

Seasonal transition from NO_x- 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 (NO_y), 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 NO_x-limited to hydrocarbon-limited conditions for O₃ production over the course of September. The transition is diagnosed by large decreases of the H₂O₂/(NO_y-NO_x) and HCHO/NO_y concentration ratios, weakening of the correlation between O₃ and NO_y-NO_x concentrations, and decrease of the slope $\Delta O_3/\Delta(NO_y-NO_x)$. A high-O₃ episode occurring in late September was associated with only 0.34 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 (NO_x = 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 NO_x 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 NO_x [Trainer et al., 1987, 1993; Chameides et al., 1988, 1992; Sillman et al., 1990a; McKeen et al., 1991a; Jacob et al., 1993]. However, Kleinman [1991] has argued from theoretical considerations that a

seasonal transition from NO_x- 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 NO_x 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 O(¹D) followed by reaction of O(¹D) with H₂O [McKeen et al., 1991b]. Photolysis of aldehydes and peroxides provide additional sources. Whether O₃ production is NO_x- or hydrocarbon-limited is determined by the pathway for odd-H loss [Sillman et al., 1990a]. If loss is principally by self-reaction of peroxy radicals, producing peroxides, then O₃ production tends to be NO_x-limited. If loss is principally by reaction of NO₂ with OH 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 NO_x emissions and resulting in a seasonal transition from NO_x- to hydrocarbon-limited conditions. The transition is theoretically possible as soon as odd-H production drops to less than 2 times the NO_x emission rate, but whether it actually takes place depends on the hydrocarbon/NO_x concentration ratio and on the mechanism for NO_x oxidation [Sillman, 1995].

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A seasonal transition in photochemical regime would be of little interest if it occurred in late fall when O₃ production is slow. However, a September transition would have important implications for the design of air pollution control strategies because O₃ 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 O₃ 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 O₃ levels in summer might be ineffective in September.

We diagnose the photochemical regime for O₃ production in the SCAPE data set by using as indicators the concentration ratios H₂O₂/(NO_y-NO_x) and HCHO/NO_y [Sillman, 1995], and the correlation between O₃ and NO_y-NO_x [Trainer et al., 1993]. Here NO_y represents the sum of all reactive nitrogen oxide species, including NO_x and its oxidation products (HNO₃, aerosol nitrate, organic nitrates). Thus NO_y-NO_x represents the sum of the products of NO_x oxidation. Nitric acid accounts for about half of NO_y-NO_x over the eastern United States in summer [Buhr et al., 1990; Parrish et al., 1993]. The H₂O₂/(NO_y-NO_x) 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_x 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 H₂O₂/(NO_y-NO_x) 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 O₃ and NO_y-NO_x at eastern U.S. sites in summer has been used previously as evidence of NO_x-limited conditions for O₃ production [Trainer et al., 1993; Kleinman et al., 1994]. The slope $\Delta O_3/\Delta(\text{NO}_y-\text{NO}_x)$ gives an estimate of the net O₃ production efficiency, i.e., the net production of O₃ per unit NO_x consumed (this estimate is an upper limit because of HNO₃ 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 Pinnacles mountain ridge site (1037-m altitude) in Shenandoah National Park, Virginia (39°N, 78°W). Concentra-

