Technical Note

Observed and modeled VOC chemistry under high VOC/NO$_x$ conditions in the Southeast United States national parks

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Abstract

In airsheds that contain high volatile organic compounds (VOCs) and low NO$_x$ ($=$ NO $+$ NO$_2$) concentrations, ozone (O$_3$) production may be significantly suppressed by NO$_x$ reactions that lead to the formation of organic nitrates. O$_3$ and its precursors (VOCs and NO$_x$) ambient levels simulated using a regional-scale photochemical model, called Multiscale Air Quality Simulation Platform, are analyzed and compared to observed data from three southeast United States national parks.

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1. Introduction

High ozone (O$_3$) concentrations are attributed to the oxidation of NO$_x$ with the presence of excessive amounts of biogenically emitted Volatile Organic Compounds(VOCs) such as isoprene (Chameides et al., 1988; Trainer et al., 1987) in the southeast US rural areas during summer (Chameides et al., 1997; Heck et al., 1984). The new 8-h O$_3$ National Ambient Air Quality Standard (NAAQS) (0.085 ppmv) is likely to bring even more suburban and rural locations into noncompliance (Chameides et al., 1997). Biogenic VOCs emitted by vegetation (Fehsenfeld et al., 1992; Lamb et al., 1993; Fuents et al., 2000) and anthropogenic VOCs emitted by human activities are both widely present in the rural areas (Hagerman et al., 1997; Kang et al., 2001). Previous studies indicate that the influence of these VOCs on O$_3$ production can be significant (Trainer et al., 1987; Liu et al., 1987; Geron et al., 1994). Recent studies indicate that the VOC emission rates used in the current air quality models (Kang et al., 2003; Palmer et al., 2003) for developing control strategies may be low by a factor of 2 to 10.

The O$_3$-production mechanism in the literature is often illustrated using O$_3$ isopleths (Dodge, 1977). When the ratios of nonmethane hydrocarbons (NMHCs) to NO$_x$ are larger than 15:1 in the Empirical Kinetic-Modeling Approach (EKMA), the maximum O$_3$ concentration is not very sensitive to the hydrocarbon concentrations. In general, the current understanding is that under non-NO$_x$-limited conditions with the increase

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of VOC concentrations O_3 production increases, but under NO_x-limited conditions, the increase of VOC concentrations has no effect on O_3 production. In this study, we have found that in airsheds containing high VOC/NO_x ratios, O_3 production may be significantly suppressed by reducing NO_x through formation of organic nitrates.

2. Measurement description

One-hour integrated ambient-air samples for the determination of VOCs were collected using canisters (a single measurement at local noon for each day) at the three US national parks: Shenandoah National Park, Big Meadows (SHEN) located at 38°31′21″ N, 78°26′09″ W (1073 m), Great Smoky Mountains National Park Cove Mountain (GRSM) located at 35°41′48″ N, 83°36′35″ W (1243 m), and Mammoth Cave National Park (MACA) at 37°13′04″ N, 86°04′25″ W (219 m) (Table 1) during June through July for the years 1995–97. Samples were collected from 10 m above the ground. Hourly average O_3, NO, NO_y, CO, SO_2, and meteorology measurements during this period are also available. In the analysis of VOC samples, standards both for retention time and quantification, were run routinely; and four internal standards were added to every chromatographic run to verify performance of the analytical system (Farmer et al., 1994). Identification of the target compounds was confirmed by mass spectrometer analysis. The method detection limit is 0.10 parts per billion carbon (ppbC), with an uncertainty of ±20%. Any target compounds not detected in the sample above 0.10 ppbC were reported as not detected (ND) and were not included in any statistical analysis. The quality of the data is further guaranteed through correlation and ratio analysis. Further details on the measurement and data analysis may be found in Kang et al. (2001).

