Relationship of ozone and carbon monoxide over North America

Mian Chin, Daniel J. Jacob, and J. William Munger
Division of Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts

David D. Parrish
NOAA Aeronomy Laboratory, Boulder, Colorado

Bruce G. Doddridge
Department of Meteorology, University of Maryland, College Park

Abstract. Observations at sites in eastern North America show a strong correlation between \( \Delta O_3 \) and CO concentrations in summer, with a consistent slope \( \Delta O_3/\Delta CO = 0.3 \). Observations in the aged Denver plume at Niwot Ridge, Colorado, also show a strong correlation but with \( \Delta O_3/\Delta CO = 0.15 \). These data offer a sensitive test for evaluating the ability of photochemical models to simulate production of \( O_3 \) over North America and its export to the global atmosphere. Application to the Harvard/Goddard Institute for Space Studies three-dimensional, continental-scale model shows that the model gives a good simulation of the observed \( O_3-\text{CO} \) correlations and of the associated \( \Delta O_3/\Delta CO \). This successful simulation lends support to model estimates of 6 Gmol d\(^{-1}\) for the net \( O_3 \) production in the U.S. boundary layer in summer (corresponding to a net \( O_3 \) production efficiency of 5.5, which is the number of \( O_3 \) molecules produced per molecule of \( NO_x \) consumed) and 70% for the fraction of the net production that is exported to the global atmosphere. Export of U.S. pollution appears to make a significant contribution to total tropospheric \( O_3 \) over the northern hemisphere in summer. Simple interpretation of observed \( \Delta O_3/\Delta CO \) as an \( O_3/\text{CO} \) anthropogenic enhancement ratio is shown to underestimate substantially anthropogenic \( O_3 \) production, because \( O_3 \) and CO concentrations are negatively correlated in the absence of photochemistry. It is also shown that concurrent observations of \( \Delta O_3/\Delta CO \) and \( \Delta O_3/\Delta (\text{NO}_x-\text{NO}_y) \) ratios can be used to impose lower and upper limits on the net \( O_3 \) production efficiency.

1. Introduction

Tropospheric \( O_3 \) is a key precursor of the hydroxyl radical which controls the oxidizing power of the atmosphere [Logan et al., 1981; Thompson, 1992]. Ozone is also one of the major pollutants which, in high concentration, can be harmful to human health and to plants. Large amounts of anthropogenic \( O_3 \) are produced over the United States in summer by photochemical oxidation of nonmethane hydrocarbons (NMHCs) in the presence of nitrogen oxides (\( NO_x = NO + NO_y \)). Quantifying this anthropogenic source of \( O_3 \) and assessing its global influence is presently a major research issue in tropospheric chemistry [Liu et al., 1987; International Global Atmospheric Chemistry (IGAC), 1992; Parrish et al., 1993].

The covariance of \( O_3 \) and CO concentrations offers a valuable constraint for quantifying the anthropogenic source of \( O_3 \). Carbon monoxide is a long-lived tracer of human activity with relatively well known sources from combustion, industry, and oxidation of hydrocarbons [Logan et al., 1981]. Several authors have used the \( O_3-\text{CO} \) correlation measured from aircraft downwind of the United States to diagnose pollution influence on \( O_3 \) [Fishman and Seiler, 1983; Fishman et al., 1987; Chameides et al., 1987, 1989; Marenco and Saitd, 1989]. Recently, Parrish et al. [1993] made a first estimate of the export of anthropogenic \( O_3 \) from North America to the North Atlantic by using the slope \( \Delta O_3/\Delta CO = 0.3 \) measured at three Canadian marine sites downwind of the United States and scaling to a \( CO \) emission inventory for the eastern United States. They concluded that export of pollution from the United States dominates over transport from the stratosphere as a source of \( O_3 \) to the lower troposphere over the North Atlantic in summer.

