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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 NO_x 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 NO_x-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 NO_x to peroxyacetyl nitrate (PAN). The net number of O₃ molecules produced per molecule of NO_x consumed (net O₃ production efficiency, accounting for both chemical production and chemical loss of O₃) has a mean value of 6.3 in the U.S. boundary layer; it is 3 times higher in the western United States than in the east because of lower NO_x 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 NO_x emitted in the United States is exported out of the U.S. boundary layer as NO_x 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 NO_x in the remote troposphere. It is estimated that export of U.S. pollution supplies 8 Gmol O₃ d⁻¹ to the global troposphere in summer, including 4 Gmol d⁻¹ from direct export of O₃ out of the U.S. boundary layer and 4 Gmol d⁻¹ from production of O₃ downwind of the United States due to exported NO_x. This U.S. pollution source can be compared to estimates of 18–28 Gmol 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 (NO_x = NO + NO₂). The NMHCs are emitted by a variety of anthropogenic and biogenic sources. The main source of NO_x is fossil fuel combustion. Production of O₃ in a fresh combustion plume is usually NMHC limited, because of high concentrations of NO_x, but shifts gradually to a NO_x-limited regime as the plume dilutes and NO_x is oxidized [Chameides *et al.*, 1988; Milford *et al.*, 1989]. Production of O₃ in rural air is primarily NO_x limited because of low concentrations

of NO_x and high concentrations of the biogenic NMHC isoprene [Trainer *et al.*, 1987; Sillman *et al.*, 1990a; Chameides *et al.*, 1992]. Three-dimensional model simulations of regional pollution episodes over the eastern U.S. indicate that NO_x 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; Altshuller, 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-

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ispheric 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 NO_x 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; Oltmans and Levy, 1993], and this view is supported by global models [Levy et al., 1985; Liu et al., 1987; Crutzen and Zimmerman, 1991; Follows 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 NO_x 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 [Sillman et al., 1990b].

The six tracers include odd oxygen (which is mainly O₃), NO_x, 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 NO_x to HNO₃ and to organic nitrates other than PANs is viewed as a terminal sink for NO_x. Anthropogenic emissions of NO_x, CO, and NMHCs 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, NO_x, 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; Spivakovsky 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-