Table 1
Observed and model predicted mean NO and NO_y concentrations (ppb)

| | NO | | NO_y[a] | |
	OBS[b]	MOD	OBS	MOD
GRSM	0.1	0.1	3.2	5.4
MACA	0.3	0.4	5.0	9.6
SHEN	NA	NA	6.1	6.6

[a]NO_y in the observed data is the measured total oxidized nitrogen compounds and in the model data, it includes NO, NO_2, N_2O_5, HNO_4, HONO, NO_3, HNO_3, and PAN.
[b]OBS: the observed mean concentrations during modeling period (14th July to 29th July, 1995), MOD: the model predicted mean concentrations during the same period, NA: the data are not available at this location.

3. Model description

The Multiscale Air Quality Simulation Platform (MAQSIP) (Odman and Ingram, 1996) is a comprehensive Eulerian grid model that has also served as a prototype for the US EPA's Models-3 concept (Dennis et al., 1996; Byun and Ching, 1999). The modeling system is configured to include a detailed treatment of horizontal and vertical advection, turbulent diffusion based on K-theory, gas-phase chemical transformations using a modified version of the CBM-IV chemical mechanism (Gery et al., 1989; Kasibhatla et al., 1997), anthropogenic and natural emissions, dry deposition, and mixing and attenuation of photolysis rates due to the presence of clouds. Further detailed model description and simulation scenarios may be founded in Kang et al. (2003).

4. Relationship between O_3 and VOCs

Fig. 1 shows data collected in three southeast United States National Parks during summers from 1995 to 1997 (Kang et al., 2001) from SHEN, elevation 1073 m, GRSM, elevation 1243 m, and MACA, elevation of 219 m. In these airsheds, when VOC concentrations are less than ~50 ppbv, O_3 concentrations increase with increasing VOC concentrations, while when VOC concentrations are greater than ~50 ppbv, O_3 concentrations decrease with increasing VOC concentrations.

5. Modeled and measured hydrocarbon reactivity

To evaluate the relative importance of any VOC species in oxidant chemistry in its reaction with OH, Mathur et al. (1994) defined a reactivity-weighted
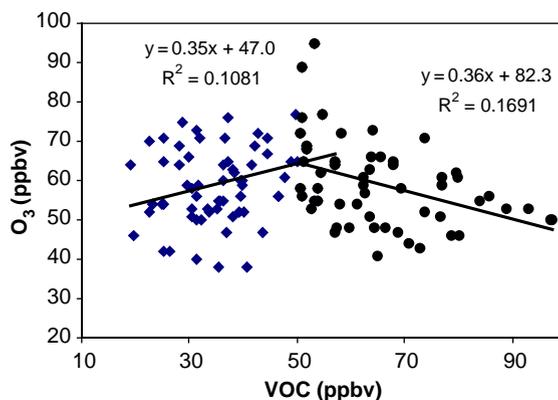
Fig. 1. Relationship between observed O_3 and VOC concentrations at three national park locations.

organic (RWOG) based on the typical reaction between a VOC species (RH) of concentration C_j and OH,

$$RH + OH \rightarrow R\bullet + H_2O \tag{1}$$
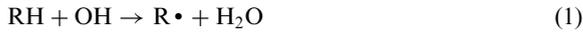
as

$$RWOG = \sum_{j}^{N} K_{OH}(j)C_j, \tag{2}$$

where N is the number of organic classes (explicit compounds and generalized reactivity classes) in the chemical mechanism and $K_{OH}(j)$ is the rate constant of the reaction between OH and the organic species (j), taken at 298°K. In this study, the concept of RWOG was extended to evaluate the impact of hydrocarbon reactivity on O_3 production. Fig. 2 indicates that with the increase of RWOG hydrocarbon reactivity, the mean daily maximum O_3 concentrations are predicted to increase initially, then reach a maximum, and decrease after that point. Observed data (the observed VOCs are lumped according to the CB4 mechanism. Refer to Kang et al., 2003 for details) are plotted for GRSM and MACA for comparison to the simulation trends. The observed values at both the national park locations are on the decreasing phase of the variation pattern, suggesting that hydrocarbon concentrations are at such a level that suppression of O_3 production is occurring.

