



## FREE TROPOSPHERIC OZONE PRODUCTION AFTER DEEP CONVECTION OF DISPERSING TROPICAL URBAN PLUMES

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**Abstract**—Ozone generation is computed in a one-dimensional photochemistry code following convective redistribution of tropical urban effluent into the free troposphere. Simulations are run at several stages of pollutant dilution by surrounding surface air. A threshold boundary layer  $\text{NO}_x$  concentration of 300 pptv is established for significant production enhancements at upper levels. Areas defined by the 300 pptv level are examined in the Gaussian dispersion framework based on a wet season plume event observed in Amazonia. Pollution travels slowly in the sluggish winds of the equatorial trough. Daily storms are likely to interrupt the effluent while coverages are still on the order of few thousand square kilometers and  $\text{NO}_x$  concentrations are above the threshold. Dry season plume sizes are difficult to assess because local concentration data are scarce, but it is conceivable that the faster trade winds lead to a several fold extension. Copyright © 1996 Elsevier Science Ltd

*Key word index:* Ozone, convection, urban plumes, air pollution, free troposphere.

### INTRODUCTION

Lower atmospheric ozone acts as a greenhouse gas (Ramanathan *et al.*, 1987; Hauglustaine *et al.*, 1994), and is also a key pollutant and oxidant (Thompson, 1992; Jacob *et al.*, 1993a, b). The species is produced during hydrocarbon oxidation through the catalytic action of the nitrogen oxides NO and  $\text{NO}_2$  ( $\text{NO}_x$ ; Crutzen, 1973; Chameides and Walker, 1973). Although organics emanate from a wide variety of sources ranging from automobiles to boreal ecosystems, the most massive inputs are from tropical forests (Singh and Zimmerman, 1992; Graedel, 1994). Crutzen (1988) has asserted that as third world economies develop and cities inject nitrogen oxides into more remote areas, catalytic production from tropical organics will be the major ozone source in the troposphere.

It has been shown over the last few years that convective mixing away from the surface enables precursor hydrocarbons and  $\text{NO}_x$  to achieve their fullest ozone generating potential (Pickering *et al.*, 1990; Lelieveld and Crutzen, 1994). Dilution from the boundary layer into a free tropospheric column significantly increases net ozone yields (Liu *et al.*, 1987; Lin *et al.*, 1988). Several groups have constructed photochemical models of enhancements in oxidant levels when tropical biomass burning plumes are convected upward (Chatfield and Delany, 1990; Pickering *et al.*, 1992a) and Pickering *et al.* (1992b) have studied a particular event in which a convective system passed through the urban plume of Manaus, Brazil. The city is the economic heart of the Amazon basin.

In the present work we apply photochemical simulations of convective outflow to generalized tropical urban plumes. Our approach is analogous to the biomass burning study of Pickering *et al.* (1992a), in which hypothetical storms pass through fire emissions at various distances. A chemical model of a convecting

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tropical airmass (Elliott *et al.*, 1995a, b) is run with an unchanging free troposphere but successively lower nitrogen oxide concentrations in the boundary layer. A typical rain forest mix of reactive organics is adopted for lower altitudes (Jacob and Wofsy, 1988, 1990; Pickering *et al.*, 1992a, b). We are able to establish a threshold for boundary layer pollutant  $\text{NO}_x$  levels which lead to augmented columnar ozone production upon deep vertical mixing. We also perform a preliminary analysis of dispersion away from large tropical cities using Gaussian techniques (Csanady, 1973; Gifford, 1982; Sillman *et al.*, 1990a, b). The goal is to estimate areas covered by boundary layer containing  $\text{NO}_x$  above the threshold. A potential seasonality is apparent in the effluent geometry. During the storm intensive tropical wet season, uplift obliterates plumes near the time that internal removal processes lower nitrogen oxides to the threshold, and slow winds translate to small coverages. During the windier dry season, dilution to many thousands of square kilometers is possible but uncertain because initial concentrations remain unknown for tropical cities.

