses at GRSM site. On the other hand, local photochemistry will continue to increase ozone concentration at the same time. The combination of the two processes results in a decrease of exceedance number right after sunrise followed by an increase in late morning (Figure 5.4a).

5.4.4 Back Trajectory Analysis

Origin of air masses carrying high level of ozone is investigated by the hybrid single-particle Lagrangian integrated trajectories (HY-SPLIT) Model [Draxler, 1997]. This technique and its actual operation routines have been elaborated elsewhere [Draxler, 1997] and will not be reported here. The PC version model is run using the output from the output wind fields of the National Climatic Data Center (NCDC)’s FNL archive data (TD-6141) for both horizontal and vertical air mass streams after January 1, 1997. Global meteorology data for the period before 1997, called the MRF Archive, are also obtained from NCDC (TD-6140). Back trajectories were initialized for each day in which 8-hr
average ozone exceeds 80 ppbv. Starting elevation of trajectories is set as 500m above ground level of the sites, although the choice of initial elevation is under considerable debate [Brankov et al., 1999]. All trajectories are tracked back to two days (48 hours), since our previous work [Tong et al., 2003a] suggests that duration of 2-3 days can provide reasonable information of O₃ regarding influence area.

Figures 5.5 shows all individual trajectories for each exceeding events at GRSM. Although the trajectories indicate transport originated from all directions, the majority can be categorized into from northwest and from southwest, consistent with previous results from a 3-year trajectory-cluster analysis for GRSM site (Tong et al., 2003a). Trajectories with high O₃ at MACA site (Figure 5.6), however, reveal dominant transport originated from southwest, with very few exceptions from north, in which direction the highly polluted Ohio River Valley located [EPA, 2000]. Such an inter-site difference suggests that high levels of O₃ can be formed under various meteorological conditions at GRSM site, while that at MACA site, which stands at northern to GRSM, are dominated by transport from southwest region. At both sites, the trajectories associated with high O₃ are generally short and display anticyclonic motions, suggesting that slow circulation during stagnant high-pressure events favors regional O₃ event. This is typical of regional-scale pollution episodes in the eastern United States [Logan, 1989; Jacob et al., 1995; Yang & Miller, 2002].

All trajectories are initialized at 1300 local time; therefore, no daytime/nighttime difference can be identified from the above analysis. It is true that there are no high ozone events at MACA site extending into nighttime (section 3.3, this study), however, GRSM site does see considerable high ozone events during nighttime. Similar back trajectory
analysis for GRSM site, with initial 2300 local time, is run and compared to daytime results to examine the effects of nighttime boundary layer. There are no strong differences between daytime and nighttime trajectories, consistent with earlier work for a mountain top site in northeast United States (Hollock, 2002). Hollock (2002) also reported that there are nearly equal numbers of trajectories associated with high O\textsubscript{3} during daytime and nighttime, suggesting that nighttime O\textsubscript{3} loss due to dry deposition at the surface may not be significant at this elevated site.

5.4.5 Case Studies

In this section we present simultaneous measurements of concentrations of trace gases and meteorological parameters during high ozone episodes. High ozone episodes have been observed mostly during summer, and extensively investigated. In this study a significant number of high ozone episodes was observed in seasons other than summer, as discussed in previous sections. Therefore, we emphasize on several typical events observed in late May and September. A variety of trace gases, O\textsubscript{3}, NO\textsubscript{y}, NO, CO, and SO\textsubscript{2}, as well as meteorological parameters such as ambient air temperature, relative humidity, wind speed and direction, solar radiation, and rain, were monitored every five minutes at both sites for the periods of interest. We first compare two September observations from both sites to examine inter-site differences, and then present two typical cases in late May and September, both at MACA site, to investigate seasonal effects on shaping high ozone episodes.
High ozone events: high elevation site vs. low elevation site

Data for two 72-hour pollution events, occurring in late August or early September, are presented in Figure 5.7 (September 06-08, 1997, MACA) and Figure 5.8 (August 30-September 01, 1996, GRSM). Both events are associated with one or more days of maximum ozone level higher than 80 ppbv, as well as at least one day of 8-hour ozone exceedance. Ozone at MACA site (Figure 5.7a) displays stronger diurnal trend than that at GRSM site (Figure 5.8a), which is a typical difference between mountaintop site and flatland sites as discussed earlier. The episode averaged ozone concentration is 53.1 ppbv at MACA site, and 70 ppbv at GRSM during the 72-hour episode, both of which are approximately 20 ppbv above their seasonal average values according to a multiple year measurement-based study [Tong et al., 2003b]. Episode average CO, SO$_2$, NO$_x$, and NO concentrations at MACA site are 207, 2.1, 9.9, and 0.45 ppbv, respectively. Except NOy, all species lie between seasonal averages for summer and fall [Table 1]. NO$_x$ concentration, however, is significantly higher than that in both seasons, suggesting that high nitrogen oxides concentration may be the main driver to elevate ozone concentration since ozone production at MACA is likely limited by available nitrogen oxides [Tong et al., 2003a; Kang et al., 2003]. Besides being rich in NO$_x$, this episode at MACA site is also found with rather regular diurnal variation of air temperature, wind direction, solar radiation, and relative humidity (Figure 5.7b). Maximum ozone is generally associated with maximum air temperature and solar radiation, and minimum relative humidity, as well as weak wind from western or northwest direction, where existing large sources of NO$_x$ from power plants, such as Paradise power plant emitting 147 thousands of tons of NOx per year located 30 kilometers west to the site. Back trajectories initialized at 500 m above ground level for different time on September 7,
1997 (Figure 5.7.c) suggest that almost all air masses approaching MACA site on that day traveled in a uniform anti-cyclonal pathway surrounding a high-pressure area south to the site. The air masses remained in the continental boundary layer for at least 48 hours, and swept over several large urban and industrial regions during that period.

