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Modeling and Analysis of Ozone and Nitrogen Oxides in the Southeast United States National Parks

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1. Introduction

High O_3 episodes are observed in several eastern US national parks, among which the Great Smoky Mountains National Park by far of the fastest increase in frequency of exceedance days (days when any 8-hour average O_3 concentration exceeding 85 ppbv). It has been well established that the southeast US rural areas are characterized with strong biogenic VOCs emissions and that O_3 production in this region is mostly NOx-limited during summer time. Thus, understanding the contribution of nitrogen oxides to O_3 formation during transport and for local photochemistry is essential to predict what effects the planned reductions in NO_x emissions from large point sources might have on observed O_3 concentrations at these southeast national parks.

Our specific interests in this study are: 1) to quantify the relative importance of point sources and mobile sources to total nitrogen oxides emissions; 2) to identify origins of air masses associated with high levels of nitrogen oxides and O_3; 3) to quantify contributions of individual chemical and physical processes, i.e., chemistry, transport, emission, and deposition, to the budget of production and removal of nitrogen oxides and O_3 in the southeast national parks.

2. Methodology

2.1. Measurements

O_3, NO_y, NO, SO_2, and CO, and meteorological parameters were measured at two enhanced monitoring sites in the southeast United States (TVA, 1995; Olszyna et al. 1998). The Great Smoky Mountains (GRSM) site (35°41′48″N, 83°36′35″W, 1243 m ASL) is located on a ridge in the Great Smoky Mountains

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National Park. The Mammoth Cave (MACA) site (37°13′04″N, 86°04′25″W, 230 m ASL) is located in Mammoth Cave National Park. 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). More detailed information of instruments, experimental techniques, and data QA/QC procedures can be found from Olszyna et al. (1998) and TVA AQ/QC manual.

2.2. *Emission Source Strength: Point vs. Mobile Sources*

According to US EPA, more than 90% of the anthropogenic NO_x ($NO_x = NO + NO_2$) emissions in the United States are from either mobile or point sources (EPA, 1997). Mobile sources emit high levels of CO, but relatively low levels of SO_2, while the reverse is true for point sources. Therefore, it is possible to valuate the relative emission strength using observed pollutant data and the techniques of regression analysis and of emission inventory analysis. The method is described in detail as follows,

Regression Analysis

NO_y is taken as the response variable in a multiple linear regression analysis and the combination of CO and SO_2 as factors. The mathematical expression of the fitted model is:

$$[NO_y] = \alpha[SO_2] + \beta[CO] + \delta \tag{1}$$

where α and β represent the linear coefficients between $[NO_y]$ and $[SO_2]$ and [CO]; δ represents the intercept. After the coefficients, α and β are parameterized, the model can be used to quantify relative contributions from mobile and point sources by plugging in measured CO and SO_2 concentrations. The terms, α, β, and δ in Eq. (1) are estimated using validated measurement data from MACA and GRSM.

Emission Inventory Analysis

Emission inventory analysis obtains the ratio (indicated by x) of NO_y from point sources ($NO_y|_p$) to mobile sources ($NO_y|_m$) from the division of two factors:

$$x = \frac{NO_{y|p}}{NO_{y|m}} = \left[\frac{NSR_p}{NCR_m}\right]\left(\frac{\mu^*[SO_2]}{[CO]-[CO]_{bg}}\right) \tag{2}$$

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. $[CO]_{bg}$ is background CO concentration independent of local processes. An adjusting parameter, μ, is introduced to account for the fraction of SO_2 oxidized into sulfate before arriving at the receptor site. Thus,

$$\text{Fraction of } NO_y \text{ attributed to mobile sources} = 1/(1+x) \tag{3-a}$$
$$\text{Fraction of } NO_y \text{ attributed to print sources} = x/(1+x) \tag{3-b}$$

2.3. Trajectory-Cluster Analysis

Origin of air masses approaching a receptor site is investigated by a combination of cluster analysis (Dorling, et al., 1992) of Hybrid Single-Particle Lagrangian Integrated Trajectories (HY-SPLIT) model output (Draxler, 1997) and emission source categorization based on EPA emission inventory (EPA, 2001). This method aims to maximize inter-group variance and to minimize within-group variance. The algorithm chosen in this study is the one proposed by Dorling (1992).

2.4. MAQSIP Model

A comprehensive 3-dimentional Eulerian grid model called Multiscale Air Quality SImulation Platform (MAQSIP) (Odman and Ingram, 1996) is employed to study the production and removal processes of nitrogen oxides and O_3 in the southeast US national parks. One of MAQSIP's 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, making it possible to conduct process budget analysis for each modeled species (Kang et al., 2003). In this study, we analyze process budgets for modeled nitrogen species and O_3.