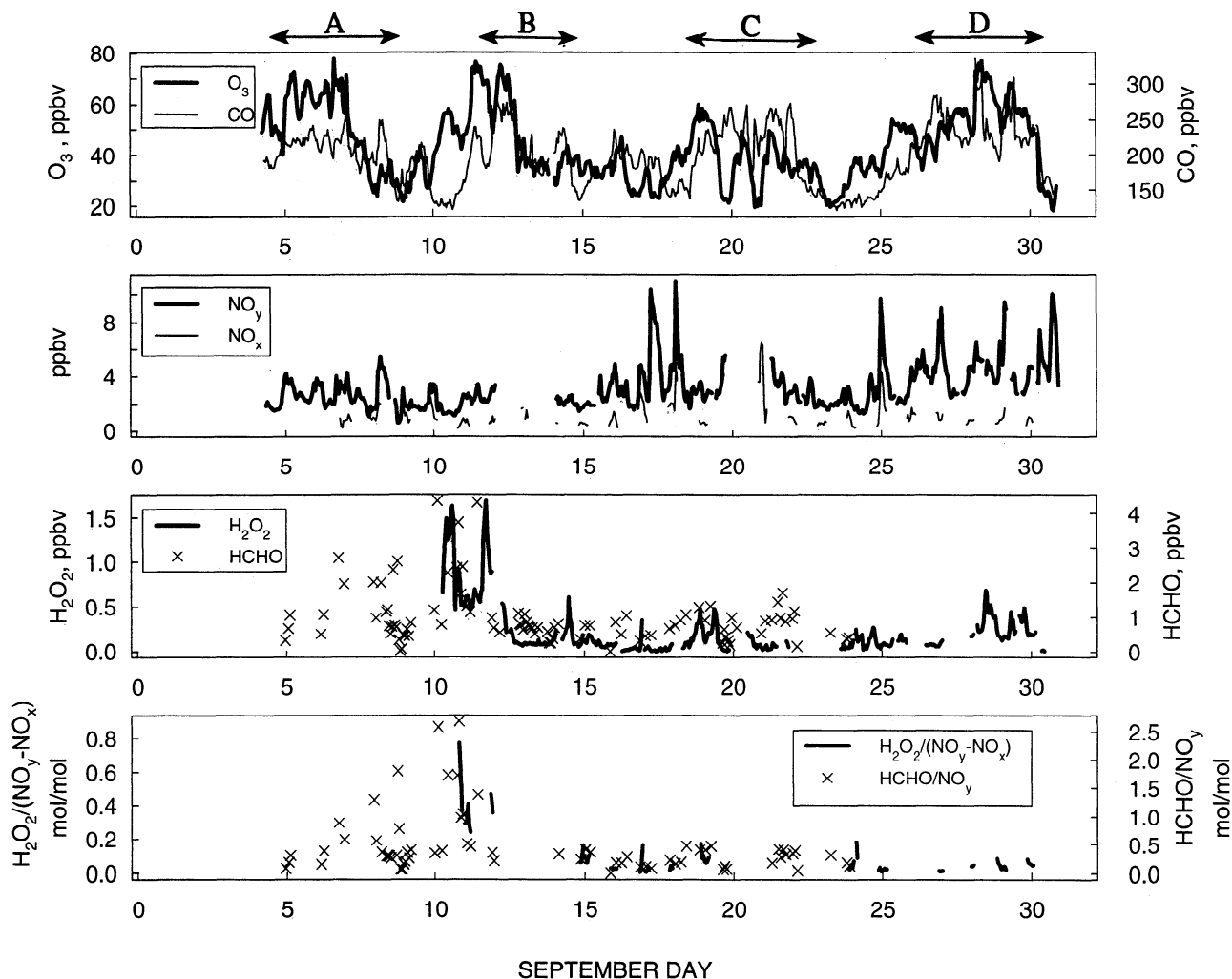


Figure 1. Time series of O₃, CO, NO_y, NO_x, H₂O₂, and HCHO concentrations and of the H₂O₂/(NO_y-NO_x) and HCHO/NO_y concentration ratios at the Pinnacles site in Shenandoah National Park during September 1990. Tick marks on the abscissa indicate local noon for the given day.

tions of O₃, CO, NO_y, and NO were measured from September 4 to October 1, 1990, using instrumentation described by Poulida *et al.* [1991] and Doddridge *et al.* [1992]. The inlet of the NO_y instrument was equipped with a 5 to 10 μm pore size Teflon filter, excluding coarse nitrate aerosol. Concentrations of H₂O₂ and organic peroxides were measured from September 10 to 30 using instrumentation described by Heikes [1992]. Concentrations of HCHO, CH₃C(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. Pierotti, 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 (Eppley 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 [Draxler, 1992]. Two-thirds of the trajectories originated in the NW quadrant.

Figure 1 shows the time series of hourly mean O₃, CO, NO_y, H₂O₂, and HCHO concentrations. Diel variations are small, as is typical of mountain sites [Aneja *et al.*, 1991; Poulida *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 19-22), 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 O₃ maxima in episodes A, B, and D

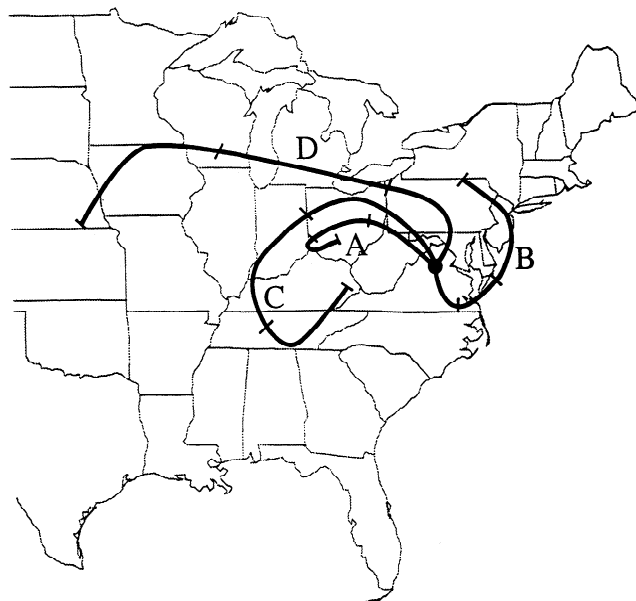


Figure 2. Three-day back trajectories for air arriving at the Pinnacles site at 12 GMT on September 6 (episode A), 13 (B), 20 (C), and 27 (D). The trajectories were generated using three-dimensional winds from the National Weather Service Nested Grid Model [Draxler, 1992]. Tick marks along the trajectories separate 24-hour segments. All four trajectories remained in the boundary layer (below 900 mbar) for the 3 days before reaching the site.

exceeded 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_y ($r = -0.05$). This result may be explained by the presence of large sources of NO_x from power plants a few hundred kilometers to the north and west of the site [Environmental Protection Agency (EPA), 1989; Moy *et al.*, 1994]. Ozone concentrations in fresh NO_x plumes are low because NO_x has not yet realized its O₃ production potential [Chin *et al.*, 1994]. Better correlation would be expected between O₃ and NO_y-NO_x [Trainer *et al.*, 1993]. Concentrations of NO₂ were not measured during SCAPE but are estimated here for daytime conditions (sun angle < 70°) by assuming photochemical steady state between photolysis of NO₂ to NO on the one hand and conversion of NO to NO₂ by reaction with O₃ and peroxy radicals on the other hand. Hourly data for the NO₂ photolysis rate constant are derived from the Eppley 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, O₃, H₂O, CO, and temperature, and fixed concentrations of 1 ppbv HCHO, 1 ppbv isoprene, and 1700 ppbv CH₄. The model uses a chemical mechanism based on recent compilations of laboratory data [Atkinson, 1990; DeMore *et al.*, 1992; Paulson and Seinfeld, 1992; Atkinson *et al.*, 1993]. Photolysis rates for species other than NO₂ are computed using a six-stream radiative transfer code for the Rayleigh scattering atmosphere with a UV surface albedo of 0.03, an O₃ column of 7.7×10^{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 NO₂ photolysis rate constant derived from the Eppley data.