6. Why O_3 production is reduced by increased hydrocarbon emissions: a hypothesis

It has been recognized that some hydrocarbons, especially biogenic hydrocarbons, react with O_3 (Atkinson, 1994). However, this reactivity is slow $(k = \sim 10^{-17} \mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ for the reaction between isoprene and O_3). Moreover, isoprene and some other reactive species can lead to the formation of organic nitrate compounds (Gery et al., 1989; Carter, 1996; Carter and Atkinson, 1996; Kasibhatla et al., 1997; Meagher et al., 1998). In the formulation of the Carbon Bond Mechanism 4 (CB4) that is popular in current chemistry/transport air quality models and is also used in this study, two universal peroxy radical operators, XO2 and XO2N, are used as surrogates for organic peroxy radicals that are produced by the oxidation of anthropogenic and biogenic hydrocarbons, mainly including the following reactions:

$$ISO3 + NO \rightarrow ISN, \tag{R1}$$

$$ISO4 + NO \rightarrow ISN, \tag{R2}$$

$$ISNT + NO \rightarrow DISN, \tag{R3}$$

$$MVI + NO \rightarrow MVNT, \tag{R4}$$
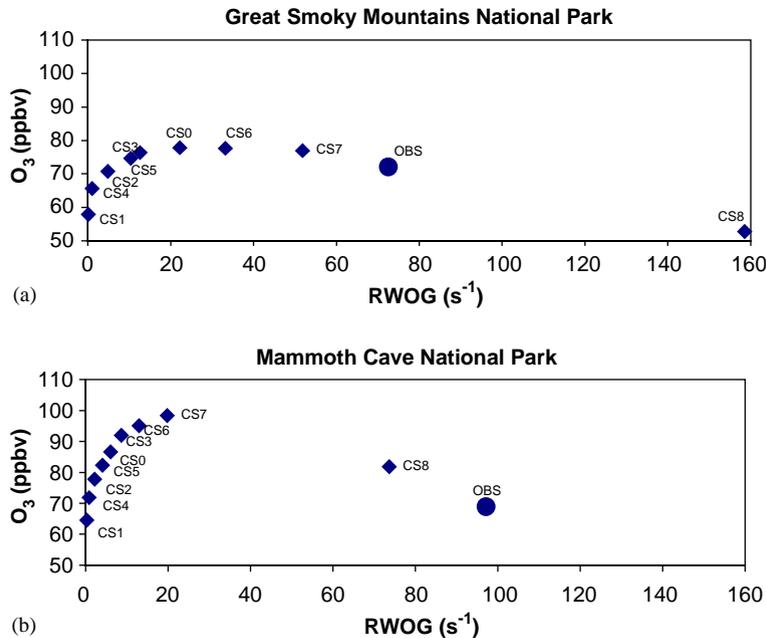
Fig. 2. (a,b) Variations of the mean daily predicted and observed maximum O_3 concentrations on a reactivity-weighted organic (RWOG) scale. OBS (dot) is observed values. Diamonds are model simulations values from different emission scenarios (CS0-CS8 are simulation scenarios, refer to Kang et al. (2003) for details).

$$BZO2 + NO_2 \rightarrow PBZN, \tag{R5}$$

$$PHO + NO_2 \rightarrow NPHN, \tag{R6}$$

$$CRO + NO_2 \rightarrow NCRE, \tag{R7}$$

Where ISO3 and ISO4: isoprene O-adduct, ISN and ISNT: nitrate of isoprene, DISN: dinitrate of isoprene, MV1: methylvinyl ketone OH-adduct, MVNT: methylvinyl ketone nitrate, BZO_2: peroxybenzoyl radical, PBZN: peroxybenzoyl nitrate, PHO: Phenoxy radical, NPHN: nitrophenol, CRO: methylphenoxy radical, and NCRE: nitrocresol.