Episode averaged CO, SO$_2$, NO$_y$, and NO concentrations at GRSM site are 201, 1.3, 3.9, and 0.11 ppbv, respectively. CO concentration is significantly larger than the seasonal average of either summer or fall [Table 1], indicating that this site was covered by high level of pollution. Lower ratios of SO$_2$/CO and NO$_y$/CO suggest that the emission sources are likely located some distance away from the site. Though NO concentration is higher than summer average, it is lower than fall average. SO$_2$ is the only measured specie that is lower than either summer or fall average [Table 1]. Washout by rain during night of August 30 and afternoon of August 31 is believed to remove considerable amount of SO$_2$ due to its high aqueous solubility. Cloud scavenges and associated heterogeneous chemistry may further lower SO$_2$, in the presence of high oxidants (O$_3$, OH, etc) concentration, to below average level. There are no as strong diurnal meteorological trends at GRSM as we saw at MACA (Figure 5.8b). Solar radiation and relative humidity are perturbed by rainfall and cloud cover. Wind in daytime is generally from north and wind speed is less than 2 m/s. For nighttime, this site is exposed to free atmosphere above NBL, and the wind speed is much stronger (> 3 m/s). The dominant nighttime wind is from southeast or south during this episode. Back trajectories, again, initialized at 500 m above ground level, on August 31 display no apparent anti-cyclonal motions developed near the site (Figure 5.8.c).
In previous study, we have reported that ozone at GRSM site displays no regular diurnal trend and the ozone peak appears in late afternoon or after sunset. This is also the case on August 30 and September 1 in this episode. Ozone on August 31 however displays rather strong diurnal variation. Presence of such an ozone peak during daytime and short after sunset is unlikely attributed to contribution from in-situ photochemical production as that happens at low elevation site. We defense this argument according to the following observations. Firstly, it is true that nitrogen oxides may be produced by lightning associated with preceding storm, and we did detect a sharp increase of NO\textsubscript{y} immediately after rain peak, but lack of sufficient solar radiation (Figure 5.8.b), caused by the same event, will prevent fresh nitrogen oxides from realizing its ozone production potential. Secondly, ozone variation is consistent with that of CO, NO\textsubscript{y}, and SO\textsubscript{2}. Simultaneous elevation of O\textsubscript{3}, NO\textsubscript{y}, and, especially, SO\textsubscript{2} and CO, can be more suitably explained by intrusion of air masses containing higher level of pollutants. Finally, ozone profile does not change in a continuous style as most photochemistry shapes. Instead, it jumps onto the high level in a short time and maintains high level of ozone for rather long time regardless of variations of temperature and solar radiation. Such a change is more likely caused by rapid atmospheric transport than by slow photochemistry. This inference is in good accord with our previous results of process budget analysis on ozone and nitrogen oxides by means of a three-dimensional transport/chemistry [Tong et al., 2003a; Kang et al., 2003].
**High ozone events: Spring vs. Fall**

Time series data for one high ozone episode in late spring (May 22-24, 1997) [Figure 5.9] and one in late fall (September 18-20, 1997) [Figure 5.10], both at MACA site, are presented in this part to investigate the possible seasonal differences and similarities between these ozone episodes. The episode-averaged concentration of ozone was 45.7 ppbv in the May event, and 40.3 ppbv in the September event, both of which are close to seasonal averages. Episode averaged CO, SO₂, NOₓ, and NO concentrations are 189, 2.5, 5.7, and 0.37 ppbv in May episode, and 171, 2.4, 6.5, and 0.38 in September episode, respectively. All species lie between seasonal averages for the two closest seasons [Table 5.1]. Both episodes are also found, as the previously discussed low-elevation cases, to have developed in conditions associated with clear sky (i.e., strong solar radiation), high temperature, low relative humidity, as well as weak anticyclones (Figures 5.9b and 5.10b), typical for most regional-scale pollution events in the eastern United States [Logan, 1989; Jacob et al., 1995; Yang & Miller, 2002]. High ozone episode at mountaintop site, such as GRSM in this study, is however not necessarily associated with such typical meteorological conditions, since meteorological conditions favoring photochemistry and accumulation are not sufficient to account for the majority of ozone influx presented at mountain top site.

Although both episodes display similarity in meteorological and chemical characteristics, analysis of their back trajectories suggests that the site was dominated by air masses originating from different regions [Figure 5.9c and 5.10c]. Air masses approaching on May 23 are mainly from upper troposphere over industrialized north region where ozone concentration is normally higher than that in surface layer. The air
masses are then transported to the site by downward motion. In the case of September episode, most air masses originated from the coastal region along Gulf of Mexico, where extensive NO\textsubscript{x} emission sources exist [EPA, 2000; Tong et al., 2003a]. Previous study based on trajectory-cluster analysis reveals that the group of air masses originated from this area is associated with highest ozone level compared to those from all other origins [Tong et al., 2003a]. Relatively high level of ozone precursors are loaded into these air masses, and are transported by winds with relative uniform wind direction along the pathway of trajectories. In the presence of strong solar radiation, these ozone precursors are able to produce ozone before reaching the measurement site. It is interesting to note that compared to the case in late May, ozone concentrations in late September case are much less weakly correlated with NO\textsubscript{y}. This is a general trend that the correlation between ozone and NO\textsubscript{y} becomes weaker from summer to fall at MACA site [Tong et al., 2003b]. Jacob et al. (1995) reported similar trend based on measurements at Shenandoah National Park, Virginia and their model simulation. They interpreted this phenomenon as a seasonal transition from NO\textsubscript{x}- to VOCs-limited conditions to ozone production [Jacob et al., 1995] caused by declined solar radiation and humidity, as well as biogenic hydrocarbon emissions.

5.5 Conclusion and Implications

Over 40% of the ozone non-attainment areas of the United States are in the Southeast [Fehsenfeld et al., 1994]. Implementation of the new National Ambient Air Quality Standard (NAAQS) proposed by US EPA in 1996 is estimated to label more Southeast locations as non-attainment areas. This study examined annual, seasonal, and
diurnal distributions, as well as some case studies of the high ozone episodes observed during a multiple-year enhanced monitoring campaign at two class I Southeast national parks, nominally, the Great Smoky Mountain (GRSM) and Mammoth Cave (MACA) national parks.

