Seasonal variation of the ozone production efficiency per unit NO$_x$ at Harvard Forest, Massachusetts

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Abstract. Weekly values of the net O$_3$ production efficiency (OPE), defined as the net number of O$_3$ molecules produced per molecule of NO$_x$ (NO + NO$_2$) consumed, are estimated from a 1990-1994 record of O$_3$, NO$_x$, NO$_y$, CO, and C$_2$H$_2$ concentrations at Harvard Forest, Massachusetts. The OPE is inferred from the slope $\Delta$O$_3$/($\Delta$NO$_y$-NO$_x$) of the linear regression between O$_3$ and NO$_y$-NO$_x$ concentrations (NO$_y$ is the sum of NO$_x$ and its oxidation products); and alternatively from the slopes $\Delta$O$_3$/$\Delta$CO and $\Delta$O$_3$/$\Delta$C$_2$H$_2$ multiplied by regional estimates of the CO/NO$_x$ and C$_2$H$_2$/NO$_x$ emission ratios. The mean OPE values inferred from $\Delta$O$_3$/($\Delta$NO$_y$-NO$_x$) are 3-5 times higher than those inferred from $\Delta$O$_3$/$\Delta$CO or $\Delta$O$_3$/$\Delta$C$_2$H$_2$; the discrepancy may be due to the effects of HNO$_3$ and O$_3$ deposition and also to uncertainties in the CO/NO$_x$ and C$_2$H$_2$/NO$_x$ emission ratios. The relative seasonal trends of the OPE derived from $\Delta$O$_3$/($\Delta$NO$_y$-NO$_x$), $\Delta$O$_3$/$\Delta$CO, and $\Delta$O$_3$/$\Delta$C$_2$H$_2$ are, however, similar. Thus $\Delta$O$_3$/($\Delta$NO$_y$-NO$_x$) increases from about 4 mol/mol in May to 8 mol/mol in June-July, and gradually decreases back to 4 mol/mol by early October. The sharp rise of the OPE from May to June is attributed to onset of emission of the biogenic hydrocarbon isoprene. The decline from July to October is attributed to decreases in isoprene emission and in solar radiation. The O$_3$ background at Harvard Forest, defined by the y intercept of the O$_3$ versus NO$_y$-NO$_x$ regression line, decreases from 40 ppbv in May to 25 ppbv in September, consistent with observations at remote sites in northern midlatitudes. The seasonal trend in the background explains why mean O$_3$ concentrations at Harvard Forest peak in May-June even though the OPE peaks in June-July.

1. Introduction

Rapid production of O$_3$ takes place over the United States in summer by photochemical oxidation of hydrocarbons in the presence of nitrogen oxides (NO$_x$ = NO + NO$_2$). Concentrations of O$_3$ in surface air are sufficiently high to have adverse effects on public health and vegetation [National Research Council, 1991]. It is well established that NO$_x$ is in general the principal limiting precursor for O$_3$ formation [Chameides et al., 1992], but there is much uncertainty regarding the factors controlling the O$_3$ yield per unit NO$_x$ (O$_3$ production efficiency, or OPE). We address this issue here by analysis of a long-term record of observations at Harvard Forest, Massachusetts.

The OPE concept was originally introduced by Liu et al. [1987] as the number of O$_3$ molecules produced per molecule of NO$_x$ oxidized. One may define either a gross OPE or a net OPE, based on consideration of either the total or the net number of O$_3$ molecules produced [Lin et al., 1988]. The OPE is a useful quantity for scaling O$_3$ production on a regional scale to the amount of NO$_x$ emitted, and also for measuring the chemical efficiency of O$_3$ production in a way that normalizes to NO$_x$ emission and is not directly dependent on transport considerations. Photochemical models suggest that the OPE should decrease with increasing NO$_x$, increase with increasing hydrocarbons and UV flux, and be relatively insensitive to temperature or humidity [Liu et al., 1987; Lin et al., 1988; Sillman et al., 1990; Walcek and Yuan, 1995]. Our analysis offers a test of these models as well as some new insights for understanding the seasonal variation of O$_3$ concentrations over the eastern United States.

