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_2H_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 $\Delta O_3/\Delta C_2H_2$ multiplied by regional estimates of the CO/NO_x and C_2H_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 $\Delta O_3/\Delta C_2H_2$; 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_2H_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 $\Delta O_3/\Delta C_2H_2$ 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 $\Delta O_3/\Delta(NO_y-NO_x)$ at Harvard Forest

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

Number of individual weeks in the Harvard Forest record (1990-1994) satisfying each successive criterion required for calculating $\Delta O_3/\Delta(NO_y-NO_x)$. Here n is the number of concurrent hourly observations for O_3, NO_x, and NO_y 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_y-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 $\Delta O_3/\Delta(NO_y-NO_x)$ of the linear regression between O_3 and NO_y-NO_x concentrations. Here ΔO_3 represents the enhancement of O_3 over the background, $\Delta(NO_y-NO_x)$ 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 Gilroy*, 1984] applied to the hourly O_3 and NO_y-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_y 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 $\Delta O_3/\Delta(NO_y-NO_x)$ only if four criteria are satisfied. First, concurrent observations of O_3, NO_x, and NO_y 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_y-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_y affected the correla-

tion. 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.

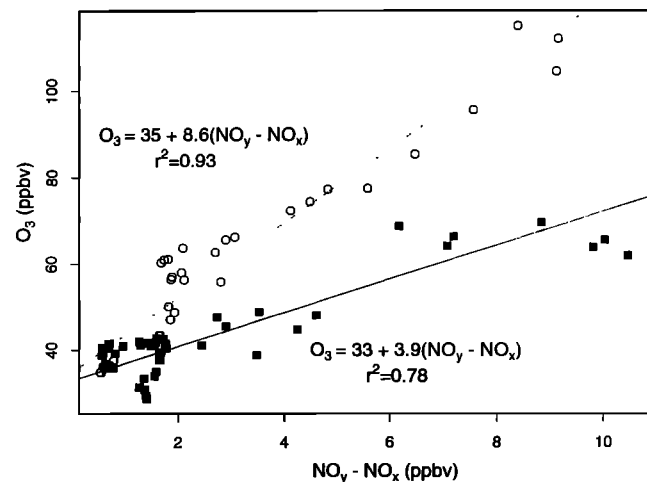For the 36 weeks where $\Delta O_3/\Delta(NO_y-NO_x)$ values were calcu-

Figure 1. Scatterplots and linear regressions (reduced-major-axis method) of O_3 versus NO_y-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.
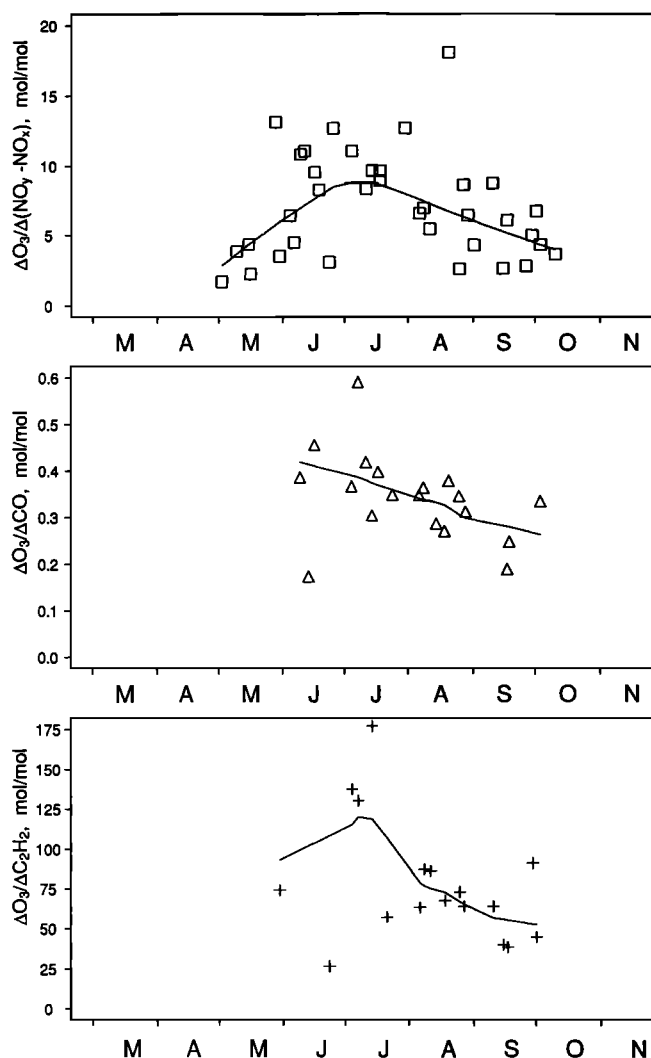
Figure 2. Enhancement ratios $\Delta O_3/\Delta(NO_y-NO_x)$, $\Delta O_3/\Delta CO$, and $\Delta O_3/\Delta C_2H_2$ at Harvard Forest, as a function of time of year. Values for individual weeks are shown as symbols. The lines are locally weighted regressions.