The photochemical model of convective storms applied here is somewhat new and is also less sophisticated dynamically than its forerunners (Pickering *et al.*, 1989; Chatfield and Delany, 1990) so that we elect to describe it at the outset in detail. The plume spreading models are well established (Gifford, 1975, 1977; Pielke, 1984; Seinfeld, 1986), so that we apply them without exposition. Manaus is adopted as an urban area archetypical for the developing tropics. Some limited pollutant distribution measurements are available to constrain its chemistry (Pickering *et al.*, 1992b). Furthermore, the simple topography of the Amazon region is amenable to the Gaussian approach (Pielke, 1984). Even so the standard dispersion models must be regarded as highly idealized, and so we use only the simplest versions of the relevant equations. Ultimately, we hope to couple our chemistry coding into a mesoscale meteorology model we have at our disposal (Pielke *et al.*, 1984; Bossert and Cotton, 1994a, b) to validate our conclusions in an Eulerian sense.

#### KINETIC NONLINEARITIES AND THE PHOTOCHEMICAL MODEL

In order for nitrogen oxides emitted in an urban zone to influence the free troposphere they must remain above catalytically effective levels through several stages of dilution. The sequence of events is illustrated schematically in Fig. 1. Concentrations in first world urban areas tend to fall in the range 50–100 ppbv during pollution episodes (Milford *et al.*, 1989; Bower *et al.*, 1991; Gladstone *et al.*, 1991; Campbell *et al.*, 1994). In underdeveloped cities lacking pollution controls the value can be several hundred ppbv (Ruiz Suarez *et al.*, 1993; Trier, 1993). Dilution of the urban

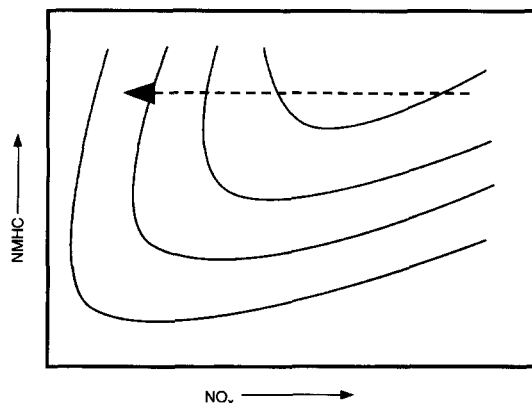


Fig. 1. A schematic trajectory for a tropical urban plume diluting into the surrounding organic rich boundary layer, superimposed on typical ozone isopleths.

plume brings the  $\text{NO}_x$  into contact with the ambient atmosphere. Tropical air contains a suite of highly reactive organics of vegetative origin (Jacob and Wofsy, 1988, 1990; Singh and Zimmerman, 1992). They are ubiquitous and so we picture them here as constant and high in concentration. A concentration trajectory in a tropical plume is shown as the dashed line, with NMHC representing nonpollution organics.

The trajectory is superimposed in the figure on a schematic of ozone production isopleths displaying the crucial nonlinearities in the tropospheric oxidant system (Crutzen, 1973; Chameides and Walker, 1973; Fishman and Crutzen, 1978; Liu *et al.*, 1987; Chatfield and Delany, 1990). Roughly speaking the contours indicate increasing ozone production during a specified photolytic period (Finlayson-Pitts and Pitts, 1986; Milford *et al.*, 1989; Dodge, 1989), usually set at a day (Pickering *et al.*, 1989). The nitrogen oxides are most effective as catalysts at intermediate concentration levels. If significant oxidant generation is to occur in the free troposphere, such levels must remain after vertical convective dilution.

The nonlinearities have complex implications for urban and regional pollution near the surface. For example, it has been noted in several works that reductions in urban  $\text{NO}_x$  emission might actually worsen air quality with respect to ozone, and that rural areas downwind of cities may sometimes bear brunt of a pollution problem (Sillman *et al.*, 1990a, b; McKeen *et al.*, 1991a, b; Jacob *et al.*, 1993a, b). Mixing into the free troposphere in major convective systems leads to dilution by a factor of ten or so (Pickering *et al.*, 1989, 1990, 1993). It is larger systems we consider here because shallow convection is a minor contributor to the global ozone budget (Feichter and Crutzen, 1990). The final storm driven dilution will generally place parcels on the contours sloping toward lower  $\text{NO}_x$  so that we do not emphasize the region  $\partial P(\text{O}_3)/\partial(\text{NO}_x) < 0$ . For tropical plumes to be important relative to the free troposphere, nitrogen oxide concentrations should remain near the isopleth

plateau region (in areas where ozone production is high) after convective redistribution.