2. Methods

Harvard Forest is a wooded tract in the town of Petersham in central Massachusetts (42°32'N, 72°11'W). The surrounding area is forested and rural. The nearest large cities are Boston and Hartford, 100 km to the east and southwest respectively. New York City is 250 km to the SW. Continuous measurement of trace gases at Harvard Forest has been conducted since 1990 from a 30-m tower extending 6 m above the forest canopy. The measurements include concentrations of O$_3$, NO$_x$, NO$_y$ (sum of NO$_x$ and its oxidation products), CO, and hydrocarbons [Munger et al., 1996; Goldstein et al., 1995]. High concentrations are associated with surface winds from the SW, indicating advection of regional...
Table 1. Data Selection for Calculating $\Delta O_3/\Delta (NO_2-NO_4)$ at Harvard Forest

<table>
<thead>
<tr>
<th>Month</th>
<th>Criterion 1</th>
<th>Criterion 2</th>
<th>Criterion 3</th>
<th>Criterion 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n&gt;10$</td>
<td>$[O_3]_{max}&gt;50$ ppbv</td>
<td>$r^2&gt;0.5$</td>
<td>$[O_3]_{background}&lt;50$ ppbv</td>
</tr>
<tr>
<td>Jan.</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Feb.</td>
<td>5</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mar.</td>
<td>7</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>April</td>
<td>10</td>
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<td>0</td>
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<tr>
<td>May</td>
<td>13</td>
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<tr>
<td>June</td>
<td>13</td>
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<tr>
<td>July</td>
<td>8</td>
<td>8</td>
<td>6</td>
<td>6</td>
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<tr>
<td>Aug.</td>
<td>11</td>
<td>8</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Sept.</td>
<td>10</td>
<td>6</td>
<td>6</td>
<td>6</td>
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<tr>
<td>Oct.</td>
<td>11</td>
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<tr>
<td>Nov.</td>
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<td>0</td>
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<tr>
<td>Dec.</td>
<td>0</td>
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</table>

Number of individual weeks in the Harvard Forest record (1990-1994) satisfying each successive criterion required for calculating $\Delta O_3/\Delta (NO_2-NO_4)$. Here $n$ is the number of concurrent hourly observations for $O_3$, NO$_x$, and NO$_2$ available between 1100 and 1700 local time for a given week; $[O_3]_{max}$ is the maximum concentration for the week; and $r^2$ and $[O_3]_{background}$ are, respectively, the linear correlation coefficient and the y intercept of the $O_3$ versus NO$_2$ NO$_x$ correlation.

pollution from the eastern United States with varying additions of urban plumes from New York City and Connecticut [Munger et al., 1996].

We estimate the net OPE from the Harvard Forest data on a weekly basis as the slope $\Delta O_3/\Delta (NO_2-NO_4)$ of the linear regression between $O_3$ and NO$_2$-NO$_x$ concentrations. Here $\Delta O_3$ represents the enhancement of $O_3$ over the background, $\Delta (NO_2-NO_4)$ represents the corresponding amount of NO$_x$ oxidized, and the ratio thus yields an estimate of the net OPE (from now on we will understand "OPE" to represent the net quantity). The estimate is an upper limit because of HNO$_3$ deposition, as discussed below. The linear regression is computed with the reduced-major-axis method [Hirsch and Gitroy, 1984] applied to the hourly $O_3$ and NO$_2$-NO$_x$ concentrations measured at 1100 1700 eastern standard time (EST); this time window is the period of maximum vertical mixing, when concentrations measured at the tower are most likely to be representative of the continental boundary layer. Concentrations of $O_3$ at Harvard Forest are at their diel maximum at 1100-1700 EST, while concentrations of NO$_x$ and NO$_2$ are at their diel minimum [Munger et al., 1996].

Our analysis covers the period from April 27, 1990 to August 31, 1994. For a given week, we calculate $\Delta O_3/\Delta (NO_2-NO_4)$ only if four criteria are satisfied. First, concurrent observations of $O_3$, NO$_x$, and NO$_2$ must be available for at least 10 hourly periods, this criterion limits the analysis to 98 weeks. Second, $O_3$ concentrations must exceed 50 parts per billion by volume (ppbv) at least once during the week, to limit the effect of variability in $O_3$ background on the slope of the regression line; this criterion excludes 31 of the 98 weeks. Third, the least-squares correlation coefficient ($r^2$) between $O_3$ and NO$_2$, NO$_x$ concentrations must be higher than 0.5; this criterion excludes 30 of the remaining 67 weeks (most of the excluded weeks had peak $O_3$ values barely above 50 ppbv). Fourth, the y intercept of the regression line ($O_3$ background) must be less than 50 ppbv, to screen periods when strong subsidence events with high $O_3$ and low NO$_x$ affected the correlation. This criterion excludes one additional week in May.