lated, r^2 ranged from 0.51 to 0.97 with a median value of 0.78. The slope $\Delta O_3/\Delta(NO_y-NO_x)$ ranged from 2 to 18 mol/mol. The mean y intercept (O_3 background) was $31\pm8(1\sigma)$ ppbv O_3. Two representative scatterplots are shown in Figure 1.

Interpretation of $\Delta O_3/\Delta(NO_y-NO_x)$ as the net OPE is subject to uncertainties related to the deposition of NO_y and O_3 and the speciation of NO_y-NO_x. Data presented by *Parrish et al.* [1993a] for rural sites in the eastern United States in summer indicate that HNO_3 accounts on average for about 40% of NO_y-NO_x during daytime, peroxyacetylnitrate (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_y-NO_x at Harvard Forest is about twice that of O_3 [*Munger et al.*, 1996]. We expect therefore $\Delta O_3/\Delta(NO_y-NO_x)$ to overestimate the actual OPE.

An alternate approach for estimating the OPE is to use the $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta C_2H_2$ ratios derived from the O_3 versus CO and O_3 versus C_2H_2 correlations. These ratios, when scaled to NO_x/CO or NO_x/C_2H_2 source ratios and applied to aged air (low

NO_x/NO_y concentration ratio), offer estimates of the OPE that are unaffected by speciation or deposition of NO_y-NO_x. The estimates are, however, lower limits because of O_3 deposition and because of nonzero NO_x/NO_y; they are, in addition, affected by variability and uncertainty in the source ratios. We calculated weekly values of $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta C_2H_2$ at Harvard Forest from the hourly O_3, CO, and C_2H_2 data at 1100-1700 EST, for those weeks satisfying the four criteria given above. The analysis was restricted to hourly periods with $NO_x/NO_y < 0.3$ 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_y data were missing as too many weeks would be affected; in those cases, we relied on the $r^2>0.5$ criterion to screen weeks significantly affected by fresh pollution. Values of $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta C_2H_2$ 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 $\Delta O_3/\Delta(NO_y-NO_x)$, $\Delta O_3/\Delta CO$, and $\Delta O_3/\Delta C_2H_2$ in the 1990-1994 data at Harvard Forest. Figure 3 shows the corresponding seasonal variations of concentrations of O_3, NO_x, NO_y, CO, and C_2H_2, temperature, and absolute humidity. The mean value of $\Delta O_3/\Delta(NOy-NO_x)$ 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 $\Delta O_3/\Delta(NO_y-NO_x)$ 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 $\Delta O_3/\Delta C_2H_2$ at Harvard Forest decrease from July to September, similarly to $\Delta O_3/\Delta(NO_y-NO_x)$. 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 $\Delta O_3/\Delta C_2H_2$, the mean summertime value is 90 mol/mol, and the estimated NO_x/C_2H_2 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 $\Delta O_3/\Delta(NO_y-NO_x)$, on the one hand, and from $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta C_2H_2$, 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 above estimates. Despite this discrepancy, we will assume for further discussion that the relative seasonal variation of $\Delta O_3/\Delta(NO_y-NO_x)$ reflects the relative seasonal variation of the OPE. Support for this assumption is offered by the strength of the O_3 versus NO_y-NO_x correlation, and by the similar relative seasonal variations found for $\Delta O_3/\Delta(NO_y-NO_x)$, $\Delta O_3/\Delta CO$, and $\Delta O_3/\Delta C_2H_2$ during June-September when data for all three quantities are available.

