Seasonal transition from NOx- to hydrocarbon-limited conditions for ozone production over the eastern United States in September

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Abstract. Concentrations of O3, CO, NO, total reactive nitrogen oxides (NOx), H2O2, and HCHO were measured from September 4 to October 1, 1990, at a mountain ridge site in Shenandoah National Park, Virginia. The data show evidence for a transition from NOx-limited to hydrocarbon-limited conditions for O3 production over the course of September. The transition is diagnosed by large decreases of the H2O2/(NOx-N02) and HCHO/(NOx) concentration ratios, weakening of the correlation between O3 and NOx concentrations, and decrease of the slope O3/NOx. A high-O3 episode occurring in late September was associated with only 34 ppbv H2O2, indicative of hydrocarbon-limited conditions. A seasonal transition in photochemical regime over the eastern United States in September would be expected from theory; the production rate of odd hydrogen radicals decreases by a factor of 2 over the course of the month, due to decreasing UV radiation and humidity, allowing HNO3 production to become the dominant sink for odd hydrogen in the boundary layer and resulting in hydrocarbon-limited conditions for O3 production. Seasonal decline of isoprene emission can greatly accentuate the transition.

1. Introduction

Ozone is produced in the troposphere by a chain reaction involving photochemical oxidation of hydrocarbons and CO in the presence of nitrogen oxides (NOx = NO + NO2) [Chameides and Walker, 1973; Crutzen, 1973]. High O3 concentrations are frequently observed in surface air over the eastern United States, because of high emissions of NOx and hydrocarbons, and represent a serious air pollution problem [National Research Council (NRC), 1991]. It is well established, based on both observations and models, that O3 production over the eastern United States in summer is limited primarily by the supply of NOx [Trainer et al., 1987, 1993; Chameides et al., 1988, 1992; Stillman et al., 1990a, McKeen et al., 1991a, Jacob et al., 1993]. However, Kleinman [1991] has argued from theoretical considerations that a seasonal transition from NOx to hydrocarbon-limited conditions should take place in the region between summer and winter. We report here evidence for such a transition using measurements made at Shenandoah National Park, Virginia, in September 1990 during the Shenandoah Cloud and Photochemistry Experiment (SCAPE). We present photochemical model calculations suggesting that a September transition is a general phenomenon in the eastern United States.

The argument of Kleinman [1991] is based on the titration of odd hydrogen by NOx in the continental boundary layer. Odd hydrogen (odd H) is the chemical family including OH and peroxy radicals (RO2). Cycling of odd H propagates the chain reaction for O3 production. The principal source of odd H in the United States boundary layer is the photolysis of O3 to O1D followed by reaction of O1D with H2O [McKeen et al., 1991b]. Photolysis of aldehydes and peroxydes provide additional sources. Whether O3 production is NOx- or hydrocarbon-limited is determined by the pathway for odd-H loss [Stillman et al., 1990a]. If loss is principally by self-reaction of peroxy radicals, producing peroxydes, then O3 production tends to be NOx-limited. If loss is principally by reaction of NO2 with O1D to produce HNO3, then O3 production tends to be hydrocarbon limited. Kleinman [1991] points out that the odd-H production rate over the eastern United States decreases by 1 order of magnitude from summer to winter, due to declining UV radiation and humidity, crossing the point where odd-H radicals can be titrated in the boundary layer by NOx emissions and resulting in a seasonal transition from NOx to hydrocarbon-limited conditions. The transition is theoretically possible as soon as odd-H production drops to less than 2 times the NOx emission rate, but whether it actually takes place depends on the hydrocarbon/NOx concentration ratio and on the mechanism for NOx oxidation [Stillman, 1995].
A seasonal transition in photochemical regime would be of little interest if it occurred in late fall when \(O_3\) production is slow. However, a September transition would have important implications for the design of air pollution control strategies because \(O_3\) concentrations during that month are still high. An analysis of data at rural sites in the eastern United States in September [Logan, 1988] indicates mean daily maximum \(O_3\) concentrations of 50-65 parts per billion by volume (ppbv), an average of 5 days per site per month with concentrations higher than 80 ppbv, and occasional violations of the federal air quality standard (120 ppbv). A \(NO_x\)-only emission control strategy designed to reduce \(O_3\) levels in summer might be ineffective in September.