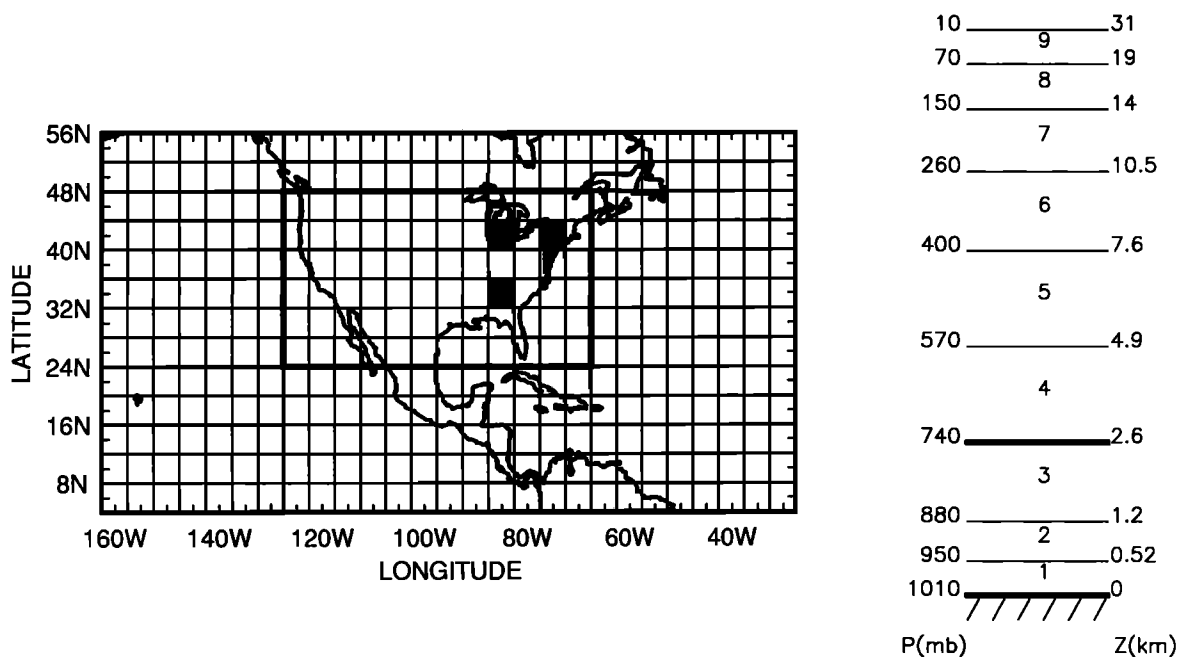


Fig. 1. Model domain and grid. The vertical grid is defined by a sigma coordinate and is shown here for an atmospheric column based at sea level. The thick line delineates the U.S. boundary layer (127.5°W to 67.5°W, 24°N to 48° N, 0-2.6 km column). The Georgia, Michigan, and New York grid boxes are identified by shading.

tion of NO_x 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 NO_x 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 NO_x 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 NO_x and

NMHC emissions (not shown) has a nearly additive effect. The strongly NO_x-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 NO_x 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 NO_x 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.