Although the level of nitrogen oxides and CO presented at MACA site are considerably higher than those at GRSM site over all seasons, the number of high ozone episodes is much larger at GRSM than at MACA. The difference is attributed to lower ozone production efficiency of NO\textsubscript{x} [Tong et al., 2003b], limited by available hydrocarbons [Kang et al., 2003], at MACA site, and influx of ozone by transport to GRSM site. Though there are no continuous increases in either annual exceedances or the 4\textsuperscript{th} highest ozone concentration at both sites, a long-term increase trend can be identified from measured data. During the first half of measurement period, i.e., 1990-1995, the 8-hour averaged ozone exceedances are 6.2 per year at GRSM site and 1.3 per year at MACA site. The later half, 1996-2002, experiences more than 3 times of increase in exceedances at both sites. The averaged ozone exceedances were 20.9 per year at GRSM site and 5.7 per year at MACA site. Similarly, the averaged 4\textsuperscript{th} highest ozone concentration increased from 89.8 ppbv to 99.0 ppbv at GRSM site, and from 78.2 ppbv to 87.3 ppbv at MACA site. Given the nationwide decreasing trend, the significant increase of high ozone events at these sites over last decade calls further efforts of implementing ozone controls in the rural Southeast US.

At GRSM site, most exceedances occur in August and September, while least number occurs in July corresponding the photochemically active season (May to September). At MACA site, the maximum exceedances are found in June. It is interesting
to note that neither site shows a mid-summer (July) maximum of ozone exceedence number. This phenomena can be partially explained by the fact that concentration of nitrogen oxides reaches its minimum in mid-summer. Another hypothesis, proposed by Kang et al. (2003), suggests that it is possible that high level of biogenic hydrocarbons emitted in July dampen ozone concentration from surpassing NAAQS standard by removal of nitrogen oxides through formation of inert organic nitrogen. Analysis of seasonal distribution of ozone exceedances also reveals that high ozone events are widely distributed in late spring, summer, and early fall. Considering the significant seasonal variations of ozone precursors as well as meteorological parameters, ozone control strategies aiming to reduce summertime ozone may not be efficient for other periods of ozone exceedances.

Diurnal distribution of exceedance occurrences shows that high ozone episodes occur most frequently around sunset, and least frequently in early morning at high elevation site. High ozone episodes can be observed at any hour during all photochemically active seasons, no matter if sunlight is available or not. Maximum exceedances at MACA site, however, are seen in the midday, and extend into a few hours after sunset. There are no ozone exceedances between midnight and early morning. Combination of transport and photochemistry can explain the mainly daytime distribution of ozone exceedances observed at MACA site. After sunset, the formation of stable NBL prevents air masses with higher level of ozone from reaching the surface while other depletion mechanism such as dry deposition and titration by fresh nitrogen oxides can work further to lower ozone to a level under exceedance standard. GRSM site, however,
is always swept by air masses containing higher level of ozone and ozone is not subject to most depletion mechanisms presented at low elevation site such as MACA.

While the air masses associated with ozone exceedances at GRSM site originated from all directions, those with high O₃ at MACA, however, reveal dominant transport originated from southwest with, very few exceptions from north. Such an inter-site difference suggests that high level of O₃ can be formed under various meteorological conditions at GRSM site, while that at MACA site, which stands at northern to GRSM, are dominated by transport from southwest region.

Case studies of typical ozone episodes, mainly in seasons other than summer, are performed to examine both inter-site and inter-season differences that contribute to shape high ozone formation. Two early September cases shows that high nitrogen oxides concentration is the main driver to elevate ozone concentration to exceedance level at MACA site while ozone transport from polluted area works to form exceedances at GRSM, a mountain top site. Almost all high ozone episodes at MACA site are found developed with clear sky, high temperature, low relative humidity, as well as weak winds traveling in a uniform anti-cyclonal pathway surrounding a high-pressure area. High ozone episodes observed at mountain site, however, are not necessarily associated with these factors, which have been viewed as typical of regional-scale pollution episodes in the eastern United States [Logan, 1989; Jacob et al., 1995; Yang & Miller, 2002]. The authors also note that compared to other cases in late May or even early September, ozone concentrations in late September case are much less weakly correlated with NOₓ. This phenomenon has been interpreted as a seasonal transition from NOₓ- to VOCs-limited conditions to ozone production [Sillman et al., 1990; Kleiman, 1991; Jacob et al.,
1995] caused by declined solar radiation and humidity, as well as biogenic hydrocarbon emissions.

The results summarized here may broach further discussion on ozone control issue in Southeast United States. Under the 1-hour average NAAQS standard, neither the Great Smoky national park nor the Mammoth Cave national park was categorized as non-attainment areas for ozone. However, application of the new 8-hour NAAQS standard renders both national parks to violate the ozone standard at least since 1995. Introducing new and more stringent NAAQS standard, as well as the unusual increasing trend in these areas against the national decreasing tendency and the considerable human exposure to ozone in these class-I national parks, calls for more attention to a more effective ozone control strategy in these rural areas. Moreover, the facts that ozone exceedances are widely distributed over spring, summer, and fall, and that maximum frequency of ozone exceedances consistently appears out of mid-summer, bring further challenge to design a successful ozone debasement strategy for rural Southeast region. Investigating seasonal characteristics of ozone key precursors and their contribution to photochemical production of ozone will be essential to make such strategy more efficient. While this study presents only data collected in the past thirteen years, more measurement data, as well as modeling study, will be needed to verify the long-term trend and evaluate the effectiveness of control policies.
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Table 5.1. Seasonal average of ozone, SO2, CO, NO, and NOy at Great Smoky Mountain (GRSM) site and Mammoth Cave (MACA) site