A more detailed interpretation of \( \Delta O_3/\Delta CO \) in terms of \( O_3 \) production requires a three-dimensional model that can resolve complicating factors such as the effect of \( O_3 \) deposition, the presence of chemical sources and sinks for CO, and spatial variability. We present here such an analysis using a continental-scale model for \( O_3 \) and its precursors over North America [Jacob et al., 1993a]. Our principal objective is to use the \( O_3-\text{CO} \) correlation as a test of the ability of the model to compute production of \( O_3 \) over the continent. The particular value of this test is that it normalizes \( O_3 \) photochemical enhancements to a long-lived tracer of human activity. Ozone concentrations alone do not offer as sensitive a test because they include a substantial and variable background advected from the model boundaries (e.g., from the oceans or from high altitude). In rural surface. (Copyright 1994 by the American Geophysical Union. Paper number 94JD00907. 0148-0227/94/94JD-00907S05.00)
air over the eastern United States, about half of the mean summertime \( \text{O}_3 \) concentration appears to be contributed by advection from outside North America [Jacob et al., 1993a]. The \( \text{O}_3 \)-\text{CO} correlation removes to a large degree the sensitivity to background. As such, it diagnoses whether the model is giving a successful simulation of \( \text{O}_3 \) for the right reasons.

Section 2 gives a brief description of the model and summarizes important previous results. Section 3 presents observed \( \text{O}_3 \)-\text{CO} correlations at sites in North America and compares model to observations. Section 4 assesses the possibility for direct interpretation of observed \( \Delta \text{O}_3/\Delta \text{CO} \) as an anthropogenic enhancement ratio. Conclusions are in section 5.

2. The Model

The three-dimensional photochemical model of Jacob et al. [1993a] covers a domain including North and Central America and important previous results. Section 3 presents observed \( \text{O}_3 \)-\text{CO} correlations at sites in North America and compares model to observations. Section 4 assesses the possibility for direct interpretation of observed \( \Delta \text{O}_3/\Delta \text{CO} \) as an anthropogenic enhancement ratio. Conclusions are in section 5.

The simulation is conducted for 3 summer months (June to August) with 2 weeks of initialization in May. Meteorological input is provided by one summer of data from a general circulation model (GCM) developed at the Goddard Institute of Space Studies (GISS) [Hansen et al., 1983]. Meteorological variables are updated every 4 hours, and model output is also sampled every 4 hours. Boundary concentrations at the edges of Figure 1 are specified as a function of latitude, altitude, and month using observations.

The GCM is intended to simulate a typical year rather than any particular year; evaluation of model results with observations must therefore focus on seasonal statistics rather than on values for any particular day. Jacob et al. [1993a] previously evaluated the model with observed statistics for the concentrations of \( \text{O}_3 \) and precursors at rural sites in the United States. The model reproduces the observed summer median \( \text{O}_3 \) concentrations to within 5 ppb in most cases, except in the south central United States where concentrations are overpredicted by 15–20 ppb due in part to insufficient ventilation. Median summertime concentrations of \text{CO} are simulated to within 30 ppb at all sites, and the spatial variance of rural \text{CO} across the United States is well captured.

A detailed discussion of the \( \text{O}_3 \) budget in the three-dimensional model is given by Jacob et al. [1993b]. The net production rate of \( \text{O}_3 \) in the U.S. boundary layer (0–2.6 km altitude) averages 6.1 Gmol \( \text{d}^{-1} \) for the 3 month period June to August. The net \( \text{O}_3 \) production efficiency \( e_{\text{N}} \) (net number of \( \text{O}_3 \) molecules produced per molecule of \( \text{NO}_x \) consumed, as defined by Lin et al. [1988]) has a mean value of 5.5 in the U.S. boundary layer and is more than 2 times higher in the western United States (9.1) than in the east (4.2) because of lower \( \text{NO}_x \) concentrations in the west. (Notice the slight changes of the values of \( \text{O}_3 \) production rate and net \( \text{O}_3 \) production efficiency from Jacob et al. [1993b], after correcting an error in saving those values.) Only 30% of the net \( \text{O}_3 \) production in the U.S. boundary layer in the model is deposited to the region; the remaining 70% is exported to the global atmosphere. This export amounts to about one fifth of
the cross-tropopause transport of O$_3$ over the entire northern hemisphere in summer. Implying that O$_3$ produced in the United States makes a significant contribution to tropospheric O$_3$ on the hemispheric scale.