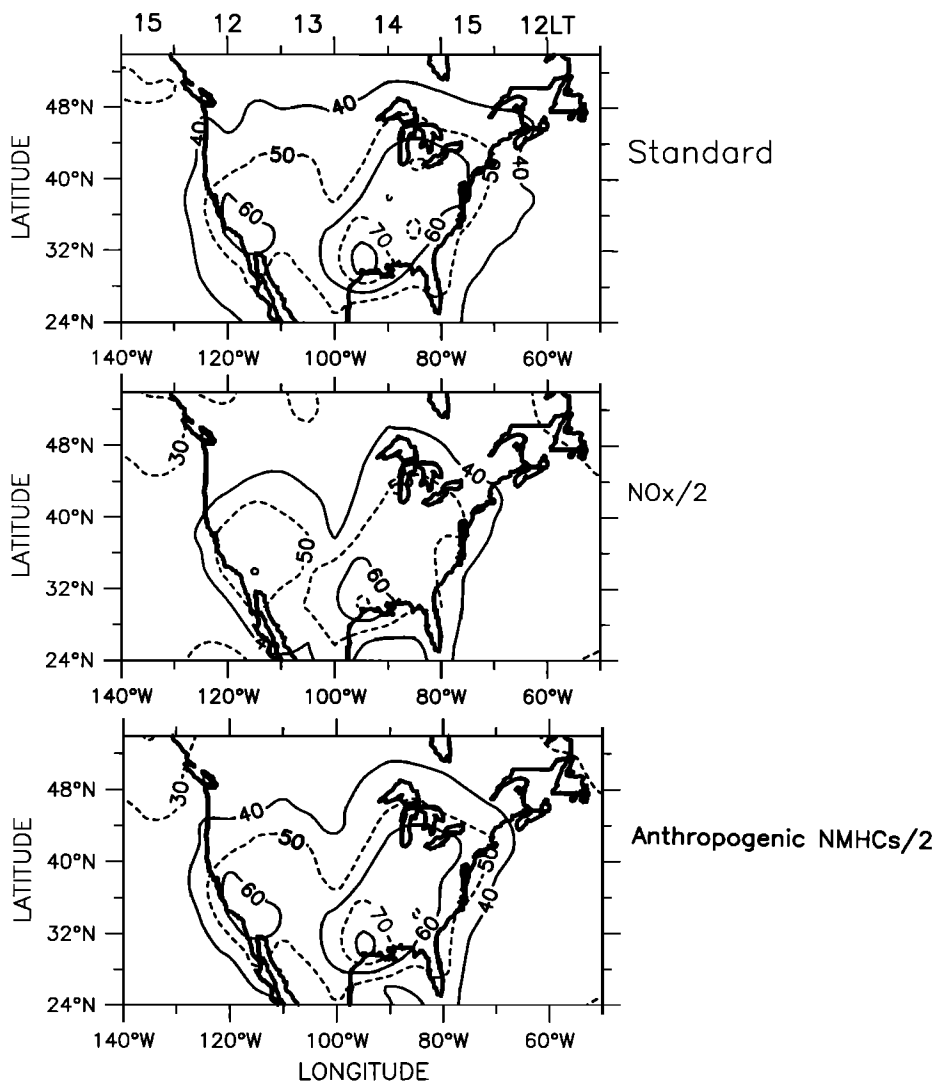


Fig. 2. Mean afternoon concentrations of O₃ (ppb) simulated in rural air in July. The concentrations are for 12-15 local time (LT) in the lowest model layer (0-500 m altitude). Results from the standard simulation with anthropogenic emissions for 1985 (top panel) are compared to results from simulations with anthropogenic NO_x or NMHC emissions reduced uniformly by 50%.