The resulting time series of daytime NO_x concentrations, including observed NO and modeled NO₂, is shown in Figure 1. The mean NO₂/NO ratio is 4.5 mol/mol and the mean NO_x/NO_y ratio is 0.31 mol/mol. The NO₂ concentrations are relatively insensitive to the modeled peroxy radical concentrations because reaction with O₃ accounts on average for 83% of the total NO sink in the model (i.e., the mean NO₂/NO ratio would be 3.7 mol/mol if reaction of NO with peroxy radicals were ignored).

A scatterplot of O₃ versus NO_y-NO_x 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 $\Delta O_3 / \Delta (NO_y - NO_x) = 18$ mol/mol obtained from the reduced-major-axis method. The relationship between O₃ and NO_y-NO_x 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; Kleinman *et al.*, 1994]. The slopes reported in these 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 O₃ and NO_y-NO_x ($r^2 = 0.23$, $n = 107$) and a lower slope ($\Delta O_3 / \Delta (NO_y - NO_x) = 7$ mol/mol), suggesting that O₃ production is less NO_x-limited than in early September. The weak correlation is due in part to occurrences of high NO_y-NO_x (4-8 ppbv) associated with relatively low O₃ (30-60 ppbv). The September 4-12 data show no such occurrences of high NO_y-NO_x that could be used for comparison. However, the summertime data of Trainer *et al.* [1993] show a strong linear relationship between O₃ and NO_y-NO_x extending up to at least 10 ppbv NO_y-NO_x, with 6 ppbv NO_y-NO_x associated on average with 80-100 ppbv O₃. The cause for the high NO_y-NO_x values in the late-September SCAPE data is