3. O$_3$-CO Correlations

Table 1 summarizes observed and simulated O$_3$-CO correlation statistics for eight nonurban sites in North America where at least 1 month of observations are available in summer (June to August). Site locations are shown in Figure 1. For continental sites we restrict our attention to the 1300–1700 LT window, when surface air is most likely representative of the boundary layer. Such a restriction is not needed at marine sites where we use data for all times of day. The model gives one value per day in the 1300–1700 LT window at any site, the exact hour depending on longitude (1300 LT in Colorado, 1500 LT on the East Coast of the United States); we use that value for constructing model statistics. All statistics in the model are constructed for June to August (n = 92 points at continental sites; n = 552 points at marine sites), even when the observations cover only a fraction of that period.

Figure 2 plots observed O$_3$ versus CO concentrations at Harvard Forest in central Massachusetts. There is no significant correlation because of a number of points with elevated CO but low O$_3$, representing fresh pollution plumes that have not yet realized their O$_3$ production potential. Production of O$_3$ over the United States in summer is mostly NO$_x$ limited [Trainer et al., 1987; Sillman et al., 1990b; McKeen et al., 1991; Chameides et al., 1992]; therefore realization of the O$_3$ production potential can be diagnosed by the NO$_x$/NO$_y$ concentration ratio where NO$_y$ represents the sum of NO$_x$ and its oxidation products [Trainer et al., 1993]. Figure 3 plots the NO$_x$/NO$_y$ concentration ratio at Harvard Forest against the standard normal distribution. Two distinctly different populations are found: NO$_x$/NO$_y$ < 0.3 (photchemically aged rural air) and NO$_x$/NO$_y$ > 0.3 (fresh pollution). The rural air data (solid circles in Figure 2) show a strong correlation between O$_3$ and CO concentrations ($r^2 = 0.78$). This correlation is insensitive to small changes in the NO$_x$/NO$_y$ criterion (using NO$_x$/NO$_y$ < 0.2 as the criterion does not alter the correlation or the slope).

Figure 4 compares model results with rural observations (diagnosed by NO$_x$/NO$_y$ < 0.3) at the five flatland and mountaintop sites listed in Table 1. The sites were chosen for the availability of concurrent observations for O$_3$, CO, NO$_x$, and NO$_y$. The measurements at Shenandoah include NO and NO$_y$ concentrations but not NO$_2$ [Doddridge et al., 1992]; we estimate the NO$_2$ concentrations at that site from NO/NO$_2$/O$_3$ photostationary steady state [Leighton, 1961], using local UV flux measurements to estimate the NO$_2$ photolysis rate constant [Madronich, 1987]. Selection of data with NO$_x$/NO$_y$ < 0.3 is not possible in the model because NO$_y$ is not a tracer; however, it is not necessary
since urban and industrial pollution plumes are isolated in the model with the subgrid scheme.

The observations at Harvard Forest, Scotia (Pennsylvania), and Kinverbsh (Alabama) show significant correlation between O$_3$ and CO concentrations, with $\Delta$O$_3$/ΔCO $\sim$ 0.3 at all three sites (Table 1). We find excellent agreement between model and observations at Harvard Forest for O$_3$ and CO concentrations and for the associated $\Delta$O$_3$/ΔCO (Figure 4a). The observations at Scotia are also well reproduced by the model, although the model has less scatter (Figure 4b). The model also reasonably agrees with the observations at Kinverbsh; although the slope in the model is somewhat higher than in the observations (Figure 4c), it overlap within the standard error. The model does not, in general, capture the extremes in the observed concentrations, in part because of spatial averaging on the 4$^\circ$ x 5$^\circ$ grid scale.