The seasonal trend of $\Delta O_3/\Delta(NO_y-NO_x)$ 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_y-NO_x
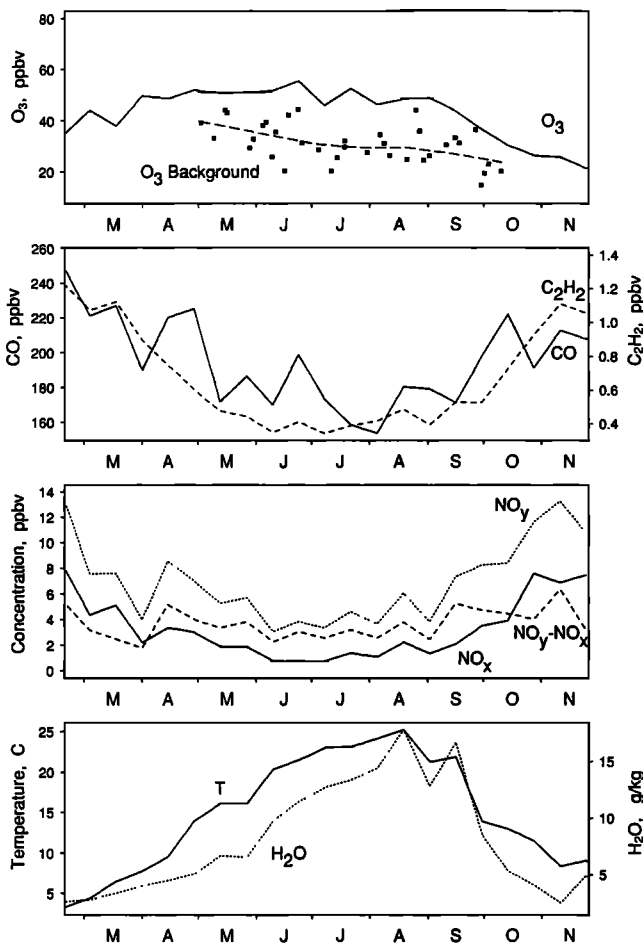
Figure 3. Mean 1990-1994 observations at Harvard Forest at 1100-1700 EST as a function of time of year. The solid squares are the O_3 background concentrations defined as the y-intercept of the O_3 versus NO_y-NO_x regression line; the corresponding dashed line is a locally weighted regression.

linear regression [Kleinman et al., 1994]. The seasonal variation of NO_y-NO_x is weak in comparison, as seasonal variations of NO_x and NO_y tend to cancel (Figure 3; see Munger et al. [1996] for further discussion). The top panel of Figure 3 shows the O_3 background values for the individual weeks where $\Delta O_3/\Delta(NO_y-NO_x)$ could be calculated (solid squares). The O_3 background decreases from 40 ppbv in early May to 20 ppbv at the end of September, a trend consistent with observed O_3 concentrations at remote sites in northern midlatitudes [Logan, 1985]. The high tropospheric background in spring may reflect downwelling of O_3 from the stratosphere [Levy et al., 1985], or photochemical production of O_3 from precursors stored at high latitudes during the winter months [Liu et al., 1987]. The decrease in the background from spring to summer could reflect in addition a more rapid deposition of O_3 to the fully leafed canopy [Munger et al., 1996].

The seasonal decrease in the O_3 background from May to September explains why mean O_3 concentrations at Harvard Forest peak in May-June, while the enhancement above background peaks in June-August (Figure 3). Observations for Harvard Forest and for nearby Montague, Massachusetts, indicate that although mean O_3 concentrations are comparable in May and June, high-O_3 episodes are more frequent in June [Logan, 1989; Munger et al., 1996], consistent with a higher OPE in June.

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 dependences and implies that leaves 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 O_3 over the eastern United States in summer [McKeen et al., 1991a]. The presence of isoprene under NO_x-limited conditions increases the OPE by depleting OH and hence slowing down the oxidation of NO_x to HNO_3 [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 HO_x radicals (OH and peroxy) that drive O_3 production. Jacob et al. [1995] found evidence for a seasonal transition from NO_x- to hydrocarbon-limited O_3 production over the eastern United States in September, reflecting a decline of the HO_x supply down to levels that can be titrated by NO_x emission. Such a transition in photochemical regime would result in a large drop of the OPE [Sillman, 1995]. The seasonal decrease of OH concentrations also increases the importance of nighttime oxidation as a sink for NO_x [Dentener and Crutzen, 1993; Munger et al., 1996], further decreasing the OPE.