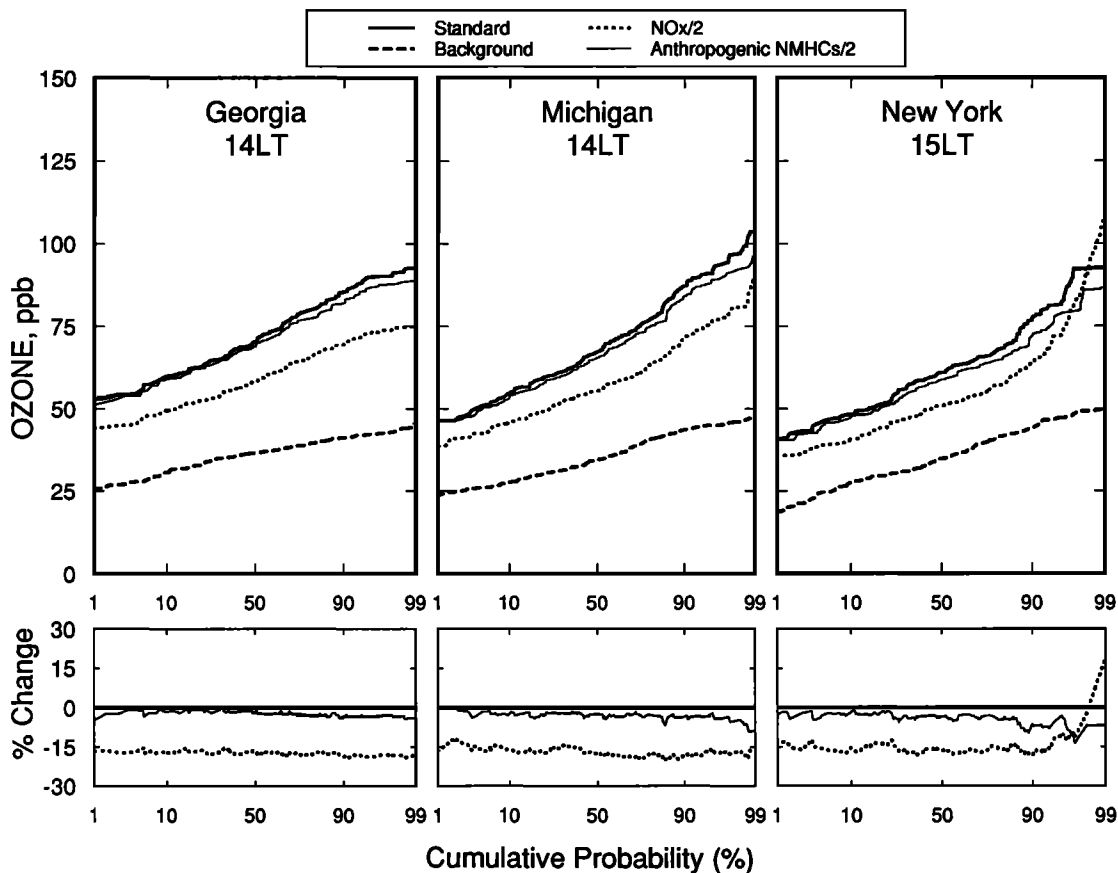


Fig. 3. Cumulative probability distributions of summer afternoon O_3 concentrations simulated for rural sites in the Georgia, Michigan, and New York grid boxes. The scale of the abscissa is such that a normal distribution would plot as a straight line (probability scale). Results from the standard simulation with anthropogenic emissions for 1985 (bold lines) are compared to results from simulations with anthropogenic NO_x or NMHC emissions reduced uniformly by 50% (dotted lines and thin lines, respectively). The dashed lines show the probability distributions for background O_3 originating from outside North America, as obtained in a simulation including no chemistry (i.e., with concentrations regulated solely by advection of boundary conditions and deposition). The bottom panels show the percent changes of the different quantiles when anthropogenic NO_x or NMHC emissions are reduced by 50%.

Under strongly NMHC-limited conditions, O_3 production increases when NO_x concentrations decrease [Sillman *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 ventilated 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. McKeen *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 anthropo-

genic 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 Possiel *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.*, this issue].

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

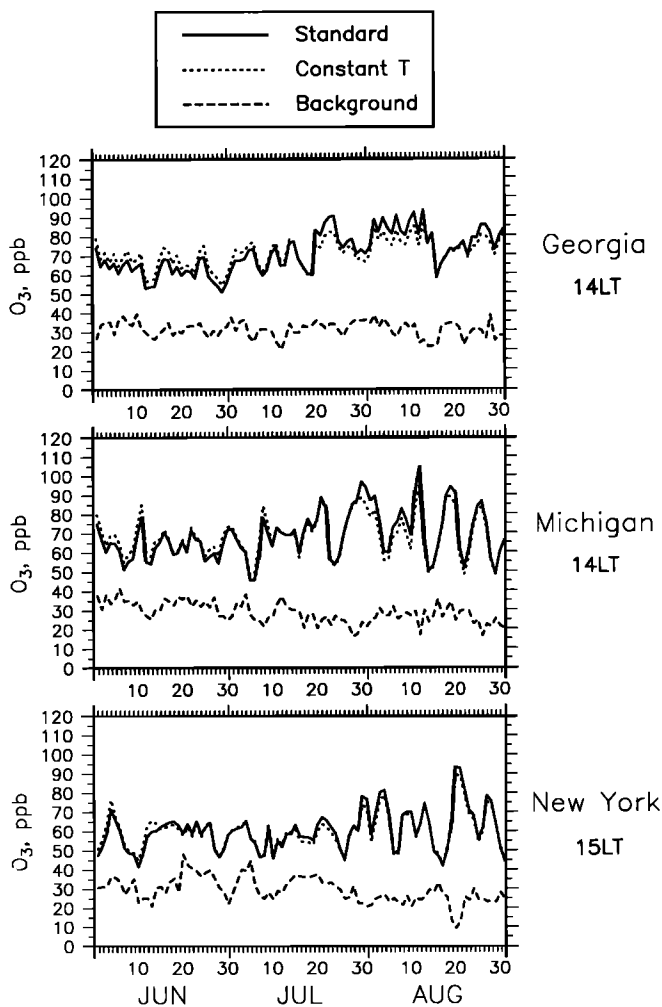


Fig. 4. Afternoon concentrations of rural O_3 simulated in the Georgia, Michigan, and New York grid boxes. Results from the standard simulation (solid lines) are compared to results from a simulation with temperature held constant in each grid box at its local mean value for June-August (dotted lines).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