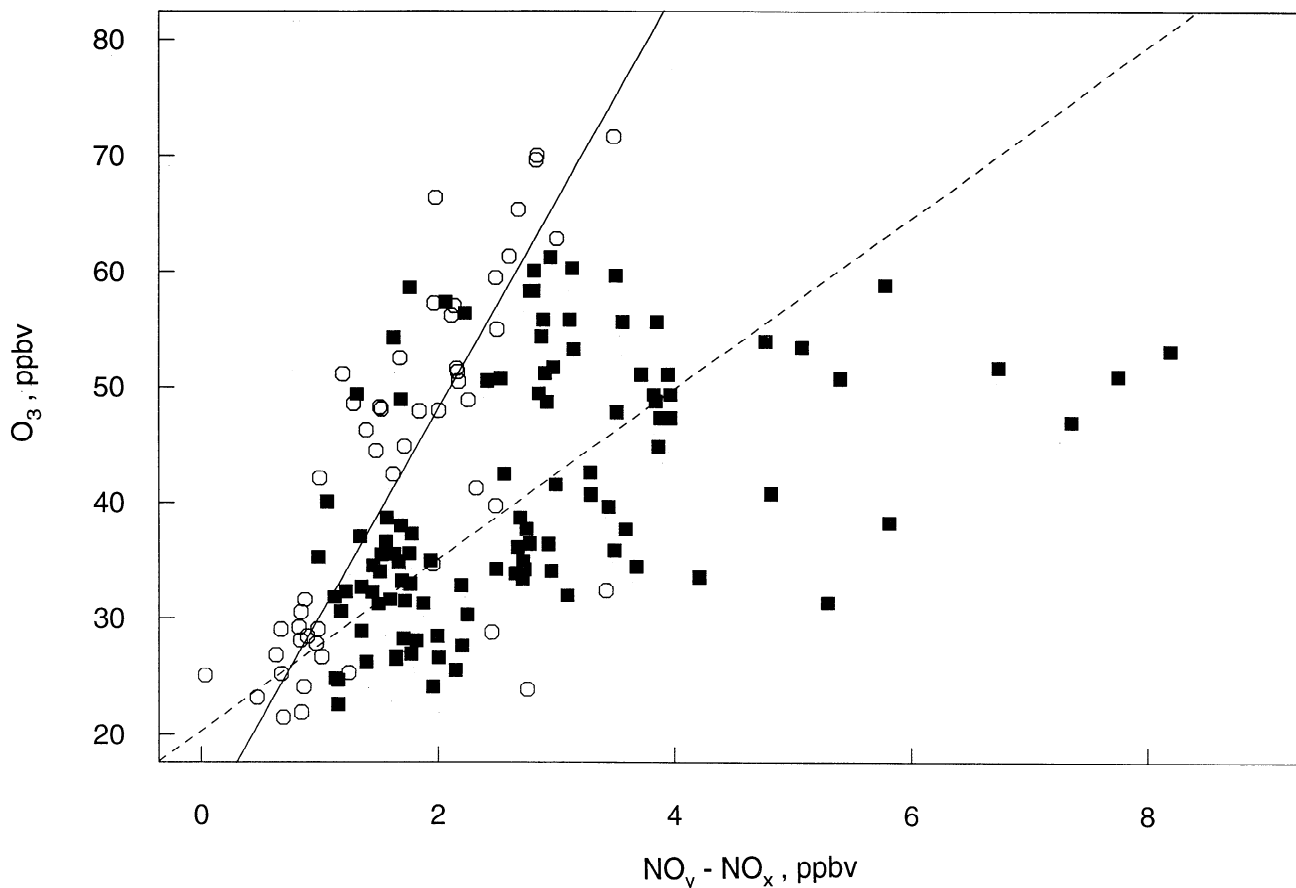


Figure 3. Scatterplot of hourly mean O₃ versus NO_y-NO_x concentrations and linear best fits (reduced-major-axis method) for September 4-12 (circles, solid line) and September 13-30 (squares, dashed line). Correlation coefficients and slopes are given in Table 1.

unclear. Inspection of back trajectories shows no obvious correlation with air mass origin.

The time series of H₂O₂ 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 H₂O₂/(NO_y-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 0.2 mol/mol given by *Sillman* [1995] as the crossover point between NO_x- and hydrocarbon-limited regimes for O₃ production.

Although our H₂O₂ record is limited, measurements at other mountain sites in the southeastern United States show that the H₂O₂ 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 [*Olszyna 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 Aneja*, 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 H₂O₂ concentrations during the month of September. Such a decrease is predicted by *Kleinman* [1991], who attributes it to the suppression of H₂O₂ formation following titration of odd-H by NO_x emissions. Aqueous-phase titration of H₂O₂ by SO₂ [*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 H₂O₂ and organic peroxides in the SCAPE data set ($r^2 = 0.68$), suggesting that the decrease of H₂O₂ during September is photochemically controlled. Organic peroxides are not rapidly consumed by oxidation of SO₂ in cloud because of their low solubility [*Jacob et al.*, 1989a].

The HCHO/NO_y 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 13-25 (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_y 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 O₃ (70-80 ppbv) during episodes B and D give an additional perspective on the transition. Mean concentrations

Table 1. Photochemical Indicators at Shenandoah National Park

Indicator	September 4-12	September 13-30	Crossover
H ₂ O ₂ /(NO _y -NO _x), mol/mol	0.40(0.24-0.77)	0.049(0.01-0.18)	0.2
HCHO/NO _y , mol/mol	0.67(0.07-2.7)	0.25(0.01-0.47)	0.2-0.4
O ₃ versus NO _y -NO _x :			
<i>r</i> ²	0.49	0.23	
ΔO ₃ /Δ(NO _y -NO _x), mol/mol	18	7	

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

in episode B were 73 ppbv O₃, 2.6 ppbv NO_y, 0.63 ppbv H₂O₂, and 2.5 ppbv HCHO (14 hours of data); in episode D they were 73 ppbv O₃, 5.2 ppbv NO_y, and 0.34 ppbv H₂O₂ (9 hours of data; HCHO was not measured). The high-O₃ periods occurred in the evening and night hours, when NO_x could not be estimated. Nevertheless, the NO_y and H₂O₂ data suggest that episode D was less NO_x-limited than episode B for a similar amount of O₃ pro-

duced. 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

	September 1	October 1
Solar declination, degrees	+7.4	-3.9
Temperature, K	293	288
H ₂ O, mol/mol	0.017	0.013
O ₃ , ppbv	55	55
HCHO, ppbv	1.4	0.7
H ₂ O ₂ , ppbv	0.8	0.2
CH ₃ C(O)CHO, ppbv	0.017	0.020
Odd-H production rate, 10 ⁵ molecules cm ⁻³ s ⁻¹		
O(¹ D)+H ₂ O → 2OH	12.7	6.0
HCHO+hν $\xrightarrow{2O_2}$ CO+2HO ₂	3.6	1.4
CH ₃ C(O)CHO+hν $\xrightarrow{2O_2}$ CO+HO ₂ +CH ₃ CO ₃	0.9	0.8
H ₂ O ₂ +hν → 2OH	0.4	<0.1
Total	18	8

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 5x10¹⁰ 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 7.7x10¹⁸ 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_y; in particular, the trends in the indicators over the course of September reflect partly a rise in NO_y-NO_x 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 O₃ 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 O₃, HCHO, CH₃C(O)CHO, and H₂O₂ 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 1.8×10^6 molecules cm⁻³ s⁻¹ on September 1 and 8×10^5 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 of radiation intensities in the bandwidth for photolysis of O₃ to O(¹D) (300-320 nm) and a 25% decline of H₂O concentrations.

The mean emission of NO_x in the eastern United States in summer is 1.9×10^{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 1.2×10^6 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 O₃ production during September could therefore be expected.

