Factors Regulating Ozone Over the United States and Its Export to the Global Atmosphere

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The factors regulating summertime O3 over the United States and its export to the global atmosphere are examined with a 3-month simulation using a continental scale, three-dimensional photochemical model. It is found that reducing NOx emissions by 50% from 1985 levels would decrease rural O3 concentrations over the eastern United States by about 15% under almost all meteorological conditions, while reducing anthropogenic hydrocarbon emissions by 50% would have less than a 4% effect except in the largest urban plumes. The strongly NOx-limited conditions in the model reflect the dominance of rural areas as sources of O3 on the regional scale. The correlation between O3 concentrations and temperature observed at eastern U.S. sites is attributed in part to the association of high temperatures with regional stagnation, and in part to an actual dependence of O3 production on temperature driven primarily by conversion of NOx to peroxyacetylinitrate (PAN). The net number of O3 molecules produced per molecule of NOx consumed (net O3 production efficiency, accounting for both chemical production and chemical loss of O3) has a mean value of 6.5 in the U.S. boundary layer; it is 3 times higher in the western United States than in the east because of lower NOx concentrations in the west. Approximately 70% of the net chemical production of O3 in the U.S. boundary layer is exported (the rest is deposited). Only 6% of the NOx emitted in the United States is exported out of the U.S. boundary layer as NOx or PAN, but this export contributes disproportionately to total U.S. influence on global tropospheric O3 because of the high O3 production efficiency per unit NOx in the remote troposphere. It is estimated that export of U.S. pollution supplies 8 Gm mol O3 d\(^{-1}\) to the global troposphere in summer, including 4 Gm mol d\(^{-1}\) from direct export of O3 out of the U.S. boundary layer and 4 Gm mol d\(^{-1}\) from production of O3 downwind of the United States due to exported NOx. This U.S. pollution source can be compared to estimates of 18-28 Gm mol d\(^{-1}\) for the cross-tropopause transport of O3 over the entire northern hemisphere in summer.

1. INTRODUCTION

This paper is the second of two describing a continental scale, three-dimensional simulation of O3 and its precursors over North America for an entire summer. The first paper [Jacob et al., this issue] described the model and evaluated it with observations. Here we use the model to examine how emissions and meteorology determine O3 concentrations over the United States, and we estimate the exports of O3 and its precursors from the U.S. boundary layer to the global atmosphere.

Ozone is produced rapidly over the U.S. in summer by photochemical oxidation of non methane hydrocarbons (NMHCs) in the presence of nitrogen oxides (NOx = NO + NO\(_2\)). The NMHCs are emitted by a variety of anthropogenic and biogenic sources. The main source of NOx is fossil fuel combustion. Production of O3 in a fresh combustion plume is usually NMHC limited, because of high concentrations of NOx, but shifts gradually to a NOx-limited regime as the plume dilutes and NOx is oxidized [Chameides et al., 1988; Milford et al., 1989]. Production of O3 in rural air is primarily NOx limited, because of low concentrations of NOx and high concentrations of the biogenic NMHC isoprene [Trainor et al., 1987; Sillman et al., 1990a; Chameides et al., 1992]. Three-dimensional model simulations of regional pollution episodes over the eastern United States indicate that NOx emission controls offer the best strategy for decreasing O3 maxima in rural areas [Possiel et al., 1990; McKeen et al., 1991]. We will take here a broader view by examining the effects of emission controls on O3 concentrations over the continental scale and over an entire summer.

Measurements of O3 concentrations at rural sites in the eastern United States indicate considerable variability from day to day and from year to year [Vukovich and Fishman, 1986; Logan, 1989]. The strongest correlation is with temperature; correlations with other meteorological variables such as wind speed and direction, pressure, cloud cover, and humidity are weak or absent [Wolff and Lioy, 1978; Clark and Karl, 1982; Korsog and Wolff, 1991]. The highest O3 concentrations tend to be regional in scale and associated with weak, warm, stagnant anticyclones [Decker et al., 1976; Alshuller, 1978; Wolff and Lioy, 1980; Logan, 1989]. The model reproduces well these different features of the observations, as shown below, and offers insights into the actual dependences of O3 concentrations on meteorological variables.