A month-by-month summary of the data selection is given in Table 1. The requirement of a weekly maximum $O_3$ higher than 50 ppbv eliminates all weeks in November-February. The requirement of $r^2>0.5$ eliminates a large number of weeks in the spring, but few in summer and none in fall; this result is due to a high $O_3$ background in spring, as discussed below. Our database of OPE values is thus limited to the May-October time window. The OPE values from November to April are certainly lower than in May-October, and possibly negative [Parrish, 1993], but cannot be quantified here.

For the 36 weeks where $\Delta O_3/\Delta (NO_2-NO_4)$ values were calculated, we used a reduced-major-axis method to determine the linear regression coefficients.

Figure 1. Scatterplots and linear regressions (reduced-major-axis method) of $O_3$ versus NO$_2$-NO$_x$ concentrations at Harvard Forest, Massachusetts, for the weeks of May 6-12, 1990 (squares, solid line) and August 24-30, 1992 (circles, dotted line). Concentrations are hourly means at 1100 1700 EST.
Figure 2. Enhancement ratios $\Delta O_3/\Delta (NO_2 - NO_x)$, $\Delta O_3/\Delta CO$, and $\Delta O_3/\Delta C_2H_4$ at Harvard Forest, as a function of time of year. Values for individual weeks are shown as symbols. The lines are locally weighted regressions, $r^2$ ranged from 0.51 to 0.97 with a median value of 0.78. The slope $\Delta O_3/\Delta (NO_2 - NO_x)$ ranged from 2 to 18 mol/mol. The mean $y$ intercept (O$_3$ background) was 31±8 (1σ) ppbv O$_3$. Two representative scatterplots are shown in Figure 1.

Interpretation of $\Delta O_3/\Delta (NO_2 - NO_x)$ as the net OPE is subject to uncertainties related to the deposition of NO$_x$ and O$_3$, and the speciation of NO$_x$-NO$_2$. Data presented by Parrish et al. [1993a] for rural sites in the eastern United States in summer indicate that NO$_x$ accounts on average for about 40% of NO$_x$ during daytime, peroxyacetyl nitrate (PAN) for 30%, and aerosol nitrate for 10%; the 20% residual may represent organic nitrates other than PAN but is also within the uncertainty of the measurements. Nitric acid is removed by wet and dry deposition on a timescale of a few days, while O$_3$ is removed by dry deposition on a timescale of a week [Jacob et al., 1993]. The dry deposition velocity of NO$_2$-NO$_x$ at Harvard Forest is about twice that of O$_3$ [Munger et al., 1996]. We expect therefore $\Delta O_3/\Delta (NO_2 - NO_x)$ to overestimate the actual OPE.

An alternate approach for estimating the OPE is to use the $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta C_2H_4$ ratios derived from the O$_3$ versus CO and O$_3$ versus C$_2$H$_4$ correlations. These ratios, when scaled to NO$_x$/CO or NO$_x$/C$_2$H$_4$ source ratios and applied to aged air (low NO$_x$/NO$_2$ concentration ratio), offer estimates of the OPE that are unaffected by speciation or deposition of NO$_2$-NO$_x$. The estimates are, however, lower limits because of O$_3$ deposition and because of nonzero NO$_2$/NO$_x$; they are, in addition, affected by variability and uncertainty in the source ratios. We calculated weekly values of $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta C_2H_4$ at Harvard Forest from the hourly O$_3$, CO, and C$_2$H$_4$ data at 1100-1700 EST, for those weeks satisfying the four criteria given above. The analysis was restricted to hourly periods with NO$_x$/NO$_2$ < 0.3 mol/mol, to exclude fresh pollution plumes where NO$_x$ has not yet realized its O$_3$ production potential [Chin et al., 1994]. We did not exclude periods when NO$_x$ or NO$_2$ data were missing for too many weeks; in those cases, we relied on the $r^2>0.05$ criterion to screen weeks significantly affected by fresh pollution. Values of $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta C_2H_4$ were obtained for a total of 19 and 17 weeks, respectively, covering the period June-September.