We diagnose the photochemical regime for \(O_3\) production in the SCAPE data set by using as indicators the concentration ratios \(H_2O_2/([NO_x]-NO_y)\) and HCHO/NO_y [Sillman, 1995], and the correlation between \(O_3\) and \([NO_x]-NO_y\) [Trainor et al., 1993]. Here \(NO_y\) represents the sum of all reactive nitrogen oxide species, including \(NO_x\) and its oxidation products (HNO_3, aerosol nitrate, organic nitrates). Thus \([NO_x]-NO_y\) represents the sum of the products of \(NO_x\) oxidation. Nitric acid accounts for about half of \([NO_x]-NO_y\) over the eastern United States in summer [Buhr et al., 1990; Parrish et al., 1991]. The \(H_2O_2/([NO_x]-NO_y)\) ratio gives a measure of the relative rates of odd-H loss by the \(NO_x\)-limited versus hydrocarbon-limited pathways, while the HCHO/NO_y ratio gives a measure of the reactivity-weighted hydrocarbon/NO_y emission ratio. Based on photochemical model calculations for the U.S. boundary layer over a range of conditions, Sillman [1995] finds that the transition from hydrocarbon- to \(NO_x\)-limited conditions should take place at a consistent \(H_2O_2/([NO_x]-NO_y)\) ratio of 0.2 mol/mol and at HCHO/NO_y ratios in the range 0.2-0.4 mol/mol.

The strong correlation observed between \(O_3\) and \([NO_x]-NO_y\) at eastern U.S. sites in summer has been used previously as evidence of \(NO_x\)-limited conditions for \(O_3\) production [Trainor et al., 1993; Klenman et al., 1994]. The slope \(\Delta O_3/\Delta([NO_x]-NO_y)\) gives an estimate of the net \(O_3\) production efficiency, i.e., the net production of \(O_3\) per unit \(NO_x\) consumed (this estimate is an upper limit because of HNO_3 deposition [Chin et al., 1994]). As the atmosphere evolves from \(NO_x\)- to hydrocarbon-limited, both the strength and the slope of the correlation would be expected to decrease [Lin et al., 1988; Sillman, 1995].

2. Observations

Air was sampled from a tower 3 m above the top of the forest canopy at the Pinacles mountain ridge site (1037-m altitude) in Shenandoah National Park, Virginia (39°N, 78°W). Concentra-

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**Figure 1.** Time series of \(O_3\), CO, \(NO_x\), \(NO_y\), \(H_2O_2\), and HCHO concentrations and of the \(H_2O_2/([NO_x]-NO_y)\) and HCHO/NO_y concentration ratios at the Pinacles site in Shenandoah National Park during September 1990. Tick marks on the abscissa indicate local noon for the given day.
tions of O$_3$, CO, NO$_3$, and NO were measured from September 4 to October 1, 1990, using instrumentation described by Pouli di et al. [1991] and Dodridge et al. [1992]. The inlet of the NO$_3$ instrument was equipped with a 5 to 10 μm pore size Teflon filter, excluding coarse nitrate aerosol. Concentrations of H$_2$O$_2$ and organic peroxides were measured from September 10 to 30 using instrumentation described by Heikes [1992]. Concentrations of HCHO, CH$_3$C(O)CHO, and CHOCHO were measured from September 5 to 24 [Munger et al., this issue]. Grab hydrocarbon samples were collected from September 4 to 14 (D. Perotti, unpublished data, 1994). Additional measurements at the site included organic acids and cloudwater composition [Keene et al., this issue; Talbot et al., this issue]. Meteorological measurements included wind speed and direction, temperature, humidity, pressure, and UV radiation zenith and nadir (Epplley Laboratory, Incorporated). Three-day back trajectories for air arriving at the site at 12 GMT each day were calculated using three-dimensional winds from the National Weather Service Nested Grid Model [Draager, 1992]. Two-thirds of the trajectories originated in the NW quadrant.

Figure 1 shows the time series of hourly mean O$_3$, CO, NO$_3$, H$_2$O$_2$, and HCHO concentrations. Diel variations are small, as is typical of mountain sites [Aneja et al., 1991; Pouli di et al., 1991]. There are four multiday pollution episodes defined by diel mean CO concentrations higher than 200 ppbv and labeled in Figure 1 as A (September 5-8), B (September 12-14), C (September 19-77), and D (September 27-30). All four episodes developed in association with weak anticyclones, as is typical of regional-scale pollution events in the eastern United States [Logan, 1989]. Back trajectories for each episode (Figure 2) suggest that the air remained in the continental boundary layer for at least 3 days before reaching the site and passed over major urban and industrial regions during that period. The O$_3$ maxima in episodes A, B, and D exceed 75 ppbv, the maximum in episode C was only 60 ppbv, likely because of cloudiness.