Eqs. (R1)–(R4) are isoprene reactions, and Eqs. (R5)–(R7) are reactions for aromatic surrogate TOL. The typical rate constants for all these reactions are in the range of $\sim 10^{-11}$–10^{-12} cm^3 molecule^{-1} s^{-1}, which are comparable to most of the VOC and OH reactions and inorganic reactions of NO and NO_2. The organic nitrate compounds formed from these reactions are stable under normal atmospheric conditions and may eventually be removed through gas and/or aerosol deposition. Fig. 3a maps the mean reduction in predicted ambient NO_x due to the above reactions, when isoprene (ISOP) hydrocarbon emissions are increased by a factor of 3, while other hydrocarbon
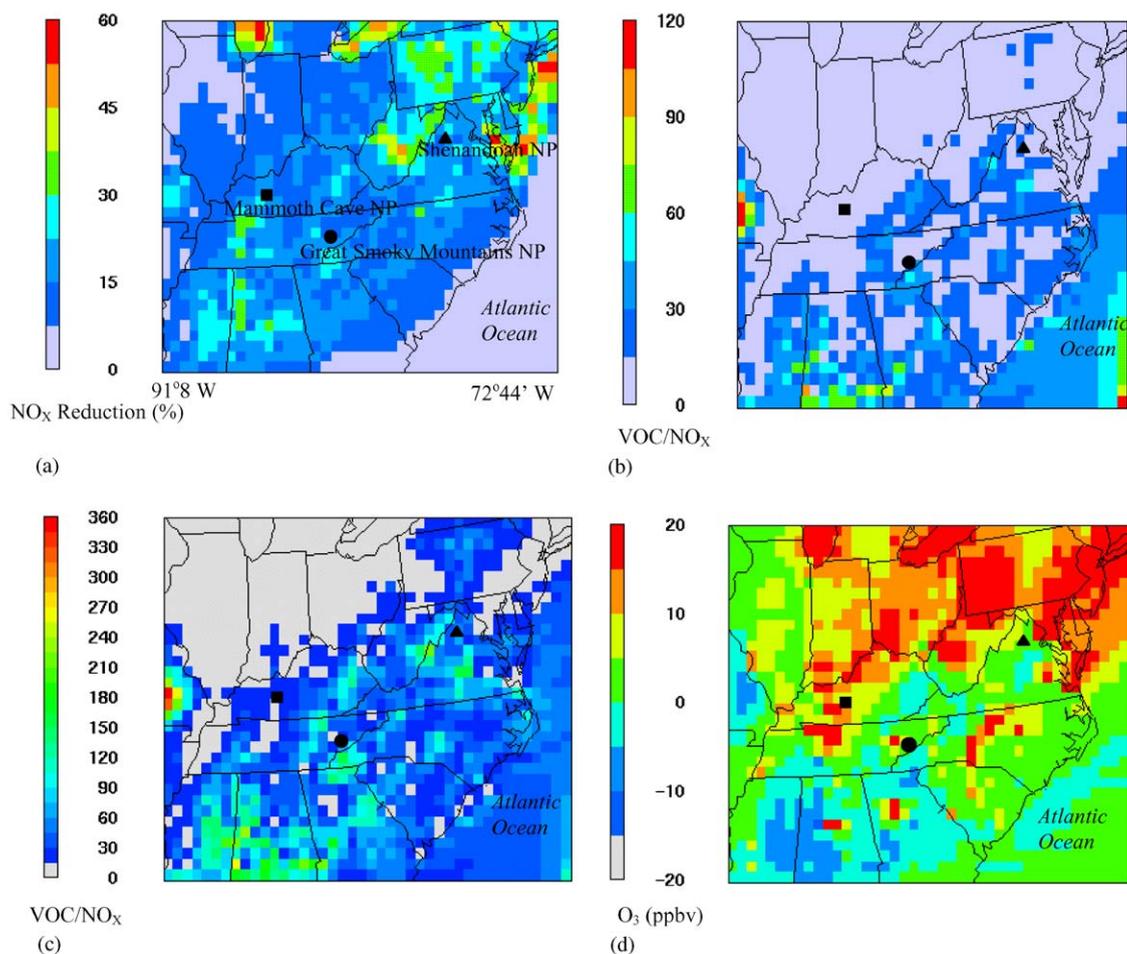
Fig. 3. Output maps from the MAQSIP simulations for the southeast United States: (a) Average NO_x reduction (%) for the scenario with tripled ISOP emissions. NO_x reduction is defined as:

$$\frac{C_{NOx}^b - C_{NOx}^d}{C_{NOx}^b} \times 100,$$

where C_{NOx}^b and C_{NOx}^d are NO_x concentrations at the Base Scenario and at the $3 \times$ ISOP Scenario with tripled ISOP emissions, respectively, (b) Average HC/NO_x ratios for the Base Scenario, (c) Average HC/NO_x ratios when ISOP emissions are increased by a factor of three, $3 \times$ ISOP Scenario, (d) Average differences between O_3 concentrations (ppbv) predicted by the $3 \times$ ISOP scenario with increased VOC from ISOP emissions and the Base Scenario.

species (PAR, ETH, OLE, TOL, XYL) (Gery et al., 1989) were kept at the same level as the Base Scenario. The mean reduction in NO_x varies from 0% to about 60% across the modeling domain with the highest reduction occurring in the northeast of the domain. However, the impact on O_3 production is not dependent just on changes in ambient NO_x, but also on the change of the hydrocarbon to NO_x ratio (VOC/NO_x). Fig. 3b and Fig. 3c present VOC/NO_x ratios for the Base Scenario and the $3 \times$ ISOP scenario with increased isoprene emissions. In the Base Scenario, less than half of the modeling domain has VOC/NO_x ratios greater than 15:1 that would be considered as NO_x-limited areas, most of these areas are located in the southeast of the modeling domain. But in $3 \times$ ISOP Scenario (Fig. 3c), the areas that have VOC/NO_x ratios greater than 15:1 extend to more than $\frac{2}{3}$ of the modeling domain. Even though the greatest reductions in ambient NO_x reduction ($>50\%$) occur in the north and northeast region of our domain, the VOC/NO_x ratios in the higher emission scenarios are still low in these regions. Some of those areas are still lower than 15:1 ratio level. Within these regions, O_3 production is not reduced by the reduction of NO_x, but rather increased because of the increase in the VOC/NOx ratio.

Fig. 3d presents the average difference between O_3 concentrations predicted by the $3 \times$ ISOP Scenario with increased ISOP emissions and the Base Scenario. In the regions with lower VOC/NO_x ratios, mainly in the northern areas of the model domain, O_3 production is increased by the higher ISOP emissions. In the regions with higher VOC/NO_x ratios, in the south and southwest of the model domain, O_3 production is suppressed by the higher ISOP emissions. This result would be obtained by high VOC/NO_x ratios either from increasing reactive organics or decreasing NO_x.

As illustrated here by the model scenarios and data collected in rural areas, when biogenic ISOP is emitted into areas otherwise characterized as having low VOC and NO_x, ozone production can be suppressed by the added emissions. The VOC/NO_x ratios as a result are far outside the normal range of isopleths O_3 charts thought to characterize urban areas. The non-linear chemistry involved is not easily labeled either as NO_x-limited or VOC-limited chemistry. This model simulation represents only a short period in July 1995, but it suggests some unexpected results that deserve further modeling and comprehensive measurements at a wider variety of rural monitoring locations to verify.

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