Results for Shenandoah National Park, Virginia (mountaintop site, 1100 m altitude) are shown in Figure 4d. The observations show no significant O$_3$-CO correlation, while the model shows a strong correlation with slope $\Delta$O$_3$/ΔCO $\sim$ 0.3. The median concentration of O$_3$ in the model is 22 ppb higher than observed, while the median concentration of CO is 30 ppb lower. Model statistics are for the lowest layer (0–500 m altitude) to account for the upslope circulation in the daytime [Poulida et al., 1991]; however, model results in layer 2 (corresponding to the actual altitude of the site) are not significantly different. The observations are from the summer of 1989, which was unusually cold, cloudy, and rainy; mean O$_3$ concentrations at the site that summer were 10 ppb lower than the average for the past six summers [Poulida et al., 1991].

Results for Niwot Ridge, Colorado (3100 m) are shown in Figure 4e. The observations at Niwot Ridge sample, in general, either relatively clean air advected from the west or boundary layer air transported upslope from the east and contaminated by the Denver metropolitan area [Parrish et al., 1990]. The O$_3$-CO correlation in the observations is driven by the Denver plume. We show in Figure 4e model results for air at the altitude of Niwot Ridge (open squares) and for the 4- to 8-hour old Denver plume resolved with the subgrid scheme (open triangles). Model results seem consistent with observations. We find that $\Delta$O$_3$/ΔCO at Niwot Ridge is markedly lower than at rural eastern U.S. sites, both in the observations and in the model (Table 1). This result can be explained by the low NO$_x$/CO emission ratio in the Denver metropolitan area (0.14) as compared to the average for the eastern United States (0.23) [EPA, 1989]. The low NO$_x$/CO emission ratio in Denver reflects the dominance of mobile sources and fuel-rich combustion in automobiles not tuned to the local altitude of 1600 m [Parrish et al., 1991].

Figure 5 compares model and observations at three Canadian marine sites [Parrish et al., 1993]. These sites are downwind of the northeastern United States in the prevailing summertime circulation [Wendland and Bryson, 1981]. The observations indicate $\Delta$O$_3$/ΔCO in the range of 0.21 to 0.30, similar to values at eastern U.S. sites (Table 1). Model results are in good agreement. The variance in the model is far less than observed, certainly in part because aged pollution plumes are forced to dilute on the 4$^\circ$ x 5$^\circ$ grid scale (no cross-gridbox advection is allowed for subgrid plumes in the model).

Our analysis indicates that $\Delta$O$_3$/ΔCO $\sim$ 0.3 is a uniform characteristic of boundary layer air over eastern North America in summer. Data for the free troposphere from the Arctic Boundary Layer Expeditions (ABLE) 3A and 3B [Harriss et al., 1992, 1994] are generally consistent with this result. Wofsy et al. [1992] measured $\Delta$O$_3$/ΔCO in the range 0.17–0.62 at 3–6 km altitude during an ABLE 3A flight along the eastern seaboard from Maine to Virginia. They measured a negative $\Delta$O$_3$/ΔCO below 1.5 km on the same flight, evidently due to O$_3$ deposition. Data from ABLE 3B show $\Delta$O$_3$/ΔCO in the range 0.20–0.69 for anthropogenic pollution plumes sampled in the free troposphere over eastern Canada [Mauzeroll et al., 1993].

4. Interpretation

We have shown that the three-dimensional model of Jacob et al. [1993a] reproduces closely the O$_3$-CO correlation and slope $\Delta$O$_3$/ΔCO for all available sites in North America except Shenandoah National Park. This finding, combined with the generally good simulation of O$_3$ and CO concentra-

![Figure 3](image-url)  
**Figure 3.** The NO$_x$/NO$_y$ concentration ratio measured at Harvard Forest (for the same time period as in Figure 2) plotted against the standard normal distribution.
tions, lends confidence in the ability of the model to compute anthropogenic production of O\textsubscript{3} over the United States and the export of O\textsubscript{3} to the global atmosphere. Detailed discussion of model results, including O\textsubscript{3} budgets, is given by Jacob et al. [1993b].