Several complications to this argument must be considered,

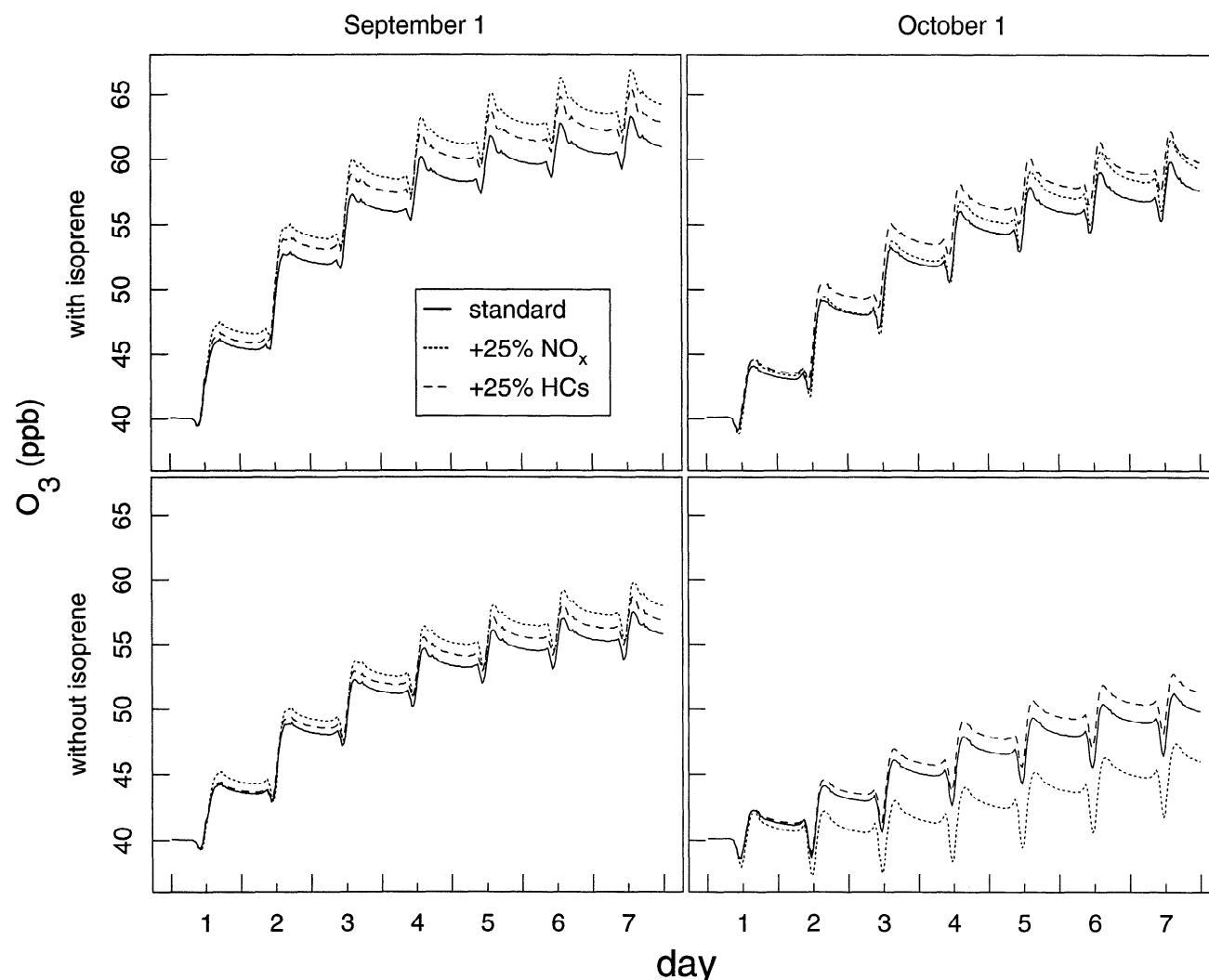


Figure 4. Ozone concentrations at 1-km altitude calculated with a one-dimensional photochemical model for conditions representative of the eastern United States on September 1 and October 1 (left and right panels, respectively), with and without isoprene emission (top and bottom panels, respectively). The sharp rise of O₃ concentrations at noon reflects the diurnal rise of the mixed layer above 1-km altitude. Results from the standard simulation described in the text are compared to results from simulations with NO_x or hydrocarbon (HCs) emissions increased by 25% (the increase in hydrocarbon emissions is applied to all non-methane hydrocarbons including isoprene).

however. For example, nighttime hydrolysis of N₂O₅ in aerosols may delay or prevent the transition by consuming NO_x without consuming odd H. Conversion of NO_x 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 $1 \times 10^{-4} \text{ s}^{-1}$ [Dentener and Crutzen, 1993], so that loss of NO_x at night is limited largely by the rate of the NO₂+O₃ reaction in the gas phase. Deposition velocities of O₃, NO₂, PAN, carbonyls, and peroxides at 10-m altitude are 0.5 cm s⁻¹ in the day and 0.1 cm s⁻¹ at night. The deposition of HNO₃ is limited by the rate of turbulent diffusion to the surface and is sufficiently fast that conversion to HNO₃ is a terminal sink for NO_x.