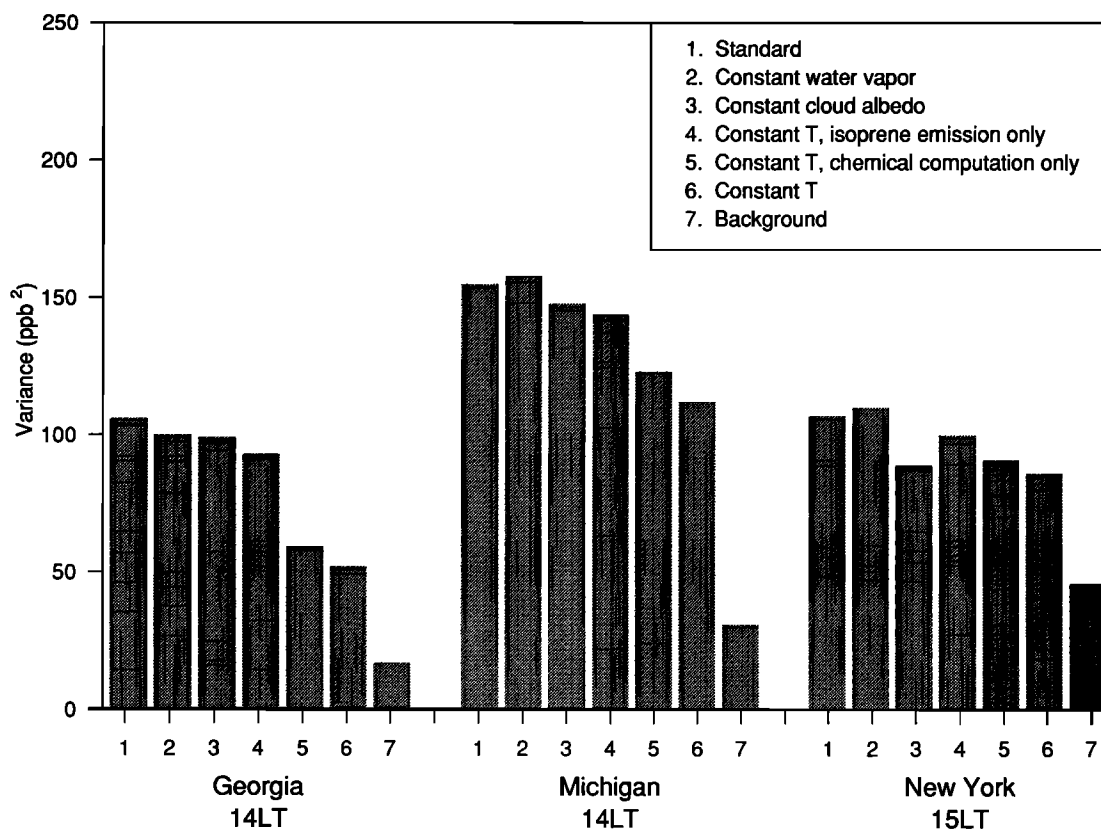


Fig. 5. Temporal variances of rural O₃ concentrations in the Georgia, Michigan, and New York grid boxes, computed from the model time series for June–August sampled at 14 or 15 LT ($n = 92$). Results are shown for the standard simulation, and for a series of sensitivity simulations with individual variables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

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 NO₂ 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; Korsog 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 [Sillman *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 Lioy, 1978; Clark and Karl, 1982].

4. GLOBAL INFLUENCE

Budgets of O₃ and NO_x 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 NO_x 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 NO_x 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 ϵ_N , defined as the net number of O₃ molecules produced per molecule of NO_x consumed [Lin *et al.*, 1988], is 3 times higher in the west ($\epsilon_N = 12.4$) than in the east ($\epsilon_N = 4.4$), due to lower NO_x concentrations in the west that reflect

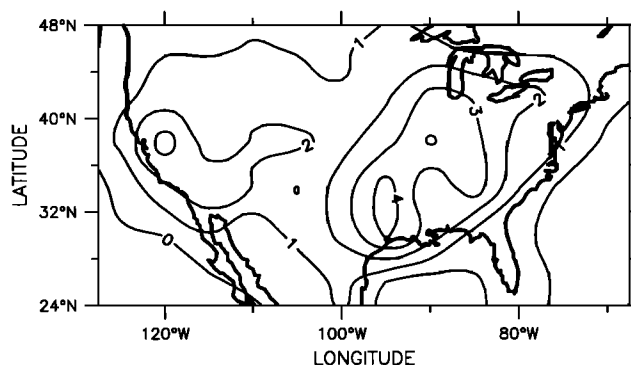


Fig. 6. Net O₃ production rates (10^6 molecules cm⁻³ s⁻¹) computed in the model for the air column extending up to ≈ 2.6 km above the surface (top of model layer 3). Values are 24-hour means for July averaged over the depth of the column.