Several of us have lately been involved in the design of photochemistry packages fast enough for deployment in massive three-dimensional problems (Kao *et al.*, 1990; Elliott *et al.*, 1993a, b; Jacobson and Turco, 1994; Shen *et al.*, 1995; Elliott *et al.*, 1995a, b). Numerical streamlining has included automation of set-up for solutions to the continuity equations, vectorization, and incorporation of the flexibility to choose from among a suite of integrators. We have emphasized family approaches in the past because of the need for speed in multiple dimensions. Most of the runs reported here were conducted in the family mode at time steps of 15 min. The present one-dimensional geometries also permit the use of more computationally intensive integrators. Accordingly, spot checking for accuracy was performed with an individual species QSSA (quasi-steady-state approximation; Hestvedt *et al.*, 1978; Isaksen *et al.*, 1978a, b; Odman *et al.*, 1992).

A surrogate hydrocarbon mechanism is adopted to represent the range of tropospheric organics (Elliott *et al.*, 1993a, b, 1995a, b; Shen *et al.*, 1995). The approach is quite similar to that of Pickering *et al.* (1989, 1992a, b, c) and Chatfield and Delany (1990) in other studies of convection and chemistry. Methane and ethane represent themselves in the scheme. Propane simulates the higher alkanes, propene the higher alkenes and isoprene the terpenoids. Fully detailed oxidation sequences are included for the surrogates (Atkinson and Lloyd, 1986; Elliott *et al.*, 1995a, b; Shen *et al.*, 1995). In particular, isoprene is oxidized according to the recent recommendations of Paulson and Seinfeld (1992). The mechanism has been tested previously in the family mode for its ability to reproduce general free tropospheric ozone chemistry at specific locations (Levy *et al.*, 1985; Liu *et al.*, 1987). Comparisons with established integrators are shown in Fig. 2, with most of the results specific to the Niwot Ridge site (Liu *et al.*, 1987; Trainer *et al.*, 1987). The Niwot runs were designed to parallel the simulations of Liu *et al.* (1987) as closely as possible. Initial conditions, column ozone abundances, humidity, temperature, time and altitude were all set to be nearly identical with the earlier work. Details of our model configuration are provided in Elliott *et al.* (1995b). One noteworthy difference lies in the chemical mechanisms. Liu *et al.* were able to include butane and its oxidation sequence explicitly. Discrepancies in the upper curve are due to the differences in the treatment of dilution into the box model (Liu *et al.*, 1987; Elliott *et al.*, 1995b). The figure is actually a set of sections through a version of the generic Fig. 1 isopleth set and so is evidence that the codes pick up the well-known tropospheric chemical nonlinearities.

Similar comparisons were made to test the ability of the program to represent nonlinearities resulting from convective mixing (Elliott *et al.*, 1995b). A one-dimensional model of stacked coupled layers

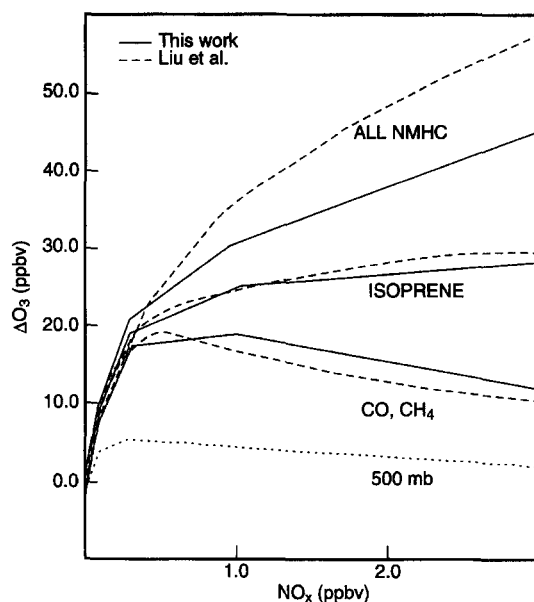


Fig. 2. Comparison of ozone production from our surrogate hydrocarbon mechanism with results from established integrators. Dashed simulations are for the Niwot Ridge site (Liu *et al.*, 1987; Trainer *et al.*, 1987). The lone dotted curve labeled 500 mbar is an upper level computation which matched the Levy *et al.* (1985) values for the free troposphere over the open ocean.

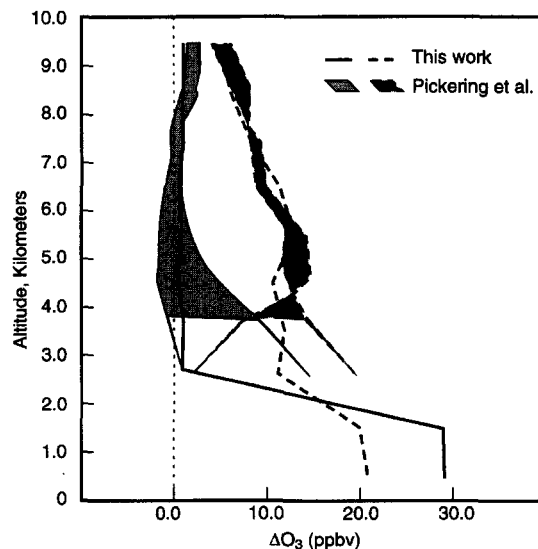


Fig. 3. Tropospheric ozone production in several calculations from the Pickering series (1989, 1990, 1991, 1992a-c, 1993; shaded areas indicate the range of results involved in the comparison) and in similar scenarios from our own work (Elliott *et al.*, 1995a, b; individual curves). Dashes indicate runs incorporating convective overturn. Shading is extended only to the point of overlap, while the lines are permitted to continue.

was constructed and run from midnight into the morning before various convective events. At average midday storm times portions of boundary layer air were lifted into the free troposphere and distributed,

with replacement air inserted to maintain mass balance. Costen *et al.* (1988) describe a related model. The detrainment profiles were calibrated using tracer redistribution results in the two-dimensional computations from the Pickering series (Pickering *et al.*, 1989, 1990, 1991, 1992a). The model was then run for several days and ozone production integrated to yield diurnal averages. The results were compared with the Pickering *et al.* calculations for several events. A typical level of agreement is shown in Fig. 3. Small discrepancies are the result of our inability to reproduce exactly the initial concentration conditions. In our runs idealized smoothed vertical profiles were used for ozone precursors which correspond only loosely with the Pickering *et al.* cases. The combination of numerical accuracy tests and agreement in comparisons such as Figs 2 and 3 suggests that our photochemical storms model provides a reasonable representation of ozone production following deep convection. Several of the Pickering cases involved hot tower type dynamics (Riehl and Malkus, 1958; Riehl and Simpson, 1979) with a clear displacement of boundary layer chemistry directly to cloud tops. In most of them, however, thorough turbulent mixing of boundary layer air occurred over the depth of the storm. We assume here in our generalized tropical calculations that the mixing is complete. In other words, material lifted from the boundary layer was detrained evenly through the free tropospheric column, from 2 to 10 km. Details of our convection parameterization can be found in Elliott *et al.* (1995b).

The radiative routines in our convection codes are described in Elliott *et al.* (1995b). Incoming solar radiation is first attenuated through Beer's law absorption by molecular oxygen and ozone. The molecular scattering field is constructed from adjustment factors tabulated in discussions of full radiative transfer studies (Luther and Gelinas, 1970; Luther and Wuebbles, 1976; Isaksen *et al.*, 1977; Nicolet *et al.*, 1982). We have taken careful note of the distinction which must be made between results from diffuse and collimated calculations (McElroy and Hunten, 1966; Madronich, 1987). Comparisons of key species such as the hydroxyl radical and the nitrogen oxides were made for the Niwot runs with results reported in Trainer *et al.* (1987). Agreement to within a few tens of percent could generally be achieved, indicating some degree of fidelity. The clear sky actinic fluxes are adjusted further according to estimates in Thompson (1984) and Madronich (1987) to represent the field in the presence of convective systems of  $\sim 10$  km depth. Sensitivity tests demonstrate that this post hoc approach provides a reasonable starting point (Elliott *et al.*, 1995b). The cloud factors are decoupled from any detailed structures implied by detrainment as matter of expedience. Shielding is turned off immediately following the convective event. Interactivity between wet chemistry, cloud particle distributions and the radiation field is an area where our simulations could be improved. Jacobson (1994) describes coupled

coding which could in principle treat the effects. Photolysis constants are calculated from the actinic field using the standard wavelength integrations described in Turco (1985).

#### NITROGEN OXIDE THRESHOLDS FOR THE TROPICS

Our tropical urban plume calculations are guided largely by results of wet and dry season campaigns conducted in the vicinity of Manaus, Brazil and emphasizing the remote boundary layer and its effects on the free troposphere (Jacob and Wofsy, 1988, 1990; Pickering *et al.*, 1992a, b). A survey of concentrations for key species in the ozone system above and within the tropical boundary layer is presented in Table 1. The data are derived from both measurements and models, but generally the two were in agreement with one another. We divide the boundary layer conceptually into the ambient and the urban plume. The Manaus plume was characterized by Pickering *et al.* (1992b) at a distance of about 50 km but with the indications that little spreading had occurred.

The concentrations we have selected to initialize our photochemistry models of convective systems are given in Table 2. For simplicity a single set of values is adopted for the wet and dry seasons. As a starting point for our computations we take the round value 10 ppbv  $\text{NO}_x$  to represent a well-mixed boundary layer containing fresh urban injections. This is broadly consistent with local concentrations of 0.1–1.0 ppmv for air within the city itself. Values for the other pollutants CO and organics are scaled up from the minima in Table 1 to approximate conditions in the fresh plume. Concentrations for isoprene and the long-lived species methane and ethane are set constant. These species are introduced primarily by the surrounding air causing dilution. We assume that ozone production within the plume is largely concealed by inward mixing of clean boundary layer air. This is consistent with sparse observations of the Manaus effluent, and again, becomes a better approximation with aging. Concentrations of nitrogen oxide reservoirs such as nitric acid and PAN were set proportional to  $\text{NO}_x$ . The proportionality factors were adjusted first to values given in Jacob and Wofsy (1988, 1990), Chatfield and Delany (1990) and Pickering *et al.* (1992a, b), then tuned through several model iterations so that no unwanted production of  $\text{NO}_x$  occurred (Elliott *et al.*, 1995b).

We have applied models of the photochemistry following convective turnover, first for the urban plume values themselves beginning at 10 ppbv of nitrogen oxides, and then diluting the urban levels with boundary layer air such that  $\text{NO}_x$  descends by half log units to the ambient level of 30 pptv. Runs were made at both solstices and equinoxes but for  $0^\circ$  latitude so that there is little difference in the photochemistry. Some typical results are collected in Fig. 4. Solid

Table 1. A survey of concentrations for ozone and its precursors in the tropical troposphere

Units	Species	Free troposphere	Boundary layer	Urban plume
ppb	O <sub>3</sub>	20 (P93; Darwin, F) 30 (P92b; Manaus, wet) 40 (P92a; Amazon, dry) 30 (CD90; Savanna, dry) 30 (JW88; Amazon, dry) 25 (G88; Amazon, dry) 20 (JW90; Amazon; dry)	10 (P92b; Manaus, wet) 10-20 (P92a; Amazon, dry) 25 (P91; Amazon, dry) 20 (JW88; Amazon, dry) 10 (JW90; Amazon, wet)	≥ 10 (P92b; Manaus, wet)
ppt	NO <sub>x</sub>	50 (P93; Darwin, F) 50 (P92b; Manaus, wet) 30 (P92a; Amazon, dry) 20 (S90; Tropical, wet) 20 (P91; Amazon, dry) 60 (JW88; Amazon, dry) 15-100 (CD90, Savanna, dry) 10 (JW90; Amazon, wet)	100 (P92b; Manaus, wet) 70 (P92a; Amazon, dry) 20 (S90; Tropical, wet) 20 (P91; Amazon, dry) 100 (JW88; Amazon, dry) 20 (JW90; Amazon, wet)	≥ 1000 (P92b; Manaus, wet)
ppb	CO	70 (P93; Darwin, F) 75 (P92b; Manaus, wet) 75 (P92a; Amazon, dry) 60 (JW88; Amazon, dry) 80 (JW90; Amazon, dry)	100 (P92b; Manaus, wet) 175 (P92a, Amazon, dry) 180 (P91, Amazon, dry) 80 (JW88; Amazon, dry)	≥ 200 (P92b; Manaus, wet)
ppm	CH <sub>4</sub>	1.6 (BR86a and b; 88)		
ppb	C <sub>2</sub> H <sub>6</sub>	2.0 (SZ92, BR 86a and b, 88)		
ppb	C <sub>3</sub> H <sub>8</sub>	0.2 (SZ92, E95b)	1.0 (Z88; Amazon, dry) 1.5 (P92a; Amazon, dry)	≥ 30.0 (Z88; Amazon, dry)
ppb	C <sub>3</sub> H <sub>6</sub>	0.1 (SZ92; E95a and b)	0.3 (Z88; Amazon, dry) 1.5 (P92a; Amazon, dry)	≥ 6.0 (Z88; Amazon, dry)
ppb	Isoprene		> 3 (P92b; Amazon, wet) 1-4 (P92a; Amazon, dry) 10 (P92c, Amazon, wet) 2 (JW88, Amazon, dry) 1 (JW90; Amazon, wet)	

- P92b Manaus plume had spread little a point of sample.
  - All saturated organics larger than C<sub>2</sub> treated as propane, unsaturated as propene.
  - Biomass burn plume NO<sub>x</sub> of the order of 2000-3000 pptv, CO 500 ppbv, O<sub>3</sub> 70 ppbv, alkanes and alkenes 1 ppbv (C85, CD90).
  - Boundary layer height; Manaus wet ~ 1 km (P92b), Savanna ~ 2 km (P92a); Manaus dry ~ 2 km (P91); JW88, 90 use 2 km dry or wet.
  - Pickering *et al.* include lightning NO<sub>x</sub> only when there is observational evidence for a major contribution. See P91 and P92b.
  - JW90 stress the contrast between pristine conditions during the wet season and pollution during the dry.
- NO<sub>x</sub> JW88, 90: Diurnal behavior averaged from complex interactions of surface mixed layer and a convective cloud layer as subsets of the boundary.
- NO<sub>x</sub> P92b: Boundary layer remotely influenced by Savanna biomass burns, 12-24 h transit away in Brazilian state of Mato Grosso.
- NO<sub>x</sub> P93: Initial NO<sub>x</sub> can only be estimated roughly from contour plots.
- NO<sub>x</sub> P93, CD90: Lightning influenced.
- Isoprene JW88, 90: Isoprene is sourced into boundary layer during the day; a rapid canopy level sink depletes the thin surface layer but leaves overall boundary concentrations intact at night.
- Isoprene P92a: Pickering gives the rough value 10 ppbv for wet season isoprene.
- Isoprene P92b: Unpublished grab samples.

J, F, M, etc.: Months.

Wet, dry: The major tropical seasons.

BR: Blake and Rowland; C: Crutzen *et al.*; CD: Chatfield and Delany; E: Elliott *et al.*; G: Garstang *et al.*; JW: Jacob and Wofsy; P: Pickering *et al.*; S: Scala *et al.*; SZ: Zimmerman *et al.*

curves are convected systems with boundary layer nitrogen oxide concentrations given sequentially above the frame. Ozone production for undistributed, storm-free scenarios is shown only for the NO<sub>x</sub> end points, 30 pptv and 10 ppbv, as the dashed curves. As expected, a small decrease in mixed-layer pro-

duction leads to a large enhancement in the free troposphere. There are several ways to define significant urban plume effects (e.g. Pickering *et al.*, 1989, 1992a; Chatfield and Delany, 1990). We might, for example, accept a convectively overturned back ground system as the baseline, or note that the

Table 2. Initial concentrations for the present model

Units		Free troposphere	Boundary layer	Urban plume
ppb	O <sub>3</sub>	30	20	20
ppt	NO <sub>x</sub>	30	30	Variable
ppb	CO	75	100	Variable
ppm	CH <sub>4</sub>	1.6	1.6	1.6
ppb	C <sub>2</sub> H <sub>6</sub>	2.0	2.0	2.0
ppb	C <sub>3</sub> H <sub>8</sub>	0.2	1.0	Variable
ppb	C <sub>3</sub> H <sub>6</sub>	0.1	1.0	Variable
ppb	Isoprene		2.0	2.0

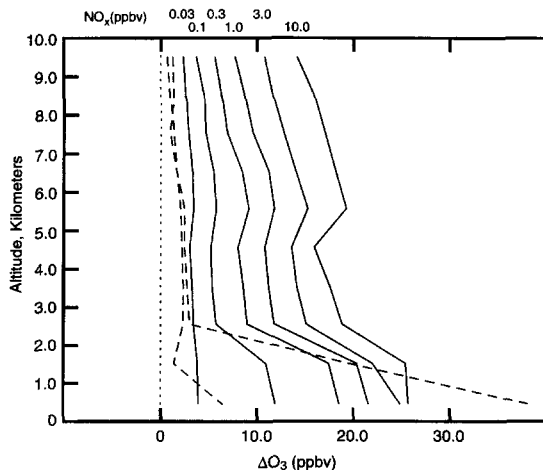


Fig. 4. Tropospheric ozone production for a series of scenarios representing dilution of an urban air mass into the tropical boundary layer. Solid curves are systems subjected to deep storms, with initial NO<sub>x</sub> concentrations given above. Vertical production profiles for nonconvected situations are shown only for NO<sub>x</sub> levels 30 pptv and 10 ppbv, as the dashed curves.

ambient free troposphere contains several tens of ppbv ozone. In either case an approximate NO<sub>x</sub> threshold is about 300 pptv. Tropical urban plumes containing this level or greater will produce of the order of 10 ppbv or more of ozone in the free troposphere following upward mixing in a convective storm. The value is derived systematically here but matches implications of the Pickering *et al.* series (1989, 1990, 1991, 1992a, b, c, 1993).

#### DISPERSION FROM TROPICAL CITIES

Having defined boundary layer NO<sub>x</sub> concentrations sufficient for free tropospheric effects, we are now in a position to investigate the areal extent of effluent with levels above the threshold. Dilution of an urban plume is calculated here in basic Gaussian spreading models (Gifford, 1975, 1977; Hanna *et al.*, 1982; Seinfeld, 1986). The dispersion is coupled in turn to time constants for chemical change within plumes, and for meteorological properties affecting them. Un-

certainties will be sufficiently large that the value of the exercise probably lies mainly in the patterns of variation it suggests. It should provide a useful guide, however, for more detailed multidimensional simulations.

Sillman *et al.* (1990a) have derived via Csanady (1973) the equation  $y_i = [y_0^2 + 8Kt]^{1/2}$  to represent the increasing width of a plume originally  $y_0$  across. The relationship is Gaussian in that tracer distributions are represented by a square wave function with a dimension of several standard deviations. The  $y_i$  was intended to simulate mixing away from cities and groups of power plants located on the North American Great Plains, but the authors employ the generalized diffusion coefficient  $10^4 \text{ m}^2 \text{ s}^{-1}$  averaged from a global range of studies (Gifford, 1982). An assumption implicit in the Sillman *et al.* expression is that atmospheric dispersion is Fickian, or in other words, that a single  $K$  applies. Fick's laws strictly describe spreading only when it involves uniform small-scale motions (Seinfeld, 1986). In the atmosphere a material cloud interacts with eddies of about its own size, and these lead to faster diffusion with growth (Gifford, 1982, 1995). The Sillman equation adopts  $K$  appropriate to the bulk of time and size scales of interest in urban plume studies. The choice of coefficient value can be verified by applying random force theory, which takes the eddy variations into account (Gifford, 1984). Barr and Gifford (1987) quote  $2 \times 10^4 \text{ m}^2 \text{ s}^{-1}$  as a reasonable average for regional dispersion, in accord with Sillman *et al.* (1990a). Stability class analysis (Gifford, 1961; Pasquill, 1971, 1974) relates diffusion rates to thermodynamic properties of the boundary layer. It suggests that lower atmospheric stability differences can lead to variations of an order of magnitude in Gaussian width. However, the concepts are valid only for plume lengths of 10 km or less. Beyond this point, larger-scale processes dominate. We adopt the round figure  $K = 10^4 \text{ m}^2 \text{ s}^{-1}$  as a point of reference for the calculations below.

From an examination of Brazilian government atlas materials (Instituto Brasileiro de Geografia, 1971) and crude maps in some of the Amazon boundary layer works (e.g. Pickering *et al.*, 1992b), we estimate  $y_0$  for a developing tropical metropolis at 10–30 km. Values for major U.S. cities are about a factor of three larger (Sillman *et al.*, 1990a). In Fig. 5 the Sillman *et al.* equation and parameters are used to estimate dilution of pollutants in tropical urban plumes as a function of time. We ignore the regime  $y_0^2 \geq 8Kt$  because our  $t$  values will be in the range half a day or more. Results for pure mixing are plotted as the solid curves. The NO<sub>x</sub> threshold of 300 pptv is marked by the hatched area.

Chemical and deposition losses will be competitive with dilution in lowering NO<sub>x</sub> concentrations. Dry season hydroxyl radical levels in the boundary layer are suppressed somewhat in tropical forests due to the presence of high concentrations of terpenoids. The OH values from Jacob and Wofsy (1988) coupled to

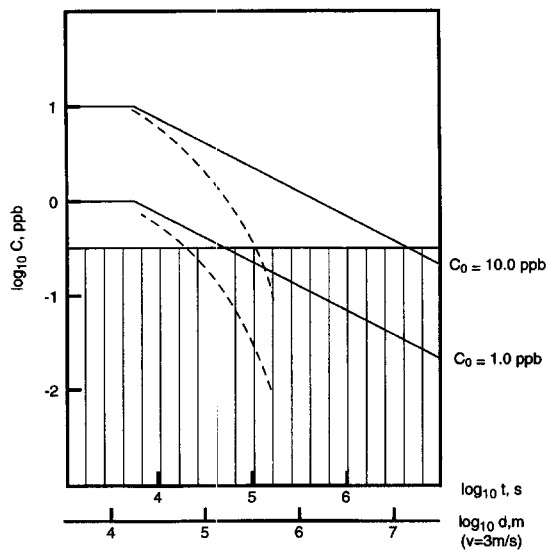


Fig. 5. Dilution and chemistry/deposition reductions in tropical urban plume  $\text{NO}_x$ . Capital C signifies a concentration, and subscript nought an initial value. Solid lines represent mixing induced changes in tracer concentrations calculated alone within a Gaussian dispersion model. Dashed curves add to dilution first order photochemical and deposition losses for the nitrogen oxides. The primary lower scale in units of seconds is readily converted to distance in meters upon multiplication by a lower limit wet season surface wind velocity of  $1 \text{ m s}^{-1}$ . The alternate scale assumes a wind of  $3 \text{ m s}^{-1}$ , which lies at the lower end of the 3 to  $5 \text{ m s}^{-1}$  range mentioned in the text.

the recombination rate for  $\text{NO}_2$  to form nitric acid (Demore *et al.*, 1990) suggest an  $\text{NO}_x$  lifetime of about a day. Recycling of  $\text{NO}_x$  from  $\text{HNO}_3$  has a time constant of weeks. Generation from peroxy nitrate species may be important in ambient air (Jacob and Wofsy, 1988, 1990) but not in our polluted plumes. During the wet season clouds retard overall photochemical activity so that hydroxyl removal should be slower. Both  $\text{NO}_2$  and  $\text{NO}$  are insoluble in the aqueous and organic liquids which are present in leaf surfaces. In the serial model for deposition, surface resistance thus tends to be the controlling factor. Deposition in the tropics is poorly constrained but Jacob and Wofsy (1988, 1990) use a value of about  $1 \text{ cm}^{-1}$  as a resistance for  $\text{NO}_2$  flux to the canopy. As a set of fast limits for  $\text{NO}_x$  removal we assume time constants of one day each for chemical and surface losses. Estimates of latitudinally dependent  $\text{NO}_x$  lifetimes from global scale studies support these figures (Logan, 1983; Penner *et al.*, 1991). Nitrogen oxide levels adjusted for removal from the boundary layer are shown as the dashed curves on Fig. 5.

Wind conditions will determine the distances to which urban pollutants can spread given the limitations defined by decay and convective overturn. Both winds and storm frequencies undergo well-understood seasonal cycles in the tropics. Because we have designated Manaus as an archetype city, the meteorology

of the Amazon basin in which it lies is now examined (Ratisbona, 1976; Paegle, 1987). Prominent features of the Amazonian climate extend to other areas of the terrestrial tropics (Riehl, 1950; Shukla, 1987). Average winds and precipitation are expected to conform loosely to the trade wind model (Nimer, 1979; Dos Santos, 1987; Molion, 1987; Paegle, 1987). Wind systems are usually easterly along the coast and in the low river valleys. When a particular region passes into the equatorial trough, it enters its wet season. Daily convection disrupts the boundary layer (Riehl, 1950; Ratisbona, 1976; Nimer, 1979; Jacob and Wofsy, 1990; Greco *et al.*, 1990) and most rain is generated by deep storms (Greco *et al.*, 1990). Average horizontal wind speeds recorded during low-level soundings have been as slow as  $1 \text{ m s}^{-1}$  (Scala *et al.*, 1990; Fitzjarrald *et