We use the model to determine the sensitivity of O₃ to NO_x 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 5×10^{10} 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 NO_x and reactive non-methane hydrocarbons

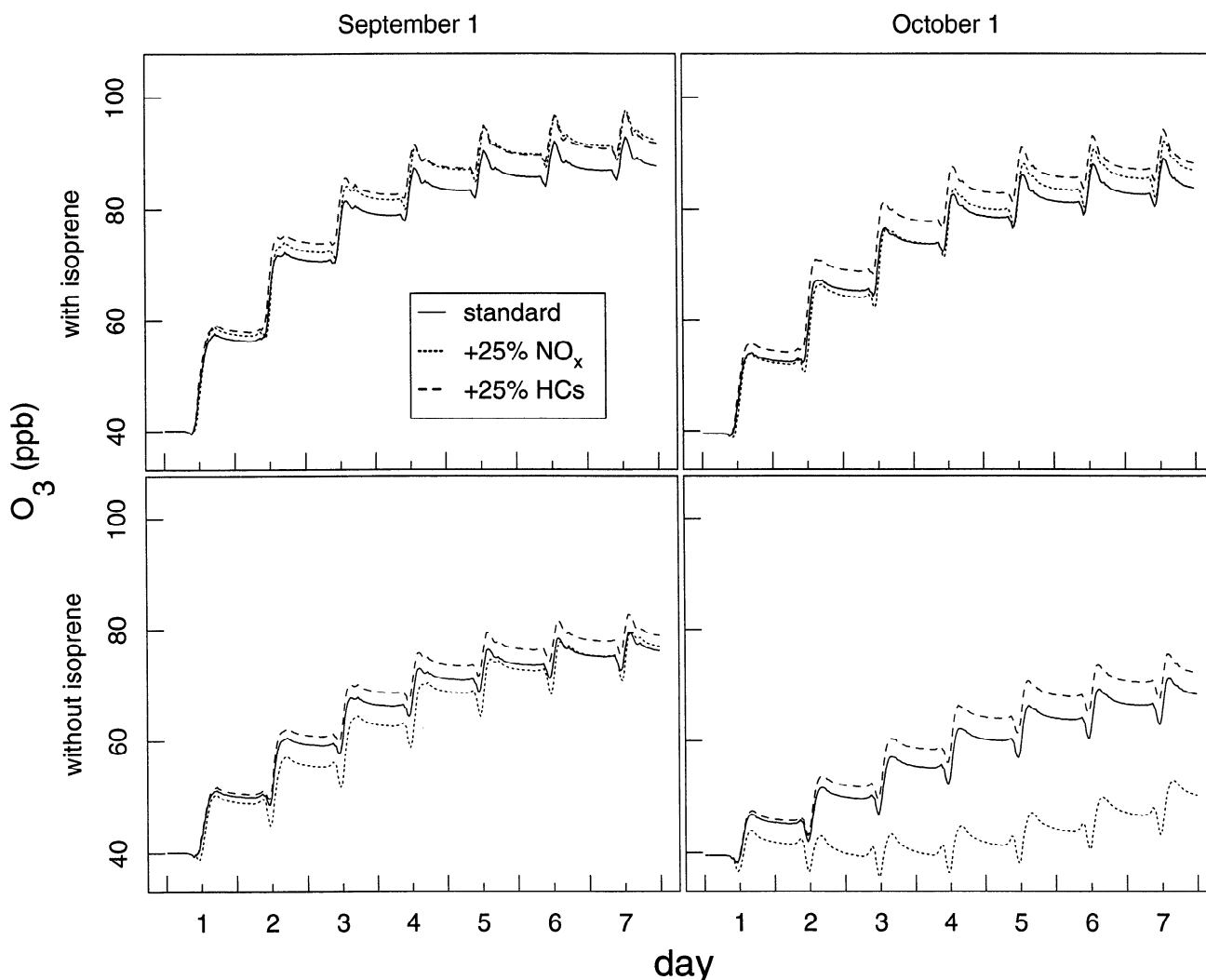


Figure 5. Same as Figure 4 but for a high-O₃ episode (see text).

for the region were taken from Table 6 of *McKeen et al.* [1991b]. On a reactivity-weighted basis [*Trainer 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 NO_x 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 NO_x and hydrocarbon emissions in the September 1 cases, and in the October 1 case with isoprene; NO_x 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 NO_x emissions, indicating strongly hydrocarbon-limited conditions.

We also applied the model to the simulation of a representative high-O₃ episode. Anthropogenic emissions were doubled from the mean values for the eastern United States given by *McKeen 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 NO_x 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, NO_y, H₂O₂, and HCHO concentrations at Shenandoah National Park indicate a seasonal transition from NO_x- to hydrocarbon-limited conditions for O₃ production during September. The transition is diagnosed by large decreases of the H₂O₂/(NO_y-NO_x) and HCHO/NO_y concentration ratios, degradation of the O₃ versus NO_y-NO_x correlation, and decrease of the slope $\Delta O_3/\Delta(NO_y-NO_x)$. The NO_x 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 [*Sillman 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 NO_x 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 valu-

able. 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 NO_x emissions on the export of NO_x out of the boundary layer and hence on tropospheric O₃ and OH. In the remote troposphere the supply of NO_x is, in general, sufficiently low that NO_x-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 NO_x concentrations may be high as a result of lightning, aircraft, and convective updrafts.