<table>
<thead>
<tr>
<th>Location</th>
<th>Season</th>
<th>O₃ (ppbv)</th>
<th>SO₂ (ppbv)</th>
<th>CO (ppbv)</th>
<th>NO (ppbv)</th>
<th>NOₓ (ppbv)</th>
<th>Tₐ (°C)</th>
<th>RH (%)</th>
<th>WS (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRSM</td>
<td>Summer</td>
<td>64.7</td>
<td>2.1</td>
<td>187.8</td>
<td>0.06</td>
<td>3.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>August 30 - September 1</td>
<td>70.0</td>
<td>1.3</td>
<td>201</td>
<td>0.11</td>
<td>3.9</td>
<td>-</td>
<td>82.5</td>
<td>2.98</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>50.5</td>
<td>2.0</td>
<td>166.1</td>
<td>0.18</td>
<td>3.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>39.0</td>
<td>2.7</td>
<td>210.5</td>
<td>0.49</td>
<td>6.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>May 22-24</td>
<td>45.7</td>
<td>2.5</td>
<td>189</td>
<td>0.37</td>
<td>5.7</td>
<td>16.7</td>
<td>71.4</td>
<td>1.14</td>
</tr>
<tr>
<td>MACA</td>
<td>Summer</td>
<td>39.7</td>
<td>1.7</td>
<td>193.8</td>
<td>0.29</td>
<td>5.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>September 6-8</td>
<td>53.1</td>
<td>2.1</td>
<td>207</td>
<td>0.45</td>
<td>9.9</td>
<td>21.1</td>
<td>81.1</td>
<td>0.48</td>
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<tr>
<td></td>
<td>September 18-20</td>
<td>40.3</td>
<td>2.4</td>
<td>171</td>
<td>0.38</td>
<td>6.5</td>
<td>20.8</td>
<td>79.5</td>
<td>0.63</td>
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<tr>
<td></td>
<td>Fall</td>
<td>31.7</td>
<td>2.9</td>
<td>191.7</td>
<td>0.75</td>
<td>7.0</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>
Figure 5.1. Locations of the two monitoring sites in national parks are indicated in red color.
Figure 5.2 Trend in 8-hr ozone exceedances and 4th highest at GRSM and SHEN, 1990-2002
Figure 5.3.a Number of high ozone events happened in each month at the Great Smoky Mountain (GRSM) National Park.
Figure 5.3.b Number of high ozone events happened in each month at the Mammoth Cave (MACA) National Park.
Figure 5.4.a Diurnal Distribution of High Ozone Event at the Great Smoky Mountain National Park. High Ozone events are defined as 8-hour averaged concentration exceeding 80 ppbv. Each of the 8 hours gets one count for a high event taking place in it.
Figure 5.4.b Diurnal Distribution of High Ozone events at the Mammoth Cave National Park. High Ozone events are defined as 8-hour averaged concentration exceeding 80 ppbv. Each of the 8 hours gets one count for a high event taking place in it.
Figure 5.5 Back trajectories of air masses associated with ozone concentration larger than 90 ppbv at GRSM site.
Figure 5.6 Back trajectories of air masses associated with ozone concentration larger than 90 ppbv at MACA site.
5.7.a Time series of $O_3$, CO, NOy, NO, and SO$_2$ at MACA site, September 6-8, 1997

![Graph showing time series of $O_3$, CO, NOy, NO, and SO$_2$ at MACA site, September 6-8, 1997.](image-url)
5.7.b Time series of $O_3$ and Meteorological Parameters at MACA site, September 6-8, 1997
5.7.c Back trajectories of MACA site on September 7, 1997
5.8.a Time series of $O_3$, CO, $SO_2$, NO, and NO$_y$ at GRSM site, August 30-September 1, 1996

(Rain)
5.8.b Time series of O3 and Meteorological Parameters at GRSM site, August 30-September 1, 1996

(Rain)
5.8.c Back trajectories of MACA site on September 7, 1997
5.9.a Time series of O₃, CO, NOₙ, NO, and SO₂ at MACA site, May 22-24, 1997
5.9.b Time series of $O_3$ and Meteorological Parameters at MACA site, May 22-24, 1997
5.9.c Back trajectories of MACA site on September 7, 1997
5.10.a Time series of O$_3$, CO, NO$_y$, NO, and SO$_2$ at MACA site, September 18-20, 1997
5.10.b Time series of \( \text{O}_3 \) and Meteorological Parameters at MACA site, September 18-20, 1997

The diagram shows the time series of \( \text{O}_3 \) (in ppbv) and meteorological parameters (RH, WDir, AirTemp, MnWSp, Radiation) over the period of September 18-20, 1997. The x-axis represents Local Time (EST), and the y-axes represent the concentrations of \( \text{O}_3 \) and the values of RH, WDir, AirTemp, MnWSp, and Radiation.
5.10.c Back trajectories of MACA site on September 19, 1997
Chapter 6. Summary, Implications and Future Research

This study presents data analysis, and interpretation of ozone (O\textsubscript{3}) and its key precursors in the rural Southeast United States. Firstly, O\textsubscript{3} and NO\textsubscript{y} chemistry is addressed based on measurements collected from three Southeast US National Parks: Shenandoah National Park, Big Meadows site (SHEN) located at 38°31'21" N, 78°26'09"W, Great Smoky Mountains National Park, Cove Mountain site (GRSM) located at 35°41'48"N, 83°36'35"W, and Mammoth Cave National Park (MACA) at 37°13'04"N, 86°04'25" W. Recognizing that nitrogen oxides are crucial to O\textsubscript{3} production in rural Southeast US, further investigation is made to identify source attribution, origin, and processes responsible for nitrogen oxides present at the measurement sites using various analytic and modeling techniques. Finally, the long-term trend and case studies of high ozone episodes observed at the national parks are examined. Recommendations of future research are also given at the end of this chapter.

6.1 Ozone and Nitrogen Oxides Chemistry

The major objective of this study is to characterize reactive nitrogen oxides and their relation to O\textsubscript{3} production at rural Southeast United States in an attempt to assess the impact of new O\textsubscript{3} NAAQS on regional attainment. Our analysis shows that whereas O\textsubscript{3} concentration at low-elevation rural site rises sharply to a short-lived afternoon maximum and drops to near zero at night, as observed in most urban or suburban areas, O\textsubscript{3} at high-elevation rural sites does not display a significant drop during nighttime. As a result,
longer-time averaged O\textsubscript{3} levels at high-elevation are much higher than those at nearby low-elevation site. We have showed that high-elevation site is more likely to violate the new O\textsubscript{3} NAAQS as the standard changed to a smaller concentration averaged over a longer time period.

We also introduced a new indicator, the (NO\textsubscript{y}-NO)/NO\textsubscript{y} ratio, to represent air mass age. O\textsubscript{3} increases with the increase of photochemical age represented by higher (NO\textsubscript{y}-NO)/NO\textsubscript{y} ratio at both high and low elevation locations. Linear relationship between O\textsubscript{3} concentration and photochemical age is found unsuitable to the whole range of air mass age for both GRSM and MACA. The current study presents a turnover point (0.9 for value of (NO\textsubscript{y}-NO)/NO\textsubscript{y}) that separates the NO\textsubscript{x}- and non-NO\textsubscript{x}-limited ozone production regimes. The regional background O\textsubscript{3} concentrations that are not directly influenced by anthropogenic emissions are estimated to be \textasciitilde35 ppbv at GRSM, and \textasciitilde43 ppbv at MACA inferred from the linear regression of O\textsubscript{3} on (NO\textsubscript{y}–NO).