Ozone concentrations in the SCAPE data set were not correlated with NO$_3$ ($r = -0.05$). This result may be explained by the presence of large sources of NO$_3$ from power plants a few hundred kilometers to the north and west of the site [Environmental Protection Agency (EPA), 1989; Mox et al., 1994]. Ozone concentrations in fresh NO$_3$ plumes are low because NO$_3$ has not yet realized its O$_3$ production potential [Chin et al., 1994]. Better correlation would be expected between O$_3$ and NO$_3$-NO$_2$ (Trainer et al., 1993). Concentrations of NO$_3$ were not measured during SCAPE but are estimated here for daytime conditions (sun angle < 70°) by assuming photochemical steady state between photolysis of NO$_3$ to NO on the one hand and conversion of NO to NO$_2$ by reaction with O$_3$ and peroxy radicals on the other hand. Hourly data for the NO$_2$ photolysis rate constant are derived from the Epplley UV radiation data using the parameterization of Madronich [1987]. The concentrations of peroxy radicals are obtained from a steady-state, zero-dimensional photochemical model constrained with hourly data for NO$_3$, H$_2$O, CO, and temperature, and fixed concentrations of 1 ppbv HCHO, 1 ppbv isoprene, and 1700 ppbv CH$_4$. The model uses a chemical mechanism based on recent compilations of laboratory data [Atkinson, 1990; DeMore et al., 1997; Pouli di and Seinfeld, 1992; Atkinson et al., 1993]. Photolysis rates for species other than NO$_2$ are computed using a six-stream radiative transfer code for the Rayleigh scattering atmosphere with a UV surface albedo of 0.03, an O$_3$ column of 7.7x10$^{18}$ molecules cm$^{-2}$ s$^{-1}$, and an aerosol optical depth for absorption of 0.13 at 310 nm varying inversely with wavelength [Logan et al., 1981]. Cloud effects are accounted for by scaling the clear-sky photolysis rate constants computed with the code to the NO$_2$ photolysis rate constant derived from the Epplley data.

The resulting time series of daytime NO$_3$ concentrations, including observed NO and modeled NO$_3$, is shown in Figure 1. The mean NO$_2$/NO ratio is 4.5 mol/mol and the mean NO$_3$/NO ratio is 0.31 mol/mol. The NO$_2$ concentrations are relatively insensitive to the modeled peroxy radical concentrations because reaction with O$_3$ accounts on average for 83% of the total NO sink in the model (i.e., the mean NO$_3$/NO ratio would be 3.7 mol/mol if reaction of NO with peroxy radicals were ignored).

A scatterplot of O$_3$ versus NO$_3$-NO$_2$ concentrations is shown in Figure 3. There is no significant correlation for the SCAPE data set as a whole. There is however significant correlation in the September 4-12 data ($r^2 = 0.49$, $n = 51$) with a slope ΔO$_3$/Δ(NO$_3$-NO$_2$) = 18 mol/mol obtained from the reduced-major-axis method. The relationship between O$_3$ and NO$_3$-NO$_2$ in the September 4-12 data is consistent with previous observations at eastern U.S. sites in summer [Olszyna et al., 1993; Trainer et al., 1993; Kleiman et al., 1994]. The slopes reported in previous studies are lower (8-14 mol/mol), but the difference appears to reflect in part the choice of statistical approach.

The September 13-30 data show a weaker correlation between O$_3$ and NO$_3$-NO$_2$ ($r^2 = 0.23$, $n = 107$) and a lower slope (ΔO$_3$/Δ(NO$_3$-NO$_2$) = 7 mol/mol), suggesting that O$_3$ production is less NO$_3$-limited than in early September. The weak correlation is due in part to occurrences of high NO$_3$-NO$_2$ (4-8 ppbv) associated with relatively low O$_3$ (30-60 ppbv). The September 4-12 data show no such occurrences of high NO$_3$ NO$_2$ that could be used for comparison. However, the summertime data of Trainer et al. [1993] show a strong linear relationship between O$_3$ and NO$_3$-NO$_2$, extending up to at least 10 ppbv NO$_3$-NO$_2$, with 6 ppbv NO$_3$-NO$_2$ associated on average with 80-100 ppbv O$_3$. The cause for the high NO$_3$ NO$_2$ values in the late-September SCAPE data is
unclear. Inspection of back trajectories shows no obvious correlation with air mass origin.