We evaluate here the potential for a more direct interpretation of \(\Delta O_3/\Delta CO\) as an O\textsubscript{3}/CO anthropogenic enhancement ratio. Parrish et al. [1993] previously used this interpretation to estimate the export of O\textsubscript{3} from the United States to the North Atlantic. They multiplied the observed \(\Delta O_3/\Delta CO = 0.3\) at the Canadian marine sites of Table 1 by a CO emission inventory for the United States east of Mississippi River (approximately east of 92\degree W) and inferred an export flux of 1.1 Gmol d\textsuperscript{-1} for anthropogenic O\textsubscript{3} out of the eastern United States (mostly, they assumed, to the North Atlantic). We find however in the model an export flux of 1.6 Gmol d\textsuperscript{-1} for anthropogenic O\textsubscript{3} out of the same region; this flux is 45\% higher than estimated by Parrish et al. [1993], even though \(\Delta O_3/\Delta CO\) in the model is indistinguishable from the observations. There are two principal reasons for the difference, as discussed below.

First, the scaling of \(\Delta O_3/\Delta CO\) as done by Parrish et al. [1993] could be improved by accounting for chemical sources and sinks of CO in addition to direct emission. Table 2 gives an inventory of CO sources and sinks for the continental boundary layer of the eastern United States in the three-dimensional model. Direct emission represents only 60\% of the total CO source; the balance is contributed by atmospheric oxidation of hydrocarbons, in particular isoprene (20\%). This chemical source is compensated by a strong chemical loss, reflecting the high concentrations of both CO and OH over the eastern United States. Overall, the net source of CO in the boundary layer of the eastern United States is 18\% higher than the emission flux.

A more fundamental difficulty in interpreting observed \(\Delta O_3/\Delta CO\) as an O\textsubscript{3}/CO anthropogenic enhancement ratio is that in the absence of photochemistry, O\textsubscript{3} would be nega-

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Observed and simulated O\textsubscript{3} and CO concentrations at five U.S. sites: (a) Harvard Forest, Massachusetts; (b) Scotia, Pennsylvania; (c) Kinterbsh, Alabama; (d) Shenandoah National Park, Virginia; and (e) Niwot Ridge, Colorado. Details of the data are given in Table 1. Solid circles are observations and open squares are model values. In Figure 4e, model results are shown also for the aged Denver plume sampled with the sub-grid-nested scheme (open triangles). Lines are linear regressions to the observations (solid) and to the model results (dashed).
tively correlated with CO due to deposition. As a result, the measured $\Delta O_3/\Delta CO$ is less than the actual anthropogenic enhancement ratio. We determined the magnitude of this effect by conducting a model simulation with $O_3$ concentrations regulated solely by advection of boundary conditions and deposition (no chemical production or loss). Figure 6 shows the results for Seal Island, Canada; without photochemistry, $O_3$ and CO concentrations are negatively correlated (crosses, top panel). We can define an $O_3$ photochemical enhancement as the difference between the $O_3$ concentrations in the standard simulation and those in the simulation including no chemistry. This photochemical enhancement of $O_3$ shows a strong positive correlation with CO (solid squares, bottom panel). The slope in the bottom panel (0.40) gives the actual $O_3$/CO enhancement ratio from U.S. pollution; it is 33% higher than $\Delta O_3/\Delta CO$ in the top panel (0.30).