Impact of the new 8-hour-80-ppbv NAAQS on rural nonattainment is addressed by examination of data from these sites from January 1996 through December 1998. Our analysis shows that under the 1-hour NAAQS, both GRSM and SHEN site were at the edge of O\textsubscript{3} violation and MACA did not violate the 1-hour NAAQS for O\textsubscript{3}. Under the new 8-hour NAAQS, however, all three national parks are in serious nonattainment of O\textsubscript{3} NAAQS. Increased number of exceedances under the new NAAQS not only categorizes these areas as nonattainment of O\textsubscript{3} pollution, but also presents a challenge to design O\textsubscript{3} control strategies for these areas. The new 8-hour NAAQS violations, compared to that of 1-hour NAAQS, are scattered into different seasons, from April to October, during which the control strategies aimed at summertime O\textsubscript{3} pollution may not be effective [Jacob et
al., 1995]. A further challenge is that there are more 8-hour exceedances observed at the high-elevation sites than at the low-elevation site. O₃ levels at high elevation site are probably subject to emissions from multiple urban areas as well as from local and remote rural sources. Therefore, this type of nonattainment is calling for control strategies to target regional scale emission sources that can exert influence on O₃ levels of these areas, rather than the current control strategies that have justifiably focused on emission controls within the nonattainment area. Further investigation is needed to examine the influencing areas and identify the seasonal characteristics of O₃ episodes to provide critical information of shaping successful O₃ control strategies in the areas of concern.

6.2 Source Attribution, Origin, and Process Budget of NOₓ

This section focuses on both observational based analysis and modeling in elucidating source attribution, influence area, and process budget of reactive nitrogen oxides at two rural southeast national parks. A regression analysis indicates mobile sources are the predominant source of NOₓ present at both sites. In the multi-variant linear equation, the coefficient of [CO], which should reflect the ratio of NOx and CO emissions, is 0.019 and 0.041 for the annual average at the Great Smoky Mountain site and at the Mammoth Cave site, respectively. These ratios are significantly lower than the EPA emission ratio for the US of [NOₓ]/[CO]=0.084. The coefficient of [SO₂], which should reflect the ratio of NOx and CO emissions, is 0.49 and 0.64 for the annual average at the Great Smoky Mountain (GRSM) site and at the Mammoth Cave (MACA) site, respectively. These ratios are in accord with the EPA emission ratio for the US of [NOₓ]/[SO₂]=0.64. Results from regression analysis also show that point sources
contribute a minimum of 23% and 27% of total NOy at GRSM and MACA, separately, during the whole measurement period. Another technique, emission inventory analysis based EPA Emission Inventory, suggests that a minimum of 26% and 45% of total NOy can be attributed to point source emission on the basis of same multiple-year continuous measurements of NOy, CO, and SO₂ at GRSM and MACA sites. The discrepancy between the two methods is largely caused by statistical uncertainty and determinations of related factors such as background CO, SO₂ adjusting parameter, as well as the molar ratios. Nevertheless, we show that a minimum of one quarter of reactive nitrogen oxides present at the two southeast national parks are emitted by point sources located within an accessible distance from the receptor sites. Given the already high level of ambient ozone in the national parks, large contribution from point sources can significantly affect attainment of the U.S. ozone standard, especially because this region is characterized by strong biogenic VOCs sources.

The influence area, or origin of nitrogen oxides, is further investigated using trajectory-cluster analysis. The results show that air masses coming from west (20% out of all air masses) and southwest (17%) sweep most frequently GRSM site, while pollutants transported from eastern sector (i.e., eastern, northeast, or southeast) have limited influence (< 10%) on air quality in the Great Smoky Mountain national park. Air masses originated from Ohio Valley or traveling through north (i.e., far north (FN) or close north (CN)), a region marked by high level of NOₓ emissions, account for more than one quarter of total trajectory number. Examination of pollutants associated with these individual clusters reveals that the highest O₃ concentrations are associated with
trajectories from the north and southwest directions, which can be tracked back to Ohio Valley region and coastal region along Gulf of Mexico, respectively.

The processes, as well as their magnitude, responsible for the formation and removal of reactive nitrogen oxides are examined using a comprehensive 3-D air quality model (MAQSIP). Process budget analysis shows that the major contributions to fresh nitrogen oxides (i.e., NO$_x$) at the two locations come from horizontal advection (58 – 62%) and local emissions (38 - 42%), and the primary removal process for NO$_x$ is local chemistry (92 – 95%). The actual magnitudes of corresponding processes at MACA are more than 3 times larger than that at GRSM, which matches the observational results (1.2-4.8 times, Tong et al., 2003). Similar analysis of oxidized nitrogen oxides, i.e., NO$_z$, reveals that 84% of NO$_z$ is the result of local chemistry at MACA, which only accounts for 32% at GRSM; the rest comes from transport. About half of NO$_z$ is removed by dry deposition at GRSM, while the rate at MACA is 87%; the rest is removed through transport. Further comparison between the process budgets of NO$_z$ and that of O$_3$ reveals the similarity among the locations as well as the contributions of each individual process at each location is apparent, especially on the production or accumulation side. Chemistry contributions of 32% and 84% to NO$_z$ correspond to 26% and 80% to O$_3$ at GRSM and MACA, respectively. The similarity between NO$_z$ and O$_3$ process budgets serves as further evidences of close association between nitrogen oxides and effective O$_3$ production at these rural locations. One may note that this modeling study is limited to summer time when biogenic emission is most active. High ozone events in southeast national parks, however, have been frequently observed in seasons other than summer, during which the ozone photochemistry may be characterized by non-NOx-limiting
condition. One of the recent findings by the NASTRO suggests that this may be an over simplification that VOC or NO\(_x\) limitation is not uniquely defined by location or emissions (NARSTO, 2002). Further efforts are needed to address the seasonal characteristics of ozone and its precursors that contribute to shape air quality in the southeast national parks.