The time series of H$_2$O$_2$ concentrations in Figure 1 offers additional evidence for a transition in photochemical regime during SCAPE. Concentrations decreased abruptly on September 12, in association with a cold front, and remained low thereafter, averaging 0.13 ppbv for September 13-30 as compared to 0.86 ppbv for September 10-12. The H$_2$O$_2$/(NO$_x$-NO$_x$) concentration ratio averaged 0.40 mol/mol on September 10-12 and 0.049 mol/mol on September 13-30; after September 12 it never rose above the value of 0.7 mol/mol given by Sillman [1995] as the crossover point between NO$_x$- and hydrocarbon-limited regimes for O$_3$ production.

Although our H$_2$O$_2$ record is limited, measurements at other mountain sites in the southeastern United States show that the H$_2$O$_2$ concentrations measured on September 10-12 during SCAPE are typical of summer values in the region, while the concentrations measured after September 12 are typical of fall values. At Whitetop Mountain, Virginia, measurements were made during July-August and on October 4-14, 1986 [Oleczyn et al., 1988]. The mean July-August concentration was 0.8 ppbv, with only 6% of observations less than 0.2 ppbv, while the mean October concentration was 0.15 ppbv with no observations above 0.6 ppbv. At Mount Mitchell, North Carolina, measurements were made during July-August and on September 14-18, 1988 [Claiborn and Anjea, 1991]. The mean July-August concentration was 0.8 ppbv, with less than 10% of values less than 0.25 ppbv, while a drop from 1.0 ppbv to 0.1 ppbv was observed during the September 14-18 period. These three data sets taken together suggest a factor of 5 or more seasonal decrease of H$_2$O$_2$ concentrations during the month of September. Such a decrease is predicted by Kleinman [1991], who attributes it to the suppression of H$_2$O$_2$ formation following titration of odd-H by NO$_x$ emissions. Aqueous-phase titration of H$_2$O$_2$ by SO$_2$ [Daum et al., 1984] would also contribute to the decrease, but should have a less systematic effect because it operates only in cloud. There is a strong correlation between H$_2$O$_2$ and organic peroxides in the SCAPE data set ($r^2 = 0.68$), suggesting that the decrease of H$_2$O$_2$ during September is photochemically controlled. Organic peroxides are not rapidly consumed by oxidation of SO$_2$ in cloud because of their low solubility [Jacob et al., 1995a].

The HCHO/NO$_x$ concentration ratio provides another indication of the transition in photochemical regime. Mean values observed in SCAPE are 0.67 mol/mol for September 5-12 and 0.25 mol/mol for September 13-23 (Figure 1). The ratio varied considerably before September 12, far less afterward, the maximum value observed after September 13 was 0.47 mol/mol. Sillman [1995] gives a crossover ratio of 0.2-0.4 mol/mol for the transition from NO$_x$- to hydrocarbon-limited conditions. The decrease of HCHO/NO$_x$ could reflect the seasonal decline of biogenic isoprene emissions in September due to senescence of vegetation [Goldstein, 1994; Jobson et al., 1994; Monson et al., 1995].

Periods of high O$_3$ (70-80 ppbv) during episodes B and D give an additional perspective on the transition. Mean concentrations

Figure 3. Scatterplot of hourly mean O$_3$ versus NO$_x$-NO$_x$ concentrations and linear best fits (reduced-major axis method) for September 4-12 (circles, solid line) and September 13-30 (squares, dashed line). Correlation coefficients and slopes are given in Table 1.
Table 1. Photochemical Indicators at Shenandoah National Park

<table>
<thead>
<tr>
<th>Indicator</th>
<th>September 4-12</th>
<th>September 13-30</th>
<th>Crossover</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂/(NOₓ, -NOₓ), mol/mol</td>
<td>0.40(0.24-0.77)</td>
<td>0.049(0.01-0.18)</td>
<td>0.2</td>
</tr>
<tr>
<td>HCHO/NOₓ, mol/mol</td>
<td>0.67(0.07-2.7)</td>
<td>0.25(0.01-0.47)</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>O₃ versus NOₓ, -NOₓ:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r²</td>
<td>0.49</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>ΔO₃/Δ(NOₓ, -NOₓ), mol/mol</td>
<td>18</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