3. Results

Figure 2 shows the seasonal variations of $\Delta O_3/\Delta (NO_2 - NO_x)$, $\Delta O_3/\Delta CO$, and $\Delta O_3/\Delta C_2H_4$ in the 1990-1994 data at Harvard Forest. Figure 3 shows the corresponding seasonal variations of concentrations of O$_3$, NO$_x$, NO$_2$, CO, and C$_2$H$_4$, temperature, and absolute humidity. The mean value of $\Delta O_3/\Delta (NO_2 - NO_x)$ increases from about 4 mol/mol in May to 8 mol/mol in June-July, and then decreases gradually to 4 mol/mol by early October. Previous summer data reported for rural sites in Pennsylvania, Georgia, and Tennessee indicate mean $\Delta O_3/\Delta (NO_2 - NO_x)$ values of 8.5, 11.3, and 12 mol/mol, respectively [Trainer et al., 1993; Kleinman et al., 1994; Olszyna et al., 1994]. These values are consistent with our results. Higher OPE values would be expected in the southeastern United States than in the northeast because of higher isoprene and lower NO$_x$ emissions [Jacob et al., 1993].

Values of $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta C_2H_4$ at Harvard Forest decrease from July to September, similarly to $\Delta O_3/\Delta (NO_2 - NO_x)$. The mean summertime $\Delta O_3/\Delta CO$ is 0.35 mol/mol, typical of observations for other sites in eastern North America [Parrish et al., 1993b; Chin et al., 1994]. Assuming an anthropogenic NO$_x$/CO source ratio of 0.12 mol/mol for the eastern United States, including both area and point sources [Environmental Protection Agency, 1995], we derive a corresponding OPE of 2.9. For $\Delta O_3/\Delta C_2H_4$, the mean summertime value is 90 mol/mol, and the estimated NO$_x$/C$_2$H$_4$ emission ratio is 57 mol/mol (mean eastern United States data from the Environmental Protection Agency [1989] cited by McKeen et al. [1991a], including all anthropogenic sources), corresponding to an OPE of 1.6.

The large difference in the OPE values estimated from $\Delta O_3/\Delta (NO_2 - NO_x)$, on the one hand, and from $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta C_2H_4$, on the other hand, stresses the potential for bias in the interpretation of these quantities as the OPE. In a three-dimensional model for O$_3$ over North America in summer, Chin et al. [1994] obtained a mean OPE of 4.2 for the eastern United States, intermediate between the two estimates. Despite this discrepancy, we will assume for further discussion that the relative seasonal variation of $\Delta O_3/\Delta (NO_2 - NO_x)$ reflects the relative seasonal variation of the OPE. Support for this assumption is offered by the strength of the O$_3$ versus NO$_x$-NO$_2$ correlation, and by the similar relative seasonal variations found for $\Delta O_3/\Delta (NO_2 - NO_x)$, $\Delta O_3/\Delta CO$, and $\Delta O_3/\Delta C_2H_4$ during June-September when data for all three quantities are available.

The seasonal trend of $\Delta O_3/\Delta (NO_2 - NO_x)$ reflects mostly the trend in the regional photochemical enhancement of O$_3$ above a background defined by the y intercept of the O$_3$ versus NO$_x$-NO$_2$ linear relationship.
4. Interpretation

The seasonal variation of the OPE derived from the Harvard Forest data appears at first look to be in phase with solar radiation and temperature. There are however some differences. The OPE is lower in May than in August, even though solar radiation is slightly higher in May. Temperatures increase from June to August (Figure 3, bottom panel) but the OPE does not. The closest coincidence of the seasonal variation of the OPE appears to be with isoprene emission. Continuous observations of isoprene emission at Harvard Forest in 1995 (A.H. Goldstein, unpublished data) show that isoprene emission is nil until early June; rises from early June through the end of June; declines through September; and shuts off abruptly in mid-September. Goldstein [1994] found similar seasonal cycles of isoprene emission for 1992-1994, overlapping our analysis period, but these data are qualitative only and cannot be used for correlation with our OPE values. It is well known that isoprene emission depends on temperature and solar radiation [e.g., Guenther et al., 1995]. However, the seasonal delay of isoprene emission until early June cannot be explained from these dependencies and implies that leaffs do not emit isoprene until they are fully expanded [Goldstein, 1994]. Previous measurements of the seasonal cycle of isoprene for a low-elevation aspen forest in Colorado [Monson et al., 1994] and for a boreal forest in Ontario [Jobson et al., 1994] also indicate a sharp onset of isoprene emission in June (after leaves are fully expanded), a decline starting in July-August, and a complete shut-off during September.