3. Results and Discussion

3.1. Source Apportionment of Nitrogen Oxides

Both methods discussed in section 2.2 have been used to quantify the relative contribution of point sources to total nitrogen oxides emissions. Relative contribution of point source to NO_y are given in Table 1 for each season at GRSM and MACA as well as results from previous studies for other locations in Eastern US sites (Stehr et al., 2000).

TABLE 1. Estimation of contribution of point sources to total NOy emissionat Eastern US sites.

Sites	Periods	Regression Analysis	Emission Inventory Analysis
GRSM, TN[a]	Spring (MAM)	23%	34%
	Summer (JJA)	16%	22%
	Fall (SON)	20%	21%
	Winter (DSF)	30%	38%
	All Data	23%	26%
SHEN, VA[b]	September-Dec.	29±5%	30±8%
MACA, KY[a]	Spring (MAM)	25%	53%
	Summer (JJA)	21%	40%
	Fall (SON)	29%	42%
	Winter (DSF)	33%	47%
	All Data	27%	45%
Wye, MD[b]	Sept.-Dec.	11±5%	16±4%
Arendiville, PE[b]	June-September	21±3%	26±6%

[a] 95% confidence interval on the mean; [b] Stehr. et al., 2000.

Both analyses show a lower fraction of NO_y from point sources in summer and fall, and higher in winter and spring. Point sources contribute 16–22% and 30–38% to total reactive nitrogen oxides in summer and winter at GRSM, and 21–40% and 33–47% at MACA.

3.2. Influence Areas Based on Trajectory-Clustering Analysis

Individual trajectories in 1996 were calculated using the HSPLIT-4 model for those days when simultaneous measurements of O_3 and NO_y were available at GRSM. The whole trajectory set was then clustered into seven groups using the clustering algorithm discussed by Dorling (1992). A seed trajectory, i.e. a trajectory that can minimize the average Root Mean Square Deviation (RMSD) for all other trajectories within a cluster, was selected out of each cluster. Figure 1 illustrates the resulting seed trajectories from each cluster. Each seed trajectory is labeled with the direction best describing the relative position of its origin and general path to the receptor site. The number in parenthesis shows the percentage of trajectories assigned to a particular cluster. Emission density of NO_y, taken from the EPA county-based emission inventory (EPA, 2001), is displayed as the background in Figure 1 to provide a visual indicator of regional emission levels that

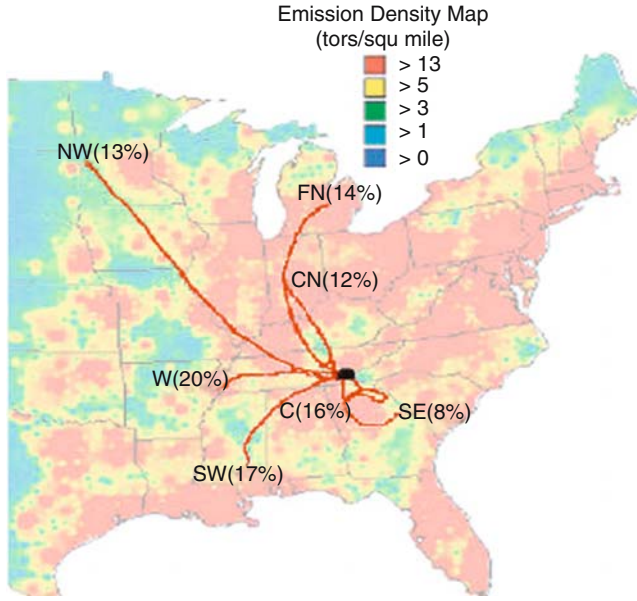

FIGURE 1. Average trajectory of air masses approaching the Great Smoky Mountain (GRSM) National Park, TN. Each average trajectory is labeled with the relative position of its origin to the receptor site. The number in the parenthesis shows the percent of the trajectories assigned to a particular cluster. The background is emission density of NO_y taken from EPA (1999).

might be loaded into those air parcels following a cluster trajectory. Figure 1 shows that air masses from west (W, 20%) and southwest (SW, 17%) sweep GRSM most frequently, while pollutants transported from the eastern half (i.e., Eastern, Northeast, or Southeast) have limited influence (< 10%) on air quality in the Great Smoky Mountain National Park.

3.3. Process Budget Analysis of Nitrogen Oxides by MAQSIP

Process budget analysis using MAQSIP shows that although 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 as large as that at GRSM, which matches the observational results (1.2-4.8 times, Tong et al., submitted manuscript, 2004). However, 84% of NO_z, the oxidized products of NO_x, is the result of local chemistry at MACA, which only accounts for 32% at GRSM; the rest comes from transport. If we compare the process budgets of NO_z with that of O_3 (Figure 2, 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. Similarity between NO_z and O_3 process budgets further demonstrates that NO_z can be used as evidence of close association between nitrogen oxides and effective O_3 production at these rural locations.