It is well known that O_3 concentrations in the eastern United States are correlated with temperature [National Research Council, 1991]. This correlation appears to reflect, in part, the dependences of isoprene emission and peroxyacetylnitrate (PAN) stability on temperature [Cardelino and Chameides, 1990; Sillman and Samson, 1995], but also the association of high temperatures with stagnation episodes [Jacob et al., 1993] and sunny skies [Walcek and Yuan, 1995]. We show in Figure 4 the relationship of $\Delta O_3/\Delta(NO_y-NO_x)$ 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 Sillman and Samson [1995] for
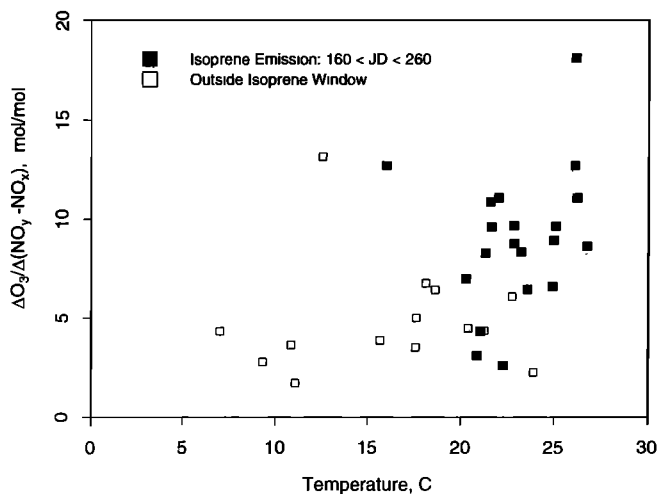
Figure 4. Relationship of $\Delta O_3/\Delta(NO_y-NO_x)$ with the weekly average temperature at 1100-1700 EST. JD is Julian (calendar) day. Solid squares identify weeks within the June 10 - September 15 seasonal time window for isoprene emission at Harvard Forest [*Goldstein*, 1994; A.H. Goldstein, unpublished data].

rural photochemistry in the eastern United States indicates an increase of $\Delta O_3/\Delta(NO_y-NO_x)$ from 5.0 to 7.5 mol/mol as temperature increases from 293K to 308K, including effects from both isoprene emission and PAN stability, but the results in Figure 4 indicate a steeper increase. The isoprene emissions assumed by *Sillman and Samson* [1995] are about 3 times lower than recommended in the recent inventories of *Geron et al.* [1994] and *Guenther et al.* [1995], possibly explaining the difference.

According to photochemical models, the OPE should decrease with increasing NO_x above 0.3 ppbv [*Lin et al.*, 1988]. We find no significant correlation between $\Delta O_3/\Delta(NO_y-NO_x)$ and NO_x in the Harvard Forest data for June-August ($r = -0.15$). This lack of correlation could, however, reflect the fact that the O_3 enhancements in polluted air parcels are due to accumulation over several days [*Kleinman et al.*, 1994], while the lifetime of NO_x is less than a day. Perhaps more meaningful is that we find no significant correlation of $\Delta O_3/\Delta(NO_y-NO_x)$ with CO, a long-lived tracer of pollution. There is a significant negative correlation with NO_y ($r = -0.52$), which could, however, reflect the effect of NO_y deposition.

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 HO_x-NO_x-hydrocarbon chemical mechanism is based on recent compilations of laboratory data. Hydrolysis of N_2O_5 in aerosols is included with a rate constant of 1×10^{-4} s^{-1}. Ultraviolet intensities are computed assuming 30% opaque cloud cover. The deposition velocity of O_3 at 10 m altitude is 0.5 cm s^{-1} in the day and 0.1 cm s^{-1} at night. The deposition of HNO_3 is limited by the rate of turbulent diffusion to the surface, and is sufficiently fast that conversion to