A strong dependence of the OPE on isoprene would be expected from current understanding of tropospheric chemistry, as illustrated by the photochemical model calculations presented in the next section. Isoprene is the principal hydrocarbon precursor of O3 over the eastern United States in summer [McKeen et al., 1991a]. The presence of isoprene under NOx-limited conditions increases the OPE by depleting OH and hence slowing down the oxidation of NOx to HNO3 [Lin et al., 1988; Fan et al., 1994]. An additional factor that may contribute to the seasonal decrease in the OPE from July to October is the decreasing supply of the HOx radicals (OH and peroxy) that drive O3 production. Jacob et al. [1995] found evidence for a seasonal transition from NOx- to hydrocarbon-limited O3 production over the eastern United States in September, reflecting a decline of the HOx supply down to levels that can be titrated by NOx emission. Such a transition in photochemical regime would result in a large drop of the OPE [Stillman, 1995]. The seasonal decrease of OH concentrations also increases the importance of nighttime oxidation as a sink for NOx [Dentener and Crutzen, 1993; Munger et al., 1996], further decreasing the OPE.

It is well known that O3 concentrations in the eastern United States are correlated with temperature [National Research Council, 1991]. This correlation appears to reflect, in part, the deniences of isoprene emission and peroxyacetyl nitrate (PAN) stability on temperature [Cardelino and Chameides, 1990; Stillman and Samson, 1995], but also the association of high temperatures with stagnation episodes [Jacob et al., 1993] and sunny skies [Walew and Yuan, 1995]. We show in Figure 4 the relationship of $\Delta O_3/\Delta NOx$ with temperature in the Harvard Forest data for individual weeks. Here temperature is the weekly average at 1100-1700 EST (results are similar when maximum weekly temperature is used). We find a marked increase of the OPE with temperature that appears attributable at least, in part, to isoprene; weekly temperatures in the 20°-25°C range are associated with lower OPE values when outside of the seasonal time window for isoprene emission. The model of Stillman and Samson [1995] for
HNO₃ is a terminal sink for NO₂. Anthropogenic emissions of NOₓ and hydrocarbons are mean values for the eastern United States as given by McKeeen et al. [1991a]. Fixed concentrations are assumed for CO (200 ppbv) and CH₄ (1700 ppbv). Low concentrations (including 30 ppbv O₃) are specified as upper boundary conditions at 1.8 km and are also used as initial conditions.

We examined the seasonality of the OPE in the model by conducting a series of 7-day simulations for conditions representative of individual months from March to October. Solar declination was specified for the middle of the month. Temperature and dew point were specified from the data in Figure 3. Isoprene emission was included from June to September with a 24-hour average flux of 2x10¹ⁱ molecules cm⁻² s⁻¹ [Guenther et al., 1995], varying with time of day as described by Jacob et al. [1989]. The isoprene emission in the June-September window was held constant, that is, it was not adjusted for month-to-month changes in temperature, in order to isolate the effect of isoprene emission from other temperature-related effects. The afternoon mixed layer depth varied from 1.3 km in March to 1.7 km in April-September to 1.5 km in October [Holzworth, 1967].

Figure 5 shows the time series of O₃, NOₓ, and NOₓ-NO₃ concentrations simulated by the model in July. Also shown is the time series of the net OPE defined as the ratio of net chemical pro-

Figure 4. Relationship of ΔO₃/Δ(NOₓ-NO₃) with the weekly average temperature at 1100-1700 EST. JD is Julian (calendar) day. Solid squares identify weeks within the June 10 September 15 seasonal time window for isoprene emission at Harvard Forest [Goldstein, 1994; A.H. Goldstein, unpublished data].

5. Photochemical Model Calculations

We used a one-dimensional photochemical model for the continental boundary layer over the eastern United States to support our analysis of the factors controlling the seasonal variation of the OPE. The model has been described previously by Jacob et al. [1995]. It resolves the boundary layer with six gridpoints extending up to 1.8 km. Vertical transport is represented by diurnally varying eddy diffusion coefficients. The gas phase NO₂-NOₓ-hydrocarbon chemical mechanism is based on recent compilations of laboratory data. Hydrolysis of N₂O₅ in aerosols is included with a rate constant of 1x10⁻⁴ s⁻¹. Ultraviolet intensities are computed assuming 30% opaque cloud cover. The deposition velocity of O₃ at 10 m altitude is 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
production of $O_3$, (P-L)$_{O_3}$, to net chemical loss of $NO_x$, (L-P)$_{NO_x}$, averaged over 24 hours for each individual day. The OPE decreases from 1.5 to 5.0 over the 7 days of simulation, principally because of rising $O_3$ concentrations and hence faster $O_3$ loss. We choose to define the model OPE representative of the 7-day simulation as the ratio of the 7-day average values of (P-L)$_{O_3}$ and (L-P)$_{NO_x}$.