Export of pollution-derived O3 and its precursors from the U.S. boundary layer may affect tropospheric O3 on the hem-
ospheric scale, considering that the chemical lifetime of O₃ is typically a week or more [Liu et al., 1987], and that the lifetime of the peroxyacetyl nitrate (PAN) reservoir for NO₃ may be longer [Singh, 1987]. Observations suggest that tropospheric O₃ in the northern hemisphere in summer is elevated ubiquitously by human activity [Logan, 1985; Fishman et al., 1990; Olmans and Levy, 1993], and this view is supported by global models [Levy et al., 1985; Liu et al., 1987; Crutzen and Zimmerman, 1991; Fioles and Austin, 1992]. We will present here quantitative estimates for the export fluxes of O₃ and its precursors from the United States, and analyze the mechanisms for export.

The model is described briefly in section 2; details are given by Jacob et al. [this issue]. The factors regulating O₃ concentrations over the United States are discussed in section 3. The exports of O₃ and NOₓ out of the U.S. boundary layer are analyzed in section 4. Conclusions are in section 5.

2. THE MODEL

The model solves the mass conservation equations for six chemical tracers on a three-dimensional gridded domain including all of North and Central America and large areas of the surrounding oceans (Figure 1). The horizontal resolution is 4° latitude x 5° longitude (≈ 400x400 km²). There are nine layers in the vertical extending from the surface to the stratosphere along a sigma (terrain following) coordinate. The grid replicates that of the Goddard Institute for Space Studies general circulation model (GISS GCM 2). A one-summer archive of GISS GCM output [Hansen et al., 1983] is used as input to the model, including 4-hour averages of dynamical variables (winds, convective mass fluxes) and 5-day averages of other meteorological variables (temperature, cloud cover, humidity). Urban and industrial plumes are represented with a subgrid nested scheme that resolves chemical non-linearity down to the 20-km scale [Stillman et al., 1990b].

The six tracers include odd oxygen (which is mainly O₃), NOₓ, PANs, CO, a lumped NMHC with a lifetime of a few days representing a typical anthropogenic mix, and a lumped NMHC with a lifetime of less than a day contributed mainly by isoprene. The PANs tracer includes peroxyacetyl nitrate (PAN) and higher peroxyacetyl nitrates. Chemical production and loss rates are computed with the detailed photochemical mechanism of Lurmann et al. [1986], modified as described by Jacob et al. [1989]. Oxidation of NOₓ to HNO₃ and to organic nitrates other than PANs is viewed as a terminal sink for NOₓ. Anthropogenic emissions of NOₓ, CO, and NMHC in North America are taken from a summer 1985 inventory compiled by the National Acid Precipitation Assessment Program (NAPAP) [Environmental Protection Agency (EPA), 1989]. Anthropogenic emissions in Central and South America are estimated from data for energy use. Biogenic emission of isoprene is computed as a function of local vegetation type, temperature, and insolation [Tingey et al., 1979; Lamb et al., 1987]. Dry deposition fluxes of O₃, NOₓ, and PANs are computed with a resistance-in-series scheme dependent on local surface type and meteorological variables.

All simulations are conducted from May 15 to August 31 of the GCM year with a time step of 4 hours. The May 15-31 period is used for initialization. Boundary conditions are specified with observed background concentrations dependent on latitude, altitude, and month [Logan, 1985; Rudolph et al., 1987; Spivakovskiy et al., 1990]. The stratospheric boundary conditions in the top two layers have negligible effect on the troposphere below because cross-tropopause transport is weak relative to horizontal transport in the troposphere across the lateral model boundaries. The background tropospheric O₃ concentrations over the model domain are thus defined mainly by advection of the tropospheric boundary conditions.