Means and ranges of observed H₂O₂/(NOₓ, -NOₓ) and HCHO/NOₓ concentration ratios; the crossover values represent the transition from NOₓ- to hydrocarbon-limited conditions for O₃ production according to the photochemical model calculations of Stillman [1995] (ratios lower than the crossover value correspond to the hydrocarbon-limited regime). The slope ΔO₃/Δ(NOₓ, -NOₓ) of the O₃ versus NOₓ, -NOₓ correlation was computed with the reduced-major-axis method.

in episode B were 73 ppbv O₃, 2.6 ppbv NOₓ, 0.63 ppbv H₂O₂, and 2.5 ppbv HCHO (14 hours of data); in episode D they were 73 ppbv O₃, 5.2 ppbv NOₓ, and 0.24 ppbv H₂O₂ (9 hours of data; HCHO was not measured). The high-O₃ periods occurred in the evening and night hours, when NOₓ could not be estimated. Nevertheless, the NOₓ and H₂O₂ data suggest that episode D was less NOₓ-limited than episode B for a similar amount of O₃ produced. A H₂O₂ concentration of 0.34 ppbv for the continental boundary layer is clearly indicative of hydrocarbon-limited conditions in photochemical models [Dommen et al., 1995].

A summary of the chemical indicator data is given in Table 1. Each of the indicators, when considered individually, would be open to interpretations other than a seasonal transition in photochemical regime. Combination of the indicators makes a stronger

Table 2. Odd Hydrogen Production Rates at Shenandoah National Park

<table>
<thead>
<tr>
<th></th>
<th>September 1</th>
<th>October 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar declination, degrees</td>
<td>+1.4</td>
<td>-3.9</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>293</td>
<td>288</td>
</tr>
<tr>
<td>H₂O₂, mol/mol</td>
<td>0.017</td>
<td>0.013</td>
</tr>
<tr>
<td>O₃, ppbv</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>HCHO, ppbv</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td>H₂O₂, ppbv</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>CH₃C(O)CHO, ppbv</td>
<td>0.017</td>
<td>0.020</td>
</tr>
<tr>
<td>Odd H production rate, 10⁵ molecules cm⁻³ s⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(¹D)+H₂O → 2OH</td>
<td>12.7</td>
<td>6.0</td>
</tr>
<tr>
<td>HCHO+hv → CO+2HO₂</td>
<td>3.6</td>
<td>1.4</td>
</tr>
<tr>
<td>CH₃C(O)CHO+hv → CO₂+HO₂+CH₃CO₃</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>H₂O₂+hv → 2OH</td>
<td>0.4</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Total</td>
<td>18</td>
<td>8</td>
</tr>
</tbody>
</table>

Odd H is the chemical family including OH and peroxy radicals. Temperatures, humidities, and concentrations of odd-H precursors are typical observations from SCAPE. The mean CH₃C(O)CHO concentration measured in SCAPE was below the detection limit of 0.05 ppbv; the values used here are from the one-dimensional photochemical model of Munger et al. [this issue], assuming an isoprene emission flux of 5×10¹⁸ molecules cm⁻² s⁻¹ (24-hour average). The odd-H production rates are 24-hour averages at 1 km altitude computed using a six-stream radiative transfer code for the Rayleigh scattering atmosphere [Logan et al., 1981] with photochemical data from DeMore et al. [1992]. We assume a UV surface albedo of 0.03, an O₃ column of 7.7×10¹⁵ molecules cm⁻² [Hilsenrath et al., 1979], an aerosol optical depth for absorption of 0.13 at 310 nm increasing inversely with wavelength, and 25% opaque cloud cover.
case. However, it should be recognized that the indicators are not truly independent since they are all based on NO$_x$; in particular, the trends in the indicators over the course of September reflect partly a rise in NO$_x$-NO for which we have no clear explanation. We present in what follows an independent model assessment of the seasonal transition in photochemical regime over the eastern United States.