### 6.3 On the High Ozone Episodes: Temporal Distributions and Case Studies

Over 40% of the ozone non-attainment areas of the United States are in the Southeast [Southern Oxidants Study (SOS), Fehsenfeld et al., 1993]. Implementation of the new National Ambient Air Quality Standard (NAAQS) proposed by US EPA in 1996 is expected to label more Southeast locations as non-attainment areas. This study examined annual, seasonal, diurnal distributions, as well as case studies of some high ozone episodes observed during a multiple-year enhanced monitoring campaign at two class I Southeast national parks, namely, the Great Smoky Mountain (GRSM) and Mammoth Cave (MACA) national parks.

Even though the level of nitrogen oxides and CO presented at MACA site are considerably higher than those at GRSM site over all seasons, the number of high ozone episodes is much larger at GRSM than at MACA. The difference is attributed to lower ozone production efficiency of NO\(_x\), limited by available hydrocarbons, at MACA site and influx of majority ozone by transport to GRSM site. There are no continuous increases in either annual exceedances or the 4\(^{th}\) highest ozone concentration at both sites, but a long-term increasing trend can be identified from measured data. During the first half of measurement period, i.e., 1990-1995, the 8-hour averaged ozone exceedances are
6.2 per year at GRSM site and 1.3 per year at MACA site. The later half, 1996-2002, experiences more than 3 times of increase at both sites. The averaged ozone exceedances are 20.9 per year at GRSM site and 5.7 per year at MACA site. Similarly, the averaged 4th highest ozone concentration has increased from 89.8 ppbv to 99.0 ppbv at GRSM site, and from 78.2 ppbv to 87.3 ppbv at MACA site. Given the nationwide decreasing trend, the significant increase of high ozone events over last decade are calling for further efforts in implementing ozone control related to rural Southeast locations.

For GRSM site, most frequent exceedances occur in August. Exceedances in July are least significant among all photochemically active seasons (May to September). As to MACA site, the maximum exceedances are found in June or August. It is interesting to note that neither site shows a mid-summer (July) maximum of ozone exceedence number. This phenomena can be partially explained by the fact that concentration of nitrogen oxides reaches its minimum in mid-summer. Another hypothesis, proposed by Kang et al. (2003), suggests that it is possible that high level of biogenic hydrocarbons emitted in July dampen ozone concentration from surpassing NAAQS standard by removal of nitrogen oxides through formation of inert organic nitrogen. Analysis of seasonal distribution of ozone exceedances also reveals that high ozone events are widely distributed in late spring, summer, and early fall. Considering the significant seasonal variations of ozone precursors as well as meteorological parameters, ozone control strategies aiming to reduce summertime ozone may not be efficient over all periods of ozone exceedences.

Diurnal distribution of exceedance occurrences shows that high ozone episodes occur most frequently after sunset, and least frequently in early morning at high elevation.
High ozone episodes can be observed in any hour during all photochemically active seasons, no matter if sunlight available or not. Maximum exceedances at MACA site, however, are seen in the midday, and extend into a few hours after sunset. There are no ozone exceedances between midnight and early morning. Combination of transport and photochemistry can explain the mainly daytime distribution of ozone exceedances observed at MACA site. After sunset, the formation of stable NBL prevents air masses with higher level of ozone from reaching the surface while other depletion mechanism such as dry deposition and titration by fresh nitrogen oxides can work further to lower ozone to a level under exceedance standard. GRSM site, however, is always swept by air masses containing higher level of ozone and ozone is not subject to most depletion mechanisms presented at low elevation site such as MACA.

While the air masses associated with ozone exceedences at GRSM site originated from all directions, those with high O₃ at MACA, however, reveal dominant transport originated from southwest with, very few exceptions from north. Such an inter-site difference suggests that high level of O₃ can be formed under various meteorological conditions at GRSM site, while that at MACA site, which stands at northern to GRSM, are dominated by transport from southwest region. This suggests that the increasing trend of ozone exceedences discussed in earlier section may bring up a larger scale air quality issue rather than just a local non-attainment problem.

Case studies of typical ozone episodes, mainly in seasons other than summer, are performed to examine both inter-site and inter-season difference that contribute to shape high ozone formation. Two early September cases show that high nitrogen oxides concentration is the main driver to elevate ozone concentration to exceedance level at
MACA site while ozone transport from polluted area works to form exceedences at GRSM, a mountain top site. Almost all high ozone episodes at MACA site are found developed with clear sky, high temperature, low relative humidity, as well as weak anticyclones traveling in a uniform anti-cyclonal pathway surrounding a high-pressure area. High ozone episodes observed at mountain site, however, are not necessary to be associated with these factors, which have been viewed as typical of regional-scale pollution episodes in the eastern United States. One should also note that compared to other cases in late May or even early September, ozone concentration in late September case are much less weakly correlated with NO\textsubscript{y}. This phenomenon has been interpreted as a seasonal transition from NOx- to VOCs-limited conditions to ozone production caused by declined solar radiation and humidity, as well as biogenic hydrocarbon emissions.

The results summarized above may broach further discussion on ozone control issue in Southeast United States. Under the 1-hour average NAAQS standard, neither the Great Smoky national park nor the Mammoth Cave national park was categorized as non-attainment areas for ozone. However, application of the new 8-hour NAAQS standard renders both national parks to violate the ozone standard at least since 1995. The more stringent NAAQS standard, as well as the unusual increasing trend in these areas against the national decreasing tendency and the considerable human exposure to ozone in these class-I national parks, is calling for more attention to implement a more effective ozone control strategy in these rural areas. Moreover, the facts that ozone exceedences are widely distributed over spring, summer, and fall, and that maximum frequency of ozone exceedences consistently appear out of mid-summer, bring further challenge to design a successful ozone debasement strategy for rural southeast region. Investigating seasonal
characteristics of ozone key precursors and their contribution to photochemical production of ozone will be essential to make such strategy more efficient. While this study presents only data collected in the past thirteen years, more measurement data, as well as modeling study, will be needed to verify the long-term trend and evaluate the functionality of control policies.
Appendix 1. Measurement and modeling of ammonia emissions at waste treatment lagoon-atmospheric interface

Viney P. Aneja, Brahm P. Malik, Quansong Tong and Daiwen Kang

Department of Marine, Earth and Atmospheric Sciences
North Carolina State University
Raleigh, NC 27695-8208, U.S.A.