Detailed evaluation of model results is presented in the companion paper. Median afternoon O₃ concentrations simulated at rural U.S. sites are typically within 5 ppb of observations, except in the south central United States where concentrations are overpredicted by 15-20 ppb. The overprediction in the south central United States is attributed to weaker-than-normal ventilation of that region in the GCM, and may also reflect insufficient resolu-

![Fig. 1. Model domain and grid. The vertical grid is defined by a sigma coordinate and is shown here for an atmospheric column based at sea level. The thick line delineates the U.S. boundary layer (1275°W to 67.5°W, 24°N to 48°N, 0-2.6 km column). The Georgia, Michigan, and New York grid boxes are identified by shading.](image-url)
tion of NO₃ point sources. The model simulates well the development of regional high-O₃ episodes over the eastern United States in association with weak anticyclones. The variance of concentrations is less than observed, certainly in part because of local effects not resolved by the model. Simulated concentrations of CO and NOₓ are in good agreement with observations, while concentrations of PANs are overpredicted by factors of 2 to 3. The overprediction of PANs is attributed to flaws in the Lurmann et al. [1986] chemical mechanism and may also reflect an underestimate of PANs deposition.

3. RURAL OZONE OVER THE UNITED STATES

Effect of Emission Controls

Figure 2 (top) shows the mean afternoon concentrations of O₃ simulated in rural surface air using the NAPAP inventory of anthropogenic emissions for 1985. Reducing NOₓ emissions uniformly by 50% from that inventory results in a mean 10-15 ppb decrease of rural O₃ over the eastern U.S. (middle). Reducing anthropogenic NMHC emissions by 50% has less than a 3 ppb effect anywhere (bottom). Reducing both anthropogenic NOₓ and NMHC emissions (not shown) has a nearly additive effect. The strongly NOₓ-limited conditions in the model reflect the importance of rural areas as sources of O₃ on the regional scale. We find that 82% of net O₃ production in the U.S. boundary layer (see Figure 1 for definition) takes place in rural air, where NOₓ concentrations are relatively low. Only 18% takes place in the urban and industrial plumes represented by our nested subgrid scheme.

Figure 3 shows the cumulative probability distributions of summer afternoon O₃ concentrations simulated in three eastern U.S. grid boxes (Georgia, Michigan, New York). The distributions are intended to be representative of rural sites in the grid boxes; they were constructed by sampling the time series of concentrations in rural air and in aged subgrid plumes on an area-weighted basis to account for occasional influence of pollution plumes over rural areas [Jacob et al., this issue]. We find that reducing NOₓ emissions by 50% from 1985 levels decreases O₃ concentrations by 15% over the full range of the summertime probability distribution, except for the highest occurrences in the New York grid box (aged New York City plume) which actually increase. Production of O₃ in the New York City plume can remain NMHC limited for a long photochemical aging time because the urban source area is large, so that dilution of the plume is slow.

Fig. 2. Mean afternoon concentrations of O₃ (ppb) simulated in rural air in July. The concentrations are for 12-15 local time (LT) in the lowest model layer (0-500 m altitude). Results from the standard simulation with anthropogenic emissions for 1985 (top panel) are compared to results from simulations with anthropogenic NOₓ or NMHC emissions reduced uniformly by 50%.
Under strongly NMHC-limited conditions, $O_3$ production increases when $NO_x$ concentrations decrease [Stillman et al., 1990a].

Reducing anthropogenic NMHC emissions by 50% decreases rural $O_3$ concentrations by less than 4% under all conditions in Figure 3, except for the highest occurrences in the Michigan and New York grid boxes (Detroit and New York City urban plumes). The Atlanta urban plume in the Georgia grid box is less sensitive to anthropogenic NMHC emissions because of higher temperatures and hence higher isoprene emissions. Ozone is particularly insensitive to anthropogenic NMHCs under relatively clean conditions (lower end of the cumulative probability distributions) because of the availability of isoprene as a rapid source of $O_3$. Anthropogenic NMHCs are typically less reactive than isoprene, and are therefore more likely to be vented outside of the U.S. boundary layer before realizing their $O_3$ production potential [Lin et al., 1988].

Our results for highly polluted conditions (higher end of the probability distributions in Figure 3) are consistent with previous studies of pollution episodes using three-dimensional regional models. McKeeen et al. [1991] found in a 4-day simulation of a regional stagnation episode over the eastern United States that reducing $NO_x$ emissions by 50% from 1985 levels would decrease afternoon $O_3$ concentrations by 12-16% in most areas but by less than 4% in the New York City plume, while reducing anthropogenic NMHC emissions by 50% would decrease $O_3$ concentrations by less than 4% in most areas but by 12-20% in the New York City plume. Simulations for the northeastern United States by Posstiel et al. [1990] and Roselle et al. [1991] indicate that reducing anthropogenic NMHC emissions by 50% from 1985 levels would decrease peak $O_3$ concentrations by less than 10% except in large urban plumes, while reducing both NMHC and $NO_x$ emissions by about 30% would decrease peak $O_3$ by 10-15% in most areas.