We now turn to the application of $\Delta O_3/\Delta CO$ as a measure of the $O_3$ production efficiency. Liu et al. [1987] pointed out that the $O_3$ production is best referenced to the loss of NO$_x$ or, on a regional scale, the emission of NO$_x$, since $O_3$ production is NO$_x$ limited. A net $O_3$ production efficiency $\varepsilon_N$ was defined by Lin et al. [1988] as the net number of $O_3$ molecules produced per NO$_x$ molecule consumed. By scaling the observed $\Delta O_3/\Delta CO$ in photochemically aged air to a CO/NO$_x$ source ratio, we can obtain an estimate of the net $O_3$ production efficiency $\varepsilon_N$; such an estimate is however a lower limit because of deposition of $O_3$. The CO/NO$_x$ source
ratio for the eastern United States, as defined in Figure 1, is 3.6 (using the net CO source in Table 2 and the NAPAP emission inventory for NOX.). From $\Delta O_3/\Delta CO = 0.3$, we obtain a net $O_3$ production efficiency $\xi_N$ of 1.7 in eastern U.S. boundary layer. In comparison a value of 8.5 for $\xi_N$ at Scotia and at Egbert, Ontario, was estimated by Trainer et al. [1993] using observations of $\Delta O_3/\Delta (NO_2,NO_x)$, and Olszyna et al. [1993] found a $\xi_N$ value of 12 at Tennessee using the same relationship; these values would be upper limits for $\xi_N$ because of rapid HNO$_3$ deposition. Our three-dimensional model gives a mean value $\xi_N = 4.2$ for the eastern United States [Jacob et al., 1993b], which is intermediate between the lower and the upper limits imposed by the observations of $\Delta O_3/\Delta CO$ and $\Delta O_3/\Delta (NO_2,NO_x)$.

We have seen that deposition of $O_3$ is an important factor limiting the potential for simple interpretation of the $O_3$-CO correlation in terms of $O_3$ production. Model results indicate that this effect is greatest in the central United States, where $O_3$ concentrations would be at a minimum in the absence of photochemistry because of the long fetch in the continental boundary layer [Jacob et al., 1993a]. Figure 7 shows $O_3$-CO correlations for the Oregon, Nebraska, Illinois, and Massachusetts grid boxes; there is no significant correlation between $O_3$ and CO in the Nebraska grid box. By subtracting the $O_3$ concentration computed in the absence of photochemistry (as in Figure 6), we obtain a strong correlation between $O_3$ photochemical enhancement and CO (solid squares in Figure 7). The slope of the linear regression analysis of the $O_3$ photochemical enhancement versus CO falls within a narrow range (0.33 to 0.49) for the four grid boxes in Figure 7 and is actually highest in the Nebraska grid box.

5. Conclusion

Observations at nonurban sites in eastern North America show a strong correlation between $O_3$ and CO concentrations in photochemically aged air (as defined by $NO_x/CO < 0.3$). The slope, $\Delta O_3/\Delta CO$, has a remarkably uniform value of about 0.3. Observations at Niwot Ridge, Colorado, indicate $\Delta O_3/\Delta CO = 0.15$ in the aged Denver plume; this low value is attributed to the low $NO_x/CO$ emission ratio in the Denver metropolitan area.

The $O_3$-CO relationship provides a sensitive test of $O_3$ production in chemical transport models. We used it to test a three-dimensional, continental-scale model of $O_3$ and precursors over North America [Jacob et al., 1993a]. The model captures successfully the $O_3$-CO correlations and reproduces closely the observed $\Delta O_3/\Delta CO$. It does not capture the full extent of variance in the observations, certainly in part because of spatial averaging on the grid scale. Simulation of the $O_3$-CO relationship lends confidence in the ability of the model to compute photochemical production of $O_3$ over North America and its export to the global atmosphere [Jacob et al., 1993b].