3. Model Calculations

Odd-H Production and NO$_x$ Emission

A simple diagnosis of the photochemical regime for O$_3$ production over the eastern United States can be made following Kleinman [1991] by comparing the rates of odd-H production and NO$_x$ emission in the region. Table 2 gives estimates of odd-H production rates at Shenandoah from photolysis of O$_3$, HCHO, CH$_3$C(O)CHO, and H$_2$O$_2$ under conditions representative of September 1 and October 1. These four photolysis reactions account for over 90% of the total odd-H source in the boundary layer according to our photochemical model calculations (see below). The odd-H production rates in Table 2 are 1.8x10$^6$ molecules cm$^{-3}$ s$^{-1}$ on September 1 and 8x10$^5$ molecules cm$^{-3}$ s$^{-1}$ on October 1. The factor of 2 decrease over the course of September is driven largely by a 40% decline in radiation intensities in the bandwidth for photolysis of O$_3$ to O(1D) (300-320 nm) and a 25% decline of H$_2$O concentrations.

The mean emission of NO$_x$ in the eastern United States in summer is 1.9x10$^{11}$ molecules cm$^{-2}$ s$^{-1}$ (1985 inventory, cited by McKeen et al. [1991b]). Seasonal variation in this emission is small [EPA, 1989]. Assuming a 1.6 km deep continental boundary layer in September [Holzworth, 1967], we derive a NO$_x$ source in the boundary layer of 1.2x10$^6$ molecules cm$^{-3}$ s$^{-1}$. This source falls between our estimates of odd-H production on September 1 and October 1. Transition to a hydrocarbon-limited regime for O$_3$ production during September could therefore be expected.

Several complications to this argument must be considered.

![Figure 4](image-url)
however. For example, nighttime hydrolysis of N₂O₅ in aerosols may delay or prevent the transition by consuming NO, without consuming odd H. Conversion of NO₃ to peroxyacetyl nitrate (PAN) consumes odd H but does not lead to a hydrocarbon-limited regime [Sillman, 1995]. Declining emission of isoprene in September would by contrast hasten the transition because oxidation of isoprene provides a significant source of odd H and also decreases the fraction of odd-H present as OH (and hence available for reaction with NO₂). We address here these complications by using a one-dimensional photochemical model for the continental boundary layer.

One-Dimensional Model

Our model is similar in structure to that used by Trainer et al. [1991] to simulate a summertime high-O₃ episode at Scotia, Pennsylvania. It resolves the boundary layer with six grid points in the vertical extending to 1.8 km. Vertical transport is represented by diurnally varying eddy diffusion coefficients. The mixed layer depth varies with time of day and peaks at 1.6 km during the afternoon hours. Ventilation of the boundary layer by the free troposphere takes place on a timescale of 4 days. The gas phase photochemical mechanism and the radiation code are as described in section 2. Hydrolysis of N₂O₅ in aerosols is included with a rate constant of 1x10⁻¹⁴ s⁻¹ [Dentener and Crutzen, 1993], so that loss of NO₃ at night is limited largely by the rate of the NO₃+O₃ reaction in the gas phase. Deposition velocities of O₁, NO₂, PAN, carbonyls, and peroxydes at 10-m altitude are 0.5 cm s⁻¹ in the day and 0.1 cm s⁻¹ at night. The deposition of HONO is limited by the rate of turbulent diffusion to the surface and is sufficiently fast that conversion to HNO₃ is a terminal sink for NO₃.

We use the model to determine the sensitivity of O₃ to NOₓ and hydrocarbon emissions for conditions representative of September 1 and October 1. The simulations are conducted for 7 days, starting from low initial concentrations (including 40 ppbv O₃) which are also taken as upper boundary conditions at 1.6 km. Fixed concentrations are assumed for CO (200 ppbv), CH₄ (1700 ppbv), C₂H₆ (2.2 ppbv), and acetone (1 ppbv). Munger et al. [this issue] estimated an isoprene emission flux of 5x10¹⁰ molecules cm⁻² s⁻¹ (24-hour average) from the SCAPE carbonyl data; as pointed out above, the HCHO data suggest a strong decline of isoprene over the course of September. We present here calculations both with and without isoprene emission. The diel variation of isoprene emission is specified following Jacob et al. [1989b].

We first applied the model to an atmosphere representative of average conditions in the eastern United States. Mean anthropogenic emissions of NOₓ and reactive non-methane hydrocarbons...
for the region were taken from Table 6 of McKee et al. [1991b]. On a reactivity-weighted basis [Trainor et al., 1991], the anthropogenic source of non-methane hydrocarbons is comparable to the biogenic source of isoprene. Meteorological and radiative conditions for September 1 and October 1 were as given in Table 2. The sensitivity of O₃ to changes in NOₓ and hydrocarbon emissions was diagnosed by conducting simulations with 25% increases in emissions (the increase in hydrocarbon emissions was applied to all non-methane hydrocarbons including isoprene).