Although $NO_x$ emission controls seem to offer the best strategy for decreasing rural $O_3$ concentrations in the eastern United States, the response is still relatively weak. A 50% reduction of $NO_x$ emissions yields only a 15% decrease of $O_3$ concentrations. There are two reasons for this weak sensitivity. First is chemical non linearity [Lin et al., 1988]; the net $O_3$ production in the U.S. boundary layer decreases by only 33% on average when $NO_x$ emissions are reduced by 50%. Second is the presence of a substantial $O_3$ background advected from outside North America, which we derive in the model by conducting a simulation with no chemistry (i.e., with concentrations regulated solely by advection of boundary conditions and deposition). The background contributes on average about half of surface $O_3$ concentrations over the eastern United States in the model (see Figure 3 and also Jacob et al. [this issue]). This contribution is less during pollution ep-
isodes, but the non-linear dependence of $O_3$ production on NO$_x$ concentration is then more pronounced, so that the response of $O_3$ to NO$_x$ emission controls remains weak over the entire probability distribution.

Sensitivity to Meteorological Variables

Figure 4 shows the time series of rural afternoon $O_3$ concentrations simulated by the model in the Georgia, Michigan, and New York grid boxes. The day-to-day variability is mainly driven by regional pollution; variability in the background is small (dashed lines) and is generally anticorrelated with pollution enhancements. The prominent oscillations in the Michigan and New York grid boxes are due to weak anticyclones traveling from central Canada across the eastern United States to the Atlantic. Ozone concentrations are low in the northerly flow on the front-side of the anticyclones, and high on the backside due to regional stagnation, consistent with observations [Jacob et al., this issue]. The Georgia grid box is less exposed to episodic influxes of cleaner air because it lies outside the principal anticyclone track, both in the GCM and in the observations [Harman, 1987].

We tested the ability of the model to reproduce the correlation between $O_3$ concentrations and temperature in the observations by using as standard the nine eastern U.S. sites of the Sulfate Regional Experiment (SURE) [Mueller and Hidy, 1983]. Continuous observations at these sites are available for June-August of 1978 and 1979. The observed $O_3$ concentrations at 14 LT are significantly correlated with temperature at eight of the nine sites, with linear correlation coefficients $r$ ranging from 0.25 to 0.67 ($n = 131-181$ points depending on the site). The same analysis in the model shows significant correlation at all nine sites with $r$ ranging from 0.50 to 0.82 ($n = 92$). The correlation coefficients are higher in the model, certainly in part because local sources of variance in the observations are not resolved.

The $O_3$-temperature correlation in the observations may reflect in part a dependence of temperature on air mass origin or solar radiation [Sillman and Samson, 1993]. We diagnosed the actual sensitivity of $O_3$ concentrations to temperature by conducting a simulation with temperature held constant in each grid box at its mean local value for June to August. Results in Figures 4 and 5 show that temperature accounts for 51% of the variance of afternoon $O_3$ concentrations in the Georgia grid box, 26% in Michigan and 20% in New York. Temperature is relatively more important in the southeast because the variability in air mass origin is less. High-$O_3$ episodes develop over the northeastern United States even when temperatures are held constant (dotted lines in Figure 4), although the peak concentrations are decreased by about 5 ppb. We see that regional stagnation, rather than high temperature, is the primary forcing factor for the occurrence of high-$O_3$ episodes. Part of the $O_3$-temperature correlation reflects the association of high temperatures with regional stagnation [Jacob et al., 1993].

The contribution of temperature to the $O_3$ concentration variance indicates a significant dependence of $O_3$ concentrations on temperature, which we examined in more detail by conducting simulations with temperatures held constant only in the chemical mechanism or in the calculation of isoprene emission. Results in Figure 5 show that most of the temperature dependence is due to the chemical mechanism, where it reflects principally the storage of NO$_x$ as PANs at low temperatures [Sillman et al., 1990a]. As pointed out above, the model overpredicts PANs concentrations, and therefore likely exaggerates the sensitivity of $O_3$ concentrations to temperature. Mean afternoon concentration ratios

Fig. 4. Afternoon concentrations of rural $O_3$ simulated in the Georgia, Michigan, and New York grid boxes. Results from the standard simulation (solid lines) are compared to results from a simulation with temperature held constant in each grid box at its local mean value for June-August (dotted lines). The dashed lines show the model background originating from outside North America.