We investigated the possibility for a more direct interpretation of observed $\Delta O_3/\Delta CO$ as an $O_3$/CO anthropogenic enhancement ratio, to be multiplied by a CO source estimate for quantitative inference of photochemical $O_3$ production and export. A first complication with this simple approach is the need to account for chemical sources and sinks of CO, even in a highly polluted region such as the eastern United States. A second complication is that $O_3$ concentrations over polluted regions include a major component advected from outside the region, which is negatively correlated with CO due to deposition at the surface. As a result, $\Delta O_3/\Delta CO$ measured at sites over the United States and downwind is

### Table 2. Budget of CO for the Boundary Layer of the Eastern United States

<table>
<thead>
<tr>
<th>Source</th>
<th>Rate, Gmol d$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic emission</td>
<td>3.3</td>
</tr>
<tr>
<td>Oxidation of isoprene</td>
<td>1.1</td>
</tr>
<tr>
<td>Oxidation of anthropogenic NMHCs</td>
<td>0.5</td>
</tr>
<tr>
<td>Oxidation of CH4</td>
<td>0.6</td>
</tr>
<tr>
<td>Reaction with OH</td>
<td>-1.6</td>
</tr>
<tr>
<td>Net CO source</td>
<td>3.9</td>
</tr>
</tbody>
</table>

This budget is based on model results from June to August for the region enclosed by thick lines in Figure 1. Anthropogenic emission is from the National Acid Precipitation Assessment Program inventory. NMHCs, nonmethane hydrocarbons.
Figure 7. Simulated O₃ and CO concentrations in June to August (1200–1500 LT) for the Oregon, Nebraska, Illinois, and Massachusetts surface grid boxes. The open squares show O₃ concentrations from the standard simulation; the solid squares show the O₃ photochemical enhancement. The slopes and correlations for standard O₃ versus CO are Oregon, slope = 0.22, r² = 0.53; Nebraska, no significant correlation (r² = 0.15); Illinois, slope = 0.31, r² = 0.61; and Massachusetts, slope = 0.29, r² = 0.81. The slopes and correlations for the O₃ photochemical enhancement versus CO are Oregon, slope = 0.39, r² = 0.74; Nebraska, slope = 0.49, r² = 0.74; Illinois, slope = 0.33, r² = 0.60; and Massachusetts, slope = 0.39, r² = 0.87.

significantly less than the O₃/CO anthropogenic enhancement ratio, and the direct interpretation of observed ΔO₃/ΔCO may underestimate substantially the O₃ production and export.

From the ΔO₃/ΔCO observed in the eastern United States scaled to a CO/NOₓ source ratio for the region, we infer a lower limit of 1.7 for the net O₃ production efficiency defined as the net number of O₃ molecules produced per molecule of NOₓ consumed. This value is a lower limit because of O₃ deposition. Observations of ΔO₃/Δ(NOₓ-NOₓ) in the eastern United States yield values of 8.5–12 for the NOₓ; these values are upper limit because of rapid HNO₃ deposition. The mean cN value of 4.2 computed in the three-dimensional model for the boundary layer of the eastern United States falls within the limits imposed by the observations of ΔO₃/ΔCO and ΔO₃/Δ(NOₓ-NOₓ).

Acknowledgments. We thank Steve Wofsy and Jennifer Logan for their comments and suggestions. This work was supported by grants to Harvard University (National Science Foundation, NSF-93-04217 and NSF-BSR-8919300; the National Aeronautics and Space Administration, NASA-NAGW-3082; Environmental Protection Agency, EPA-R814533-01-0; Department of Energy, Northeastern Center of the Global Environmental Change; and the Packard Foundation), grants to the University of Maryland (Environmental Protection Agency, EPA-R814526 and National Science Foundation, ATM-86-19491 and ATM-90-14841), and part of the Climate and Global Change Program by the National Oceanic and Atmospheric Administration.

References


M. Chin, D. J. Jacob, and W. Munger, Division of Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138. B. G. Doddridge, Department of Meteorology, University of Maryland, College Park, MD 20742. D. D. Parrish, NOAA Aeronomy Laboratory, Boulder, CO 80303.

(Received November 23, 1993; revised March 25, 1994; accepted April 1, 1994.)