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References

- Aneja, V.P., S. Businger, Z. Li, C.S. Claiborn, and A. Murthy, Ozone climatology at high elevations in the southern Appalachians, *J. Geophys. Res.*, **96**, 1007-1021, 1991.
- Atkinson, R., Gas-phase tropospheric chemistry of organic compounds: a review, *Atmos. Environ.*, **24(A)**, 1-42, 1990.
- Atkinson, R., D.L. Baulch, R.A. Cox, R.F. Hampson Jr., J.A. Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry, supplement IV, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, **21**, 1125-1568, 1993.
- Buhr, M. P., D. D. Parrish, R. B. Norton, F. C. Fehsenfeld, R. E. Sievers, and J. M. Roberts, Contribution of organic nitrates to the total reactive nitrogen budget at a rural eastern U.S. site, *J. Geophys. Res.*, **95**, 9809-9816, 1990.
- Chameides, W.L., and J.C.G. Walker, A photochemical theory of tropospheric ozone, *J. Geophys. Res.*, **78**, 8751-8760, 1973.
- Chameides, W.L., R.W. Lindsay, J. Richardson, and C.S. Kiang, The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, *Science*, **241**, 1473-1475, 1988.
- Chameides, W.L., et al., Ozone precursor relationships in the ambient atmosphere, *J. Geophys. Res.*, **97**, 6037-6055, 1992.
- Chin, M., D.J. Jacob, J.W. Munger, D.D. Parrish, and B.G. Doddridge, Relationship of ozone and carbon monoxide over North America, *J. Geophys. Res.*, **99**, 14,565-14,573, 1994.
- Claiborn, C.S., and V.P. Aneja, Measurements of atmospheric hydrogen peroxide in the gas phase and in cloud water at Mt. Mitchell, North Carolina, *J. Geophys. Res.*, **96**, 18,771-18,787, 1991.
- Crutzen, P. J., A discussion of the chemistry of some minor con-