PANs/NO$_x$ (ppb/ppb) at rural sites in the eastern United States are 2-3 in the model and 0.5-1 in the observations [Buhr et al., 1990; Parrish et al., 1993a]. The presence of a substantial PANs reservoir in the observations nevertheless implies a significant coupling of $O_3$ concentrations and temperature through PANs decomposition.

The effect of temperature on isoprene emission makes only a small contribution to the variance of $O_3$ concentrations (Figure 5) because $O_3$ production is primarily NO$_x$ limited. We conducted sensitivity simulations with isoprene emission increased or decreased uniformly by a factor of 2 from the standard simulation, corresponding in the model to a 7 K change in temperature; $O_3$ concentrations changed by at most 4 ppb. Shuttling off isoprene emission completely in the model led to 5-15 ppb decreases of $O_3$ concentrations over most of the eastern United States, consistent with previous results from regional models [McKeen et al., 1991; Roselle et al., 1991]. We conclude that although isoprene emission enhances $O_3$ concentrations substantially relative to an isoprene-free atmosphere, the temperature dependence of isoprene emission is too weak to make a major contribution to the $O_3$-temperature correlation.
The sensitivity of O₃ concentrations to cloud cover was examined using the same approach as for temperature. Cloud cover moderates O₃ production, principally by slowing down NOₓ photolysis; however, the cloud albedoes in the model (5-day averages) rarely exceed 0.4, corresponding to a 40% decrease in photolysis. Because this effect is relatively small, the contribution of cloud cover to the O₃ concentration variance is less than the contributions of dynamics or temperature. Our result is consistent with observations, which show only weak correlations of daytime O₃ concentrations with cloud cover [Kelly et al., 1986; Korngog and Wolff, 1991]. It may however be that the weak sensitivity in the model is due to the 5-day averaging of cloud cover, while the weak correlation in the observations is due to the transient nature of clouds.

None of the other model variables make any significant contribution to the variance of O₃ concentrations. In particular, water vapor is unimportant because of canceling influences on photochemistry [Stillman et al., 1990a]. This result is consistent with observations, which show that water vapor is not a significant predictor of O₃ concentrations at eastern U.S. sites [Wolff and Loy, 1978; Clark and Karl, 1982].

4. Global Influence

Budgets of O₃ and NOₓ in the U.S. Boundary Layer

Figure 6 shows the net O₃ production rates (chemical production minus chemical loss) computed in the U.S. boundary layer in July. We define here the U.S. boundary layer as the region bounded by the thick line in Figure 1, and extending vertically to ≈ 2.6 km above ground level (top of model layer 3). Production is maximum in a band between Texas and Michigan, reflecting a combination of high NOₓ emissions, high isoprene emission, and weak ventilation [Jacob et al., this issue]. The average net O₃ production rate in the U.S. boundary layer for June to August is 6.4 Gmol d⁻¹, including 2.9 Gmol d⁻¹ in the western United States (west of 97.5°W) and 3.5 Gmol d⁻¹ in the eastern United States. The near symmetry in O₃ production between west and east is remarkable considering that NOₓ emissions are much weaker in the west (0.25 Gmol d⁻¹) than in the east (0.93 Gmol d⁻¹). The net O₃ production efficiency εₙ, defined as the net number of O₃ molecules produced per molecule of NOₓ consumed [Lin et al., 1988], is 3 times higher in the west (εₙ = 12.4) than in the east (εₙ = 4.4), due to lower NOₓ concentrations in the west that reflect

Fig. 5. Temporal variances of rural O₃ concentrations in the Georgia, Michigan, and New York grid boxes, computed from the model time series for June-August sampled at 14 or 15 LT (n = 92). Results are shown for the standard simulation, and for a series of sensitivity simulations with individual variables held constant in each grid box at their local mean value for June-August.