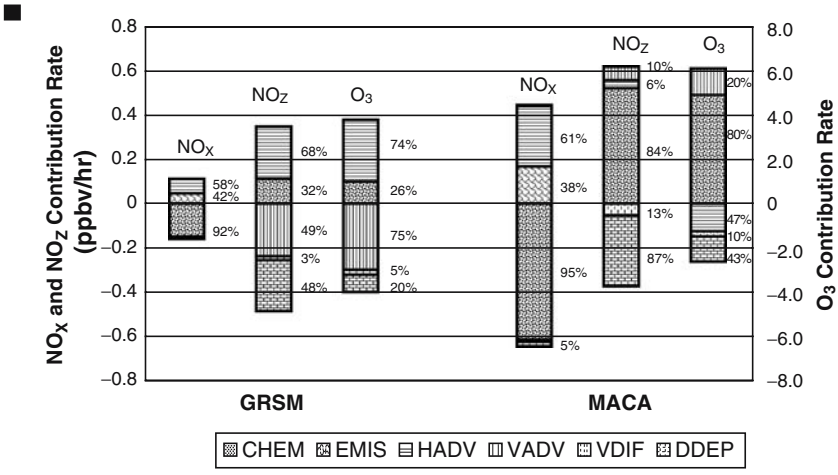

FIGURE 2. Process budget analysis of NO_x, NO_z, and O_3 using MAQSIP in the chosen domain during the 1995 summer time.

4. Conclusions

This study focuses on both observation-based and modeling analyses in elucidating source attribution, influence area, and process budget of reactive nitrogen oxides at two rural southeast national parks. Using two independent observation-based techniques, we demonstrate that point sources contribute a minimum of 23%~26% and 27%~45% of total NO_y at GRSM and MACA respectively. The influencing area, or origin of nitrogen oxides, is investigated using trajectory-cluster analysis. The result shows that air masses from western and southwest regions sweep over GRSM most frequently, while pollutants transported from the eastern half has limited influence (< 10%) on the air quality in the Great Smoky Mountain National Park. Processes budget analysis using MAQSIP reveals similarities between NO_z and O_3 process budgets, which serve as further evidences of close association between nitrogen oxides and effective O_3 production at these rural locations.

Acknowledgements This research was funded by the National Park Service, Air Resources Division, cooperative agreement #4000-7-9003. The authors thank Dr. Rohit Mathur in MCNC for his help in the modeling and data processing, and Ms. Binyu Wang at North Carolina State University for her assistance in statistical analysis. Thanks to Bob Carson, Scott Berenyi, and Jim Renfro (NPS), and to Ken Olszyna (TVA) for their efforts in collecting the measurement data.

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Speaker: Tong

Questioner: A. Ebel

Question: Budget calculations have been carried out for different processes, among them horizontal and vertical advection. What is the net effect of both in the examples presented in the paper?

Answer: The net effects of horizontal and vertical advections can be calculated from figure 2 in our full manuscript, as well in the corresponding figures in my presentation.

Questioner: S. T. Rao

Question: Have you looked at ozone data in the post-1998 period to assess whether ozone has been improving in the southeast? As you know, there are substantial decreases in the NOx emissions in the post 2001 period. It would be good to examine the linkages between emission reductions and ozone concentrations.

Answer: This has been covered in another one of our papers, which talks about ozone observations after 1998 from the same sites. It has been reported that NOx cut so far has not contributed too much to O_3 reductions, since the benefits of decreasing emissions of NOx are partially offset by an increase in the O_3 production efficiency of remaining NOx.

Questioner: D. Cohan

Question: In regressing NO_y against SO_2 and CO, how do you account for the fact that the ratios of these pollutants change during transport from an emissions source to a receptor?

Answer: We have applied an oxidizing parameter to account for the pollutants change during transport in the emission inventory analysis. For regression analysis, we assume the coefficients obtained by regression analysis of real-world measurements have taken into account the changes due to transformations during transport.

Questioner: R. Bornstein

Question: Could the reduction in reactive organics be postponing the location of ozone max to the Parks, and thus have caused the increase in "bad" days from the '80's to the '90's?

Answer: It depends. Our budget analysis shows that while local photochemistry is important at Mammoth Cave national park, O_3 in the Great Smoky Mountains national park is dominated by transport and regional O_3 background. Apparently both sites are subject to upwind emissions, particularly that of NOx.