- stituents in the stratosphere and troposphere, *Pure Appl. Geophys.*, 106, 1385-1399, 1973.
- Daum, P.H., S.E. Schwartz, and L. Newman, Acidic and related constituents in liquid-water clouds, *J. Geophys. Res.*, 89, 1447-1458, 1984.
- DeMore, W.B., S.P. Sander, D.M. Golden, M.J. Molina, R.F. Hampson, M.J. Kurylo, C.J. Howard, and A.R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ. 92-1*, Pasadena, Calif., 1992.
- Dentener, F.J., and P.J. Crutzen, Reaction of N₂O₅ on tropospheric aerosols: impact on the global distributions of NO_x, O₃, and OH, *J. Geophys. Res.*, 98, 7149-7163, 1993.
- Doddridge, B.G., R.R. Dickerson, R.G. Wardell, K.L. Civerolo, and L.J. Nunnermacker, Trace gas concentrations and meteorology in rural Virginia, 2, Reactive nitrogen compounds, *J. Geophys. Res.*, 97, 20631-20646, 1992.
- Dommen, J., A. Neftel, A. Sigg, and D.J. Jacob, Ozone and hydrogen peroxide during summer smog episodes over the Swiss Plateau: Measurements and model simulations, *J. Geophys. Res.*, in press, 1995.
- Draxler, R.D., Hybrid single-particle Lagrangian integrated trajectories (HY-SPLIT): Version 3.0, User's guide and model description, *NOAA Tech. Memo. ERL ARL-195*, Air Resour. Lab., Nat. Oceanic and Atmos. Admin., Silver Spring, Maryland, 1992.
- Environmental Protection Agency (EPA), The 1985 NAPAP emission inventory (version 2): Development of the annual data and modeler's tapes, *EPA Rep. EPA-600/7-89-012a*, Research Triangle Park, N.C., 1989.
- Goldstein, A.H., Non-methane hydrocarbons above a midlatitude forest: biogenic emissions and seasonal concentration variations, Ph.D. thesis, Harvard Univ., Cambridge, Mass., 1994.
- Heikes, B.G., Formaldehyde and hydroperoxides at Mauna Loa Observatory, *J. Geophys. Res.*, 97, 18,001-18,013, 1992.
- Hilsenrath, E., D.F. Heath, and B.M. Schlessinger, Seasonal and interannual variations in total ozone revealed by Nimbus 4 backscattered ultraviolet experiment, *J. Geophys. Res.*, 84, 6969-6979, 1979.
- Holzworth, G.C., Mixing depths, wind speeds and air pollution potentials for selected locations in the United States, *J. Appl. Meteorol.*, 6, 1039-1044, 1967.
- Jacob, D.J., E.W. Gottlieb, and Michael J. Prather, Chemistry of a polluted cloudy boundary layer, *J. Geophys. Res.*, 94, 12,975-13,002, 1989a.
- Jacob, D. J., S. Sillman, J. A. Logan, and S. C. Wofsy, Least-independent-variables method for simulations of tropospheric ozone, *J. Geophys. Res.*, 94, 8497-8509, 1989b.
- Jacob, D.J., J.A. Logan, G.M. Gardner, R.M. Yevich, C.M. Spivakovsky, S.C. Wofsy, S. Sillman, and M.J. Prather, Factors regulating ozone over the United States and its export to the global atmosphere, *J. Geophys. Res.*, 98, 14,817-14,826, 1993.
- Jobson, B.T., Z. Wu, H. Niki, and L.A. Barrie, Seasonal trends of isoprene, C₂-C₅ alkanes, and acetylene at a remote boreal site in Canada, *J. Geophys. Res.*, 99, 1589-1599, 1994.
- Keene, W.C., B.W. Mosher, D.J. Jacob, J.W. Munger, R.W. Talbot, R.S. Artz, J.M. Maben, B.C. Daube, and J.N. Galloway, Carboxylic acids in clouds at a high elevation forested site in central Virginia, *J. Geophys. Res.*, this issue.
- Kleinman, L.I., Seasonal dependence of boundary layer peroxide concentrations: The low and high NO_x regimes, *J. Geophys. Res.*, 96, 20,721-20,733, 1991.
- Kleinman, L., et al., Ozone formation at a rural site in the southeastern United States, *J. Geophys. Res.*, 99, 3469-3482, 1994.
- Lin, X., M. Trainer, and S.C. Liu, On the nonlinearity of tropospheric ozone production, *J. Geophys. Res.*, 93, 15,879-15,888, 1988.
- Logan, J.A., The ozone problem in rural areas of the United States, in Proceedings of the NATO Advanced Research Workshop on Regional and Global Ozone and Its Environmental Consequences, *NATO ASI Ser. C, vol. 227*, edited by I.S.A. Isaksen, pp. 327-344, D. Reidel, Norwell, Mass., 1988.
- Logan, J. A., Ozone in rural areas of the United States, *J. Geophys. Res.*, 94, 8511-8532, 1989.
- Logan, J.A., M.J. Prather, S.C. Wofsy, and M.B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, 86, 7210-7254, 1981.
- Madronich, S., Intercomparison of NO₂ photodissociation and U.V. radiometer measurements, *Atmos. Environ.*, 21, 569-578, 1987.
- McKeen, S.A., E.-Y. Hsie, and S.C. Liu, A study of the dependence of rural ozone on ozone precursors in the Eastern United States, *J. Geophys. Res.*, 96, 15,377-15,394, 1991a.
- McKeen, S.A., E.-Y. Hsie, M. Trainer, R. Tallamraju, and S.C. Liu, A regional model study of the ozone budget in the eastern United States, *J. Geophys. Res.*, 96, 10,809-10,845, 1991b.
- Monson, R.K., P.C. Harley, M.E. Litvak, M. Wildermuth, A.B. Guenther, P.R. Zimmerman, and R. Fall, Environmental and developmental controls over the seasonal pattern of isoprene emission from aspen leaves, *Oecologia*, 99, 260-270, 1994.
- Moy, L. A., R. R. Dickerson, and W. F. Ryan, How meteorological conditions affect tropospheric trace gas concentrations in rural Virginia, *Atmos. Environ.*, 28, 2789-2800, 1994.
- Munger, J. W., D. J. Jacob, B. C. Daube, L. W. Horowitz, W. C. Keene, and B. G. Heikes, Formaldehyde, glyoxal, and methylglyoxal in air and cloudwater at a rural mountain site in central Virginia, *J. Geophys. Res.*, this issue.**
- National Research Council (NRC), *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, National Academy Press, Washington, D.C., 1991.
- Olszyna, K.J., J.F. Meagher, and E.M. Bailey, Gas-phase, cloud and rain-water measurements of hydrogen peroxide at a high-elevation site, *Atmos. Environ.*, 22, 1699-1706, 1988.
- Olszyna, K.J., E.M. Bailey, and J.F. Meagher, O₃ and NO_y relationships at a rural site in Tennessee, *Eos Trans. AGU*, 74, (66), 1993.
- Parrish, D.D., et al., The total reactive oxidized nitrogen levels and the partitioning between the individual species at six rural sites in eastern North America, *J. Geophys. Res.*, 98, 2927-2939, 1993.
- Paulson, S.E., and J.H. Seinfeld, Development and evaluation of a photooxidation mechanism for isoprene, *J. Geophys. Res.*, 97, 20,703-20,715, 1992.
- Poulida, O., R.R. Dickerson, B.G. Doddridge, J.Z. Holland, R.G. Wardell, and J.G. Watkins, Trace gas concentrations and meteorology in rural Virginia, 1, Ozone and carbon monoxide, *J. Geophys. Res.*, 96, 22,461-22,475, 1991.
- Sillman, S., The use of NO_y, HCHO, H₂O₂ and HNO₃ as indicators for ozone-NO_x-hydrocarbon sensitivity in urban locations, *J. Geophys. Res.*, in press, 1995.
- Sillman, S., J. A. Logan, and S. C. Wofsy, The sensitivity of ozone to nitrogen oxides and hydrocarbons in regional ozone episodes, *J. Geophys. Res.*, 95, 1837-1852, 1990a.

- Sillman, S., J. A. Logan, and S. C. Wofsy, A regional-scale model for photochemical production of ozone in the United States with subgrid representation of urban and power plant plumes, *J. Geophys. Res.*, *95*, 5731-5748, 1990b.
- Talbot, R.W., B.W. Mosher, B.G. Heikes, D.J. Jacob, J.W. Munger, B.C. Daube, W.C. Keene, J.M. Maben, and R.S. Artz, Carboxylic acids in the rural continental atmosphere over the eastern United States during SCAPE, *J. Geophys. Res.*, this issue.
- Trainer, M., E.J. Williams, D.D. Parrish, M.P. Buhr, E.J. Allwine, H.H. Westberg, F.C. Fehsenfeld, and S.C. Liu, Models and observations of the impact of natural hydrocarbons on rural ozone, *Nature*, *329*, 705-707, 1987.
- Trainer, M., et al., Observations and modeling of the reactive nitrogen photochemistry at a rural site, *J. Geophys. Res.*, *96*, 3045-3063, 1991.
- Trainer, M., et al., Correlation of ozone with NO_y in photochemically aged air, *J. Geophys. Res.*, *98*, 2917-2925, 1993.
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