Fig. 6. Net O₃ production rates (10⁶ molecules cm⁻³ s⁻¹) computed in the model for the air column extending up to ≈ 2.6 km above the surface (top of model layer 3). Values are 24-hour means for July averaged over the depth of the column.
both weaker emissions and deeper boundary layer mixing. Summer afternoon mixing depths in the GCM are typically 2-2.5 km over the western United States and 1-1.5 km over the eastern United States, consistent with observations [Holzworth, 1967], and reflecting the stronger insolation and more arid terrain in the west.

Export of O3 and NOx

Net photochemical production of O3 in the U.S. boundary layer in the model exceeds slightly the loss from deposition (6.4 versus 5.2 Gmol d\(^{-1}\) in June to August), so that the United States is a net exporter of O3. Export of pollution O3 from the United States is in fact much higher than this balance would indicate because part of the O3 deposited to the United States is exogenous. We extracted this exogenous background in a simulation with no chemistry, i.e., with O3 concentrations regulated solely by advection of boundary conditions and deposition. The residual "pollution O3" represents the effect of net photochemical production over the model domain. We find that 70% of pollution O3 produced in the U.S. boundary layer is exported, representing an export flux of 4.3 Gmol d\(^{-1}\); the remaining 30% are deposited within the region. The residence time of pollution O3 in the U.S. boundary layer is 2.5 days (4 days against export, 8 days against deposition).

Parrish et al. [1993b] estimated recently an export flux of 1.1 Gmol d\(^{-1}\) for pollution O3 out of the eastern United States in summer. They arrived at this estimate by using variance ratios of O3 and CO concentrations measured at Canadian island sites, and scaling to the NAPAP inventory for CO emissions east of the Mississippi River (roughly east of 90\(^{\circ}\)W). We report elsewhere [Chin and Jacob, 1993] that the model reproduces well the variance ratios observed by Parrish et al. [1993b] and by other investigators in the eastern United States and downwind. We find however that the export flux of pollution O3 produced in the United States east of 90\(^{\circ}\)W is 1.6 Gmol d\(^{-1}\), i.e., 45% higher than estimated by Parrish et al. [1993b]. Chin and Jacob [1993] point out that the export estimate of Parrish et al. [1993b] is low because NMHC oxidation must be accounted for as a source of CO, and because anticorrelation between background O3 and CO causes the variance ratio of O3 and CO concentrations to underestimate the actual O3/CO pollution ratio.

Figure 7 shows the mean transport fluxes of pollution O3 in the model in July. Export out of the U.S. boundary layer is principally by vertical transport to the free troposphere (70% of total export) and by advection to Canada in the boundary layer (13%). Ventilation to the free troposphere is particularly vigorous over the Rocky Mountains due to strong convergence of airflow from the western and south central United States [Wendland and Bryson, 1981]. Influx of pollution O3 from the western United States to the Rocky Mountains is facilitated by deep mixed layers, with strong winds at altitude, and also by subsidence along the west coast which forces pollution from California to the east.

Figure 8 shows the mean transport fluxes of NOx in the model in July. The lifetime of NOx against oxidation to HNO3 and to stable organic nitrates is 10 hours on average in the U.S. boundary layer. Net export of NOx out of the U.S. boundary layer (averaging 0.07 Gmol d\(^{-1}\) for June to August) represents only 6% of NOx emissions in the region because of the short lifetime. Vertical transport to the free troposphere accounts for 87% of NOx export and is strongest over the northeastern United States where NOx emissions are high. Net export of PANs in the model is near zero (<0.01 Gmol d\(^{-1}\)) because of conversion of NOx to PANs in

![Fig. 7. Mean fluxes of pollution O3 computed in the model boundary layer in July. The fluxes represent the effect of net photochemical production of O3 over the model domain, and are obtained by subtracting the fluxes of background O3 from the fluxes of O3 computed in the standard simulation. The horizontal fluxes (top panel) are averages for the column extending up to \(= 2.6 \text{ km}\) above the surface (top of layer 3). The vertical fluxes (bottom panel) are computed at \(= 2.6 \text{ km}\) above the surface (through the top of model layer 3), and point upwards when positive.](image-url)
Fig. 8. Mean fluxes of NO$_x$ computed in the model boundary layer in July. The horizontal fluxes (top panel) are averages for the column extending up to a 2.6 km above the surface (top of layer 3). The vertical fluxes (bottom panel) are computed at a 2.6 km above the surface (through the top of layer 3), and point upward when positive.