HNO_3 is a terminal sink for NO_x. Anthropogenic emissions of NO_x and hydrocarbons are mean values for the eastern United States as given by *McKeen et al.* [1991a]. Fixed concentrations are assumed for CO (200 ppbv) and CH_4 (1700 ppbv). Low concentrations (including 30 ppbv O_3) 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 2×10^{11} 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 O_3, NO_x, and NO_y-NO_x 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-
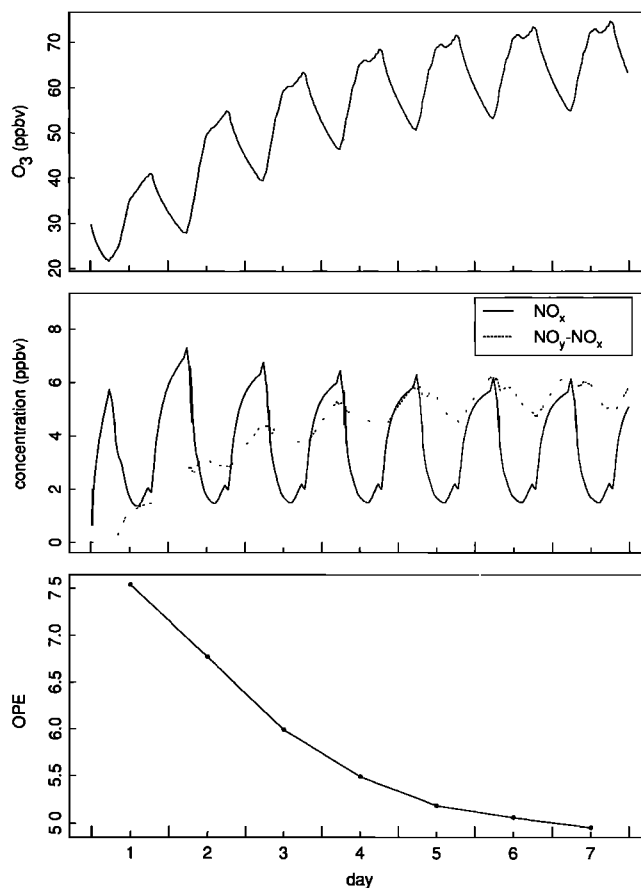

Figure 5. Surface air concentrations of O_3, NO_x, and NO_y calculated with a one-dimensional photochemical model for Harvard Forest in July, and net OPE for successive days calculated as the ratio of the net chemical production of O_3 to the net chemical loss of NO_x averaged over 24 hours in the 0-1.8 km column.
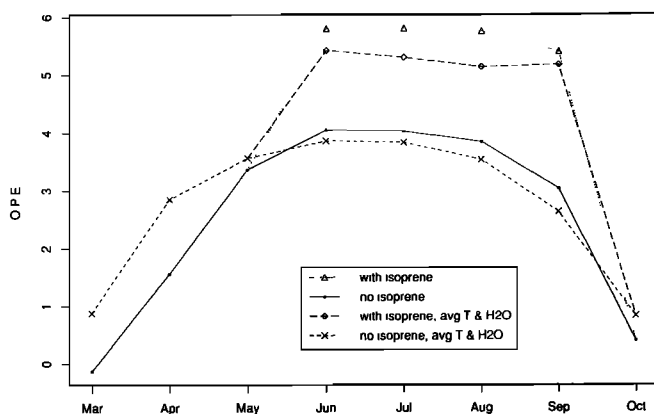
Figure 6. Seasonal variation of the net OPE computed in the one-dimensional model. The solid line shows results from the standard simulation accounting for seasonal changes of solar declination, temperature, and humidity, but without isoprene emission. The dotted line shows the effect of including isoprene emission at a constant value from June to September. The dashed lines show results of simulations with temperature and specific humidity held constant from March to October at their mean values for the period, without isoprene emission (short dashes) and with isoprene emission from June to September (long dashes).

duction 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 7.5 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 back to negative values. The summertime OPE in the model is 30% lower than the mean observed value of $\Delta O_3/\Delta(NO_y-NO_x)$ 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 $\Delta O_3/\Delta(NO_y-NO_x)$, but the model does not capture the observed decrease of $\Delta O_3/\Delta(NO_y-NO_x)$ 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_x 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; *Jobson 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_x 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_2 concentrations. The data show a sharp rise in the OPE from May to June-July, which is attributed to onset of isoprene emission, and a gradual decrease from July to October. 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 5-15 ppbv 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 summer 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 defined 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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