John H. Overton

1911 Fountain Ridge Road
Chapel Hill, NC 27514, U.S.A.

Global emission of ammonia is approximately 75 Tg N/yr (1 Tg = 10^{12} g). The major global source is excreta from domestic animals, ~32 Tg N/yr. Waste treatment lagoons are used to treat the excreta of hogs in North Carolina. Proteins and nitrogen-rich compounds in the lagoon are converted to ammonia, through a series of biological and chemical transformation. The process of ammonia emission has been investigated using two different model approaches: (1) Coupled Mass Transfer and Chemical Reaction Model, and (2) Equilibrium Model. A sensitivity analysis is performed with the models and the model results are compared and contrasted with ammonia emission experiments performed at swine waste treatment facilities in NC using an emission flux chamber system.

Results of model predictions of flux indicate an exponential increase in ammonia flux with increasing lagoon temperature and pH, a constant increase with increasing lagoon total ammoniacal nitrogen (TAN), and a second degree increase with the increasing wind speed. In addition, the fluxes predicted by the coupled mass transfer and chemical reaction model are consistently larger than fluxes predicted by the equilibrium model. In comparison to experimental values of flux, model predictions agreed well, with the experimental values lying in different positions between the two model predictions under different physical and chemical conditions. Further, when compared to diurnal and seasonal experimental flux values the coupled mass transfer and chemical reaction model would corroborate the results in calm meteorological conditions (wind speed U_{10} \leq 1.5 m/s). However, the observed results are better predicted by the equilibrium model on unstable occasions when wind speeds are higher than 2.0 m/s and physical transfer process functions dominantly.

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Appendix 2. Measurements and Analysis of Criteria Pollutants in New Delhi, India

Viney P. Aneja, A. Agarwal*, Paul A. Roelle, Sharon B. Phillips, Quansong Tong, Nealson Watkins and Richard Yablonsky

Department of Marine, Earth and Atmospheric Sciences
North Carolina State University, Raleigh, NC 27695-8208 USA

* Center for Science and Environment, New Delhi, 110062, India

Ambient concentrations of Carbon Monoxide (CO), Nitrogen Oxides (NO$_x$), Sulfur Dioxide (SO$_2$) and Total Suspended Particulates (TSP) were measured from January 1997 to November 1998 in the center of downtown (the Income Tax Office (ITO) located on B.S.G. Marg) New Delhi, India. The data consists of 24-hour averages of SO$_2$, NO$_x$, TSP; and 8 and 24-hour averages of CO. The measurements were made in an effort to characterize air pollution in the urban environment of New Delhi and assist in the development of an Air Quality Index. The yearly average CO, NO$_x$, SO$_2$ and TSP concentrations for 1997 and 1998 were found to be 4810 ± 2287 μg m$^{-3}$ and 5772 ± 2116 μg m$^{-3}$; 83 ± 35 μg m$^{-3}$ and 64 ± 22 μg m$^{-3}$; 20 ± 8 μg m$^{-3}$ and 23 ± 7 μg m$^{-3}$; 409 ± 110 and 365 ± 100 μg m$^{-3}$ respectively. In general, the maximum CO, SO$_2$, NO$_x$ and TSP values occurred during the winter with minimum values occurring during the summer, which can be attributed to a combination of meteorological conditions and photochemical activity in the region. The ratio of CO to NO$_x$ (~50) indicates that mobile sources are the predominant contributors for these two compounds in the urban air pollution problem in New Delhi. The ratio of SO$_2$ to NO$_x$ (~0.6) indicates that point sources are contributing to SO$_2$ pollution in the city. The averaged background CO concentrations in New Delhi were also calculated (~1939 μg m$^{-3}$) which exceed those for Eastern USA (~500 μg m$^{-3}$). Further, all measured concentrations exceeded the US National Ambient Air Quality Standards (NAAQS) except for SO$_2$. TSP was identified as exceeding the standard on the most frequent basis.

Published in:
Appendix 3. Measurement and modeling of ammonia emissions at waste treatment lagoon-atmospheric interface

Viney P. Aneja, Brahm P. Malik, Quansong Tong and Daiwen Kang

Department of Marine, Earth and Atmospheric Sciences
North Carolina State University
Raleigh, NC 27695-8208, U.S.A.

John H. Overton

1911 Fountain Ridge Road
Chapel Hill, NC 27514, U.S.A.

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Results of model predictions of flux indicate an exponential increase in ammonia flux with increasing lagoon temperature and pH, a constant increase with increasing lagoon total ammoniacal nitrogen (TAN), and a second degree increase with the increasing wind speed. In addition, the fluxes predicted by the coupled mass transfer and chemical reaction model are consistently larger than fluxes predicted by the equilibrium model. In comparison to experimental values of flux, model predictions agreed well, with the experimental values lying in different positions between the two model predictions under different physical and chemical conditions. Further, when compared to diurnal and seasonal experimental flux values the coupled mass transfer and chemical reaction model would corroborate the results in calm meteorological conditions (wind speed \( U_{10} \leq 1.5 \text{ m/s} \)). However, the observed results are better predicted by the equilibrium model on unstable occasions when wind speeds are higher than 2.0 m/s and physical transfer process functions dominantly.

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Appendix 4. Trace Gases in the Great Smoky Mountains National Park, TN:
Sources Identification, Origin, and Budget Analysis

Quansong Tong, and Viney P. Aneja

Department of Marine, Earth and Atmospheric Sciences,
North Carolina State University, Raleigh, NC, USA 27695-8208

John D. Ray

Air Resource Division, National Park Science, Denver, Colorado 80225-0287

Trace gas species ozone (O\textsubscript{3}), reactive nitrogen oxides (NO\textsubscript{y}), carbon monoxide (CO), and sulfur dioxide (SO\textsubscript{2}), were measured continuously in the Great Smoky Mountains (GRSM) National Park, TN, from 1995 to 1998 at an enhanced monitoring site. Following four analyses were performed: i) regression analysis; ii) emission inventory analysis; iii) back trajectory analysis; and iv) budget analysis. Multiple linear regression analysis, by taking NO\textsubscript{y} as response variable and CO and SO\textsubscript{2} as factors, reveals that the ratios of [NO\textsubscript{y}]/[CO] are 4.8 for midday and 4.5 for midnight, respectively, while the ratio of [NO\textsubscript{y}]/[SO\textsubscript{2}] displays wide variation both seasonally and diurnally. Regression analysis also provides the background concentrations of CO as 155, 134, 112, 138, and 134 ppbv for spring (March, April and May), summer, fall, winter and overall datasets, respectively. Emission inventory analysis shows that mobile sources dominate NO\textsubscript{x} emissions (72~77\%) in the GRSM national park. Back trajectory analyses suggest the influence of Midwestern originating air masses, stagnant meteorological conditions and vertical transport. Budget analysis of NO\textsubscript{y} using Multiscale Air Quality Simulation Platform (MAQSIP) model shows that the influx by horizontal advection contributes 85\% to the total NO\textsubscript{y} sources, and the dominating processes of NO\textsubscript{y} removal are vertical advection (45\%) and dry deposition (41\%).