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 O_3 and NO_x

Net photochemical production of O_3 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 O_3 . Export of pollution O_3 from the United States is in fact much higher than this balance would indicate because part of the O_3 deposited to the United States is exogenous. We extracted this exogenous background in a simulation with no chemistry, i.e., with O_3 concentrations regulated solely by advection of boundary conditions and deposition. The residual "pollution O_3 " represents the effect of net photochemical production over the model domain. We find that 70% of pollution O_3 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 O_3 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 O_3 out of the eastern United States in summer. They arrived at this estimate by using variance ratios of O_3 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 ra-

tios 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 O_3 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 O_3 and CO causes the variance ratio of O_3 and CO concentrations to underestimate the actual O_3/CO pollution ratio.

Figure 7 shows the mean transport fluxes of pollution O_3 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 O_3 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 NO_x in the model in July. The lifetime of NO_x against oxidation to HNO_3 and to stable organic nitrates is 10 hours on average in the U.S. boundary layer. Net export of NO_x out of the U.S. boundary layer (averaging 0.07 $Gmol\ d^{-1}$ for June to August) represents only 6% of NO_x emissions in the region because of the short lifetime. Vertical transport to the free troposphere accounts for 87% of NO_x export and is strongest over the northeastern United States where NO_x emissions are high. Net export of PANs in the model is near zero ($<0.01\ Gmol\ d^{-1}$) because of conversion of NO_x to PANs in

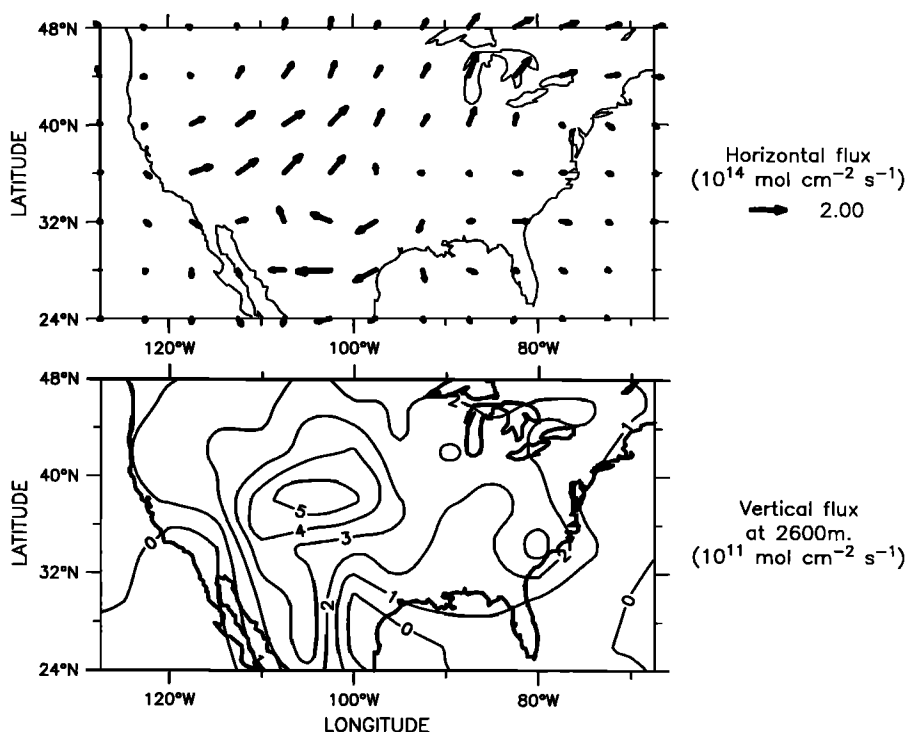


Fig. 7. Mean fluxes of pollution O_3 computed in the model boundary layer in July. The fluxes represent the effect of net photochemical production of O_3 over the model domain, and are obtained by subtracting the fluxes of background O_3 from the fluxes of O_3 computed in the standard simulation. The horizontal fluxes (top panel) are averages for the column extending up to ≈ 2.6 km above the surface (top of layer 3). The vertical fluxes (bottom panel) are computed at ≈ 2.6 km above the surface (through the top of model layer 3), and point upwards when positive.