the middle troposphere followed by subsidence, resulting in a substantial PANs influx to the U.S. boundary layer. This result is consistent with one-dimensional photochemical model calculations by Kasting and Singh [1986] for northern mid-latitudes continental air in summer, showing zero net flux of PAN at 2-km altitude. We have, however, little confidence in our ability to simulate the export of PANs since concentrations are overpredicted. Kasibhatla et al. [1993] find in a global three-dimensional simulation of nitrogen oxides that 20% of NO$_x$ emitted from the United States in July is exported as NO$_x$ (including NO$_x$, PAN, and HNO$_x$). We find here that only 5% is exported as NO$_x$ or PANs, but HNO$_x$ (which we do not simulate as a tracer) could account for a large fraction of total NO$_x$ export.

Global Influence

Mean export fluxes of pollution O$_3$, NO$_x$, and PANs out of the U.S. boundary layer in the model summer are 4.3, 0.07, and $<0.01$ Gmol d$^{-1}$, respectively. The exported NO$_x$ produces O$_3$ in the remote troposphere, but this production cannot be computed adequately in the model because of the limited spatial domain. We estimate instead the eventual O$_3$ yield from the exported NO$_x$ with a separate photochemical model calculation of the gross O$_3$ production efficiency $\varepsilon_G$ [Liu et al., 1987], defined as the gross number of O$_3$ molecules produced per molecule of NO$_x$ consumed ($\varepsilon_G$ differs from $\varepsilon_X$ in that it does not account for O$_3$ chemical loss). We obtain $\varepsilon_G$ = 57 in a diel steady-state calculation for an air parcel at 4-km altitude in northern mid-latitudes summer with 40 ppt NO$_x$ [Carroll et al., 1992; Sandholm et al., 1993], 50 ppb O$_3$, 100 ppb CO, temperature 265 K, 50% relative humidity, clear skies, surface albedo 0.1, and an O$_3$ column of 325 Dobson units. The calculation ignores the loss of NO$_x$ from hydrolysis of N$_2$O$_5$ on aerosol surfaces because we assume that the background aerosol surface area in the middle troposphere (where most of the NO$_x$ is exported) is small. The value of $\varepsilon_G$ depends on a number of variables, in particular the concentration of NO$_x$ [Liu et al., 1987]. The above calculation with 100 ppt NO$_x$ yields $\varepsilon_G$ = 36. Assuming $\varepsilon_G$ = 57, we derive an O$_3$ source of 4.0 Gmol d$^{-1}$ from export of NO$_x$ out of the U.S. boundary layer. This source is of similar magnitude to direct export of anthropogenic O$_3$.

We thus estimate that export of U.S. pollution supplies 8 Gmol d$^{-1}$ O$_3$ to the global troposphere in summer (4.3 Gmol d$^{-1}$ from direct export, 4.0 Gmol d$^{-1}$ from export of NO$_x$). This source can be compared to estimates of 18-28 Gmol d$^{-1}$ for the cross-tropopause flux of O$_3$ in the northern hemisphere in summer [Danielsen and Mohren, 1977; Gillet and Shapiro, 1980; Mahman et al., 1980]. We conclude that U.S. pollution makes a substantial contribution to tropospheric O$_3$ on the hemispheric scale. The United States are responsible for about 30% of total NO$_x$ emissions from fossil fuel combustion in the northern hemisphere [Dignon, 1992]. Scaling our results to the remaining 70% suggests that fossil fuel combustion and stratospheric input represent O$_3$ sources of comparable magnitude in the northern hemisphere troposphere in summer.

5. CONCLUSION

We have used a continental scale, three-dimensional simulation of tropospheric photochemistry over North America in summer to reach a number of conclusions regarding regional and global influences of U.S. emissions on tropospheric O$_3$. Some of the conclusions appear robust; others are uncertain and stress the need for further work.