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Appendix 5. Measurements, Modeling and Analysis of Ozone, NMHCs, and Other Trace Gases in the Southeast US National Parks

Quansong Tong, Daiwen Kang, and Viney P. Aneja

Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC, USA 27695-8208

John D. Ray
Air Resource Division, National Park Science, Denver, Colorado 80225-0287

Ambient ozone concentrations found in the lower troposphere continues to be a major air pollution problem in the United States. Ozone (O$_3$), as well as nonmethane hydrocarbons (NMHCs), reactive nitrogen oxides (NO$_x$), and carbon monoxide (CO), and sulfur dioxide (SO$_2$), were measured in three Southeast United States national parks from 1995 to 1998 at three enhanced monitoring sites. Emission inventory analysis shows that mobile sources dominate NO$_x$ emissions (72~77%) in the GRSM national park. Multiple linear regression analysis, by taking NO$_y$ as response variable and CO and SO$_2$ as factors, reveals that the ratios of [NO$_y$/[CO] are 4.8 for midday and 4.5 for midnight, respectively, while the ratio of [NO$_y$/[SO$_2$] displays wide variation both seasonally and diurnally. Back trajectory analyses suggest the influence of Midwestern originating air masses, stagnant meteorological conditions and vertical transport. Budget analysis of ozone using Multiscale Air Quality SImulation Platform (MAQSIP) model shows in-situ photochemistry can contribute ~50% of ozone at high elevation site and ~80% at low elevation site.

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A&WMA annual South Atlantic States Section meeting, Research Triangle Park, NC, December 4, 2002.
High ozone episodes observed in rural areas present a serious environmental problem. This study, using both observation-based and modeling techniques, attempts to address chemistry and transport of \( O_3 \) and its key precursors that shape \( O_3 \) pollution in the rural Southeast US. Ozone (\( O_3 \)), as well as nonmethane hydrocarbons (NMHCs), reactive nitrogen oxides (\( NO_x \)), and carbon monoxide (CO), and sulfur dioxide (\( SO_2 \)), were measured in three Southeast United States national parks from 1995 to 1998 at three enhanced monitoring sites. Anthropogenic sources are found dominating the \( NO_x \) emission in the Southeast US. Back trajectory analysis reveals the origin and transport of those air masses containing high level of air pollutants. Budget analysis of ozone using Multiscale Air Quality Simulation Platform (MAQSIP) model shows in-situ photochemistry can contribute \( \sim 50\% \) of ozone at high elevation site and \( \sim 80\% \) at low elevation site. Biogenic VOC components dominate the chemical reactive-based concentration (\( \sim 75\% \)) and are responsible for most high ozone episodes observed in the Southeast National Parks.

**Presented at:**
Appendix 7. Characterizations of fine particulate matter (PM$_{2.5}$) in the Southeast United States

Binyu Wang, Quansong Tong and Viney P. Aneja

Department of Marine, Earth and Atmospheric Sciences
North Carolina State University, Raleigh, NC, USA 27695-8208, USA

Characteristics of ambient fine particulate matter (PM$_{2.5}$) have been investigated with measurement data from seven diversely located sites in Southeast United States during 2000 and 2001. Three of those are categorized as rural sites, while two as inland urban and two as coastal urban sites. The data and interpretation focus on chemical composition, meteorological correlation, and origin of PM$_{2.5}$ presented at the seven measurement sites. Analysis of chemical species provides that sulfate (SO$_4^{2-}$) (27~37%), ammonium (NH$_4^+$) NH$_4^+$ (11~19%), and organic matter (OM)(28~33%) are the common dominant components of PM$_{2.5}$ identifiable at all sites. Total PM$_{2.5}$ mass concentrations are higher during warm seasons (summer and fall) than that in cold season (spring and winter), suggesting summer condition favors the formation of secondary aerosol components such as sulfate and organic matter. Secondary organic carbon (OC$_{sec}$) accounts for approximately 45% of total organic carbon, and about 10% of total PM$_{2.5}$.

Interactions between PM$_{2.5}$ mass and meteorology exhibits a negative dependence on wind speed, and a positive association with temperature. No obvious correlation between PM$_{2.5}$ and relative humidity is found. Finally, origin of pollutant sources is addressed using the combination of back trajectory analysis (HYSPLIT4 model) and hierarchical cluster analysis. Application of this technique to YRK site (Yorkville, GA) reveals that air masses from Northeast direction, extended to North Carolina, are associated with highest PM$_{2.5}$ mass concentration. Massive emission of ammonia in North Carolina and its effect on PM through gas-to-particulate formation is proposed as one way to account for the phenomena.

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The inorganic compounds in the fine particulate matter (PM\textsubscript{fine}) consist of primarily ammonium, sodium, sulfate, nitrate, and chloride, and exist as a solid and/or liquid phase in the particles. Concentrations of these aerosol salts are changed by the transfer time scale between gas to particle phase which is function of the ambient temperature, relative humidity, and their gas phase constituent concentrations in the atmosphere. An observational based analysis of ammonia, acid gases, and fine particles coupled with dispersion model provided the mean $k_S$ rate constant between NH\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} aerosol $\sim 2.29(\pm 2.51) \times 10^{-4}$ m$^3$/$\mu$ mole/sec. The rate constant was found to increase as temperature increases, and decreases with increasing relative humidity. We investigated that the products of measured products of ammonia and nitric acid were generally higher than the theoretical equilibrium constants.

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