Figure 4 shows the simulated O₃ concentrations at 1-km altitude. We find a positive dependence of O₃ on NOₓ and hydrocarbon emissions in the September 1 cases, and in the October 1 case with isoprene; NOₓ is more limiting in the September 1 cases while hydrocarbons are more limiting in the October 1 case. The October 1 case without isoprene shows a negative dependence of O₃ on NOₓ emissions, indicating strongly hydrocarbon-limited conditions.

We also applied the model to the simulation of a representative high-O₃ episode. Anthropogenic emissions were double from the mean values for the eastern United States given by McKee et al. [1991b]. We assumed clear skies, high temperature, and humidity (September 1 values in Table 2); the only difference between the September 1 and October 1 simulations was the solar declination. Results are shown in Figure 5. Ozone concentrations in the October 1 cases reach 80 ppbv after 4 days with isoprene present and 60 ppbv without isoprene present. Hydrocarbon limitation of O₃ production is more severe than in the previous simulation. The October 1 case without isoprene shows a precipitous O₃ decrease when NOₓ emissions are increased by 25%, reflecting an abrupt transition in photochemical regime of the type described by Kleinman [1991].

4. Conclusions

Measurements of O₃, CO, NO, NOₓ, H₂O₂, and HCHO concentrations at Shenandoah National Park indicate a seasonal transition from NOₓ-limited to hydrocarbon-limited conditions for O₃ production during September. The transition is diagnosed by large decreases of the H₂O₂/(NOₓ•NOₓ) and HCHO/NOₓ concentration ratios, degradation of the O₃ versus NOₓ NOₓ correlation, and decrease of the slope ΔO₃/Δ(NOₓ•NOₓ). The NOₓ emissions in the area around Shenandoah National Park include an unusually high contribution from power plants [EPA, 1989], so that O₃ production in the region might have a particularly high tendency to be hydrocarbon-limited [Silliman et al., 1990b]. However, our model calculations suggest that the seasonal transition in photochemical regime during September should be a general phenomenon in the eastern United States. The transition is driven by seasonal declines of UV radiation, humidity, and isoprene emission, allowing HNO₃ production to become the dominant sink for odd H in the boundary layer. We would expect the reverse transition to take place in April.

A hydrocarbon-limited regime for O₃ production over the eastern United States from September to April would have important implications for the design of O₃ pollution control strategies. A strategy relying solely on NOₓ emission controls might be successful in summer but inadequate in spring or fall. We caution that the work presented here is preliminary; the data are sparse and the model calculations largely illustrative. Additional time series of observations are required to confirm and generalize the results observed in Shenandoah. Thorough documentation of high-O₃ episodes occurring in spring and fall would be particularly valuable. Simulations using a regional three-dimensional model are needed to better quantify the seasonal variations in photochemical regime across the range of conditions found in the eastern United States.

From a global perspective the main effect of hydrocarbon-limited photochemistry in polluted boundary layers would be to amplify the effect of changes in anthropogenic NOₓ emissions on the export of NOₓ out of the boundary layer and hence on tropospheric O₃ and OH. In the remote troposphere the supply of NOₓ is, in general, sufficiently low that NOₓ-limited conditions should persist year-round. One possible exception is the upper troposphere, where odd H production is slow (because of low humidity) and where NOₓ concentrations may be high as a result of lightning, aircraft, and convective updrafts.

Acknowledgments. This work was supported by National Science Foundation grants to Harvard University (ATM-8812157, ATM-9304217), the Universities of Rhode Island and Maryland (ATM-9015789), and the University of Virginia (ATM-8911815) and by a Packard Foundation grant to Harvard. The H₂O₂ measurements were supported by the Electric Power Research Institute under contract RP-2023-12. We thank K. Civerolo and B.G. Dodridge (U. of Maryland) and M. Lee (U. of Rhode Island) for their help in the field, and R. Shetter (NCAR) and R. Arnst (EPA) for the loan of equipment. We are indebted to the Mountain Cloud Chemistry Program and particularly John Sigmon, Patricia Thompson, David Knwitz, and Michael Reiter for the use of their facilities. The Shenandoah National Park Service provided on-site housing and laboratory space.

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(Received January 1, 1994; revised October 25, 1994; accepted November 22, 1994.)