We find that NO$_x$ emission controls offer the only viable strategy for decreasing summertime levels of O$_3$ in the rural United States. This result is consistent with previous regional model
studies focusing on pollution episodes. The response of \( O_3 \) to NO\(_x\) emission controls is however relatively weak; a 50% reduction of NO\(_x\) emissions affords only a 15% decrease of \( O_3 \) concentrations in the eastern United States under most conditions. Part of the reason is chemical non linearity and part is the presence of a substantial \( O_3 \) background advected from outside North America. This background, specified in our model by boundary conditions, has a natural component but may also include significant contributions from Asian, European, and North American pollution circulated on a hemispheric scale. Abating \( O_3 \) concentrations in the United States may thus call for an international strategy of emission controls; this issue needs to be explored further with a hemispheric scale model.

The occurrence of regional high-\( O_3 \) episodes over the eastern United States in summer appears to be driven primarily by regional stagnation, rather than by high temperatures. The consistent correlation observed between \( O_3 \) concentrations and temperature at eastern U.S. sites reflects in part an association of high temperatures with air mass origin, and in part an actual dependence of \( O_3 \) production on temperature driven by the equilibrium between NO\(_x\) and PAN. The model overpredicts PAN concentrations and therefore probably exaggerates the dependence of \( O_3 \) production on temperature. Nevertheless, the presence of substantial PAN concentrations in the observations at U.S. sites suggests significant coupling of \( O_3 \) concentrations and temperature through PAN decomposition.

The net \( O_3 \) production efficiency \( \epsilon_{O_3} \), defined as the net number of \( O_3 \) molecules produced per molecule of NO\(_x\) consumed, has a mean model value of 6.3 in the U.S. boundary layer. This value appears to be well constrained by the good simulation of \( O_3 \) concentrations and the good representation of boundary layer ventilation. Values of \( \epsilon_{O_3} \) are about 3 times higher in the western United States than in the east because of lower NO\(_x\) concentrations in the west, reflecting both weaker NO\(_x\) emissions and deeper mixing. Reducing NO\(_x\) emissions in the western United States is thus far more effective for decreasing \( O_3 \) production on a per molecule basis than reducing NO\(_x\) emissions in the east.

On average, 70% of the net \( O_3 \) production in the U.S. boundary layer is exported (4.3 Gmol d\(^{-1}\)), while 30% is deposited within the region. This result appears robust since the characteristic times for \( O_3 \) deposition and boundary layer ventilation are fairly well constrained. Most of the export is by ventilation to the free troposphere. The export is particularly strong over the Rocky Mountains because of convergence of air from the western and south-central United States. Pollution from California is forced eastward toward the Rocky Mountains by strong subsidence along the Pacific coast.

Net export of NO\(_x\) out of the U.S. boundary layer in the model represents only 6% of emissions in the region, reflecting the short lifetime of NO\(_x\) against oxidation to stable products. Net export of PANs is negligible because the PANs outflow is balanced by conversion of NO\(_x\) to PANs in the middle troposphere, followed by subsidence of PANs to the boundary layer. However the model overpredicts PANs, leaving much uncertainty in the computed budget for that species. We estimate that the small fraction of NO\(_x\) exported from the U.S. boundary layer contributes as much \( O_3 \) on the global scale as the 94% oxidized within the boundary layer, reflecting the high \( O_3 \) production efficiency per unit NO\(_x\) in the remote troposphere computed from photochemical mechanisms. There are however no good observations to evaluate this \( O_3 \) production efficiency.

Our best estimate is that export of U.S. pollution supplies 8 Gmol \( O_3 \) d\(^{-1}\) to the global troposphere in summer (4.3 Gmol d\(^{-1}\) from direct export, 4.0 Gmol d\(^{-1}\) from export of NO\(_x\)). The estimate of \( O_3 \) export appears reliable, but the estimate of the \( O_3 \) source from NO\(_x\) export is highly uncertain. A source of 8 Gmol d\(^{-1}\) represents about one third of the cross-tropopause transport of \( O_3 \) over the entire northern hemisphere. We conclude that U.S. pollution makes a substantial contribution to tropospheric \( O_3 \) on the hemispheric scale.

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REFERENCES


Chin, M., and D.J. Jacob, Relationship of \( O_3 \) and CO concentrations over North America and its implication on \( O_3 \) production and transport (abstract), *EOS Trans. AGU*, 74(16), Spring Meeting suppl., 65, 1993.


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