Figure 6 shows the seasonal variation of the OPE computed in the above manner. The OPE is negative in March as photochemistry is a net sink for $O_3$. It rises to a maximum value of 5.7 in June-September, and decreases abruptly in October to negative values. The sumnetime OPE in the model is 30% lower than the mean observed value of $\Delta O_3/\Delta (NO_2-N_2O_5)$ at Harvard Forest; the difference could be due to a number of factors as discussed above. The sharp rise in the model OPE from May to June is consistent with that observed for $\Delta O_3/\Delta (NO_2-N_2O_5)$, but the model does not capture the observed decrease of $\Delta O_3/\Delta (NO_2-N_2O_5)$ from July to September.

The principal factors controlling the seasonal variation of the OPE in the model are isoprene emission, UV radiation, and humidity. Figure 6 shows the results of sensitivity simulations exploring the role of these different factors. The simulations without isoprene emission show little increase in OPE from May to June, but a significant OPE decline starting in August. The decline reflects the decreasing supply of HO$_2$ radicals, forcing a transition to a hydrocarbon-limited regime. This transition is delayed to October when isoprene is present [Jacob et al., 1995]. Observations of the seasonal cycle of isoprene [Goldstein, 1994; Johnson et al., 1994; Monson et al., 1994] all indicate a decrease in emission from July to September, which could perhaps explain the seasonal decrease of the OPE at Harvard Forest. Even in the absence of isoprene, OPE values in the model are higher in September than in April, due to the higher absolute humidity in September and hence the larger source of HO$_2$ radicals. In a sensitivity calculation with temperature and absolute humidity taken to be seasonally invariant (short-dashed line in Figure 6), the OPE values in April and September are similar.

6. Conclusions

Weekly values of the net $O_3$ production efficiency per unit $NO_x$ (OPE) were estimated at Harvard Forest from a 5-year record of $O_3$, $NO_x$, $NO_y$, CO, and $C_2H_4$ concentrations. The data show a sharp rise in the OPE in the model in the period from early May to late July, which is attributed to the onset of isoprene emission, and a gradual decrease from July to September. Our results support photochemical model predictions that isoprene is a major factor enhancing $O_3$ production per unit $NO_x$. Three-dimensional models for the eastern United States in summer indicate that isoprene emission increases surface $O_3$ levels by 5-15ppbv relative to isoprene-free conditions [McKeen et al., 1991b; Roselle et al., 1991; Jacob et al., 1993]. Isoprene emission in these models appears to be underestimated by about a factor of 3 relative to more recent estimates [Geron et al., 1994; Guenther et al., 1995], so that the magnitude of the $O_3$ enhancement associated with isoprene would be underestimated. The photochemical model calculations presented in this paper, including isoprene emission from Guenther et al. [1995], indicate a 50% increase in OPE in the model due to isoprene emission. Because of the importance of isoprene for $O_3$ production and for other aspects of tropospheric photochemistry [Fehsenfeld et al., 1992], there is a clear need to better understand the factors controlling its emission by vegetation.

The seasonal variations derived in this work for the OPE and for the regional $O_3$ background can be used to interpret the seasonal variation of $O_3$ concentrations observed in the eastern United States. The high-$O_3$ season extends from May to September [Logan, 1985; Vukovich, 1994]; the trend within this time window varies considerably from year to year and from site to site but there is a tendency for earlier seasonal maxima in the northeastern United States than in the southeast [Vukovich, 1994]. Our analysis suggests that the extent of the high-$O_3$ season is largely determined by the seasonal window of isoprene emission (June-September). The later seasonal maxima of $O_3$ in the southeastern United States than in the northeast may be explained by a later senescence of vegetation. The relatively high mean $O_3$ concentrations observed in May, before the onset of isoprene emission, appear to be due in part to an elevated tropospheric background.

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References


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