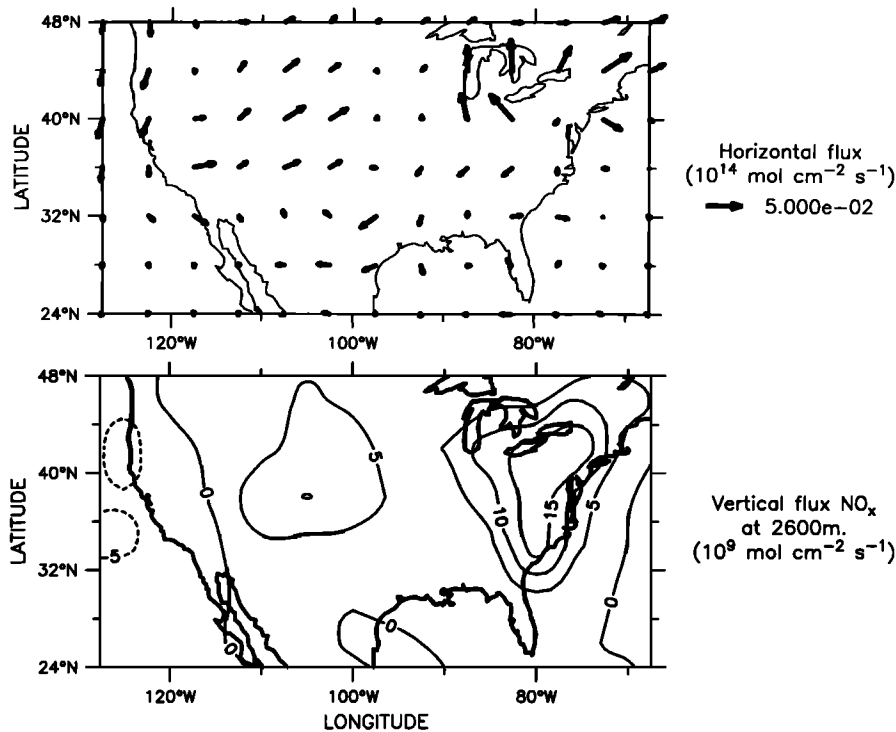


Fig. 8. Mean fluxes of NO_x computed in the model boundary layer in July. The horizontal fluxes (top panel) are averages for the column extending up to ≈ 2.6 km above the surface (top of layer 3). The vertical fluxes (bottom panel) are computed at ≈ 2.6 km above the surface (through the top of layer 3), and point upwards 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_y (including NO_x , PAN, and HNO_3). We find here that only 6% is exported as NO_x or PANs, but HNO_3 (which we do not simulate as a tracer) could account for a large fraction of total NO_y 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 ϵ_G [*Liu et al.*, 1987], defined as the gross number of O_3 molecules produced per molecule of NO_x consumed (ϵ_G differs from ϵ_N in that it does not account for O_3 chemical loss). We obtain $\epsilon_G = 57$ 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_2O_5 on aerosol surfaces because we assume that the background aero-

sol surface area in the middle troposphere (where most of the NO_x is exported) is small. The value of ϵ_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 $\epsilon_G = 36$. Assuming $\epsilon_G = 57$, 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 Mohnen*, 1977; *Gidel and Shapiro*, 1980; *Mahlman 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 ϵ_N , 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 ϵ_N 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 $8 \text{ Gmol } O_3 \text{ d}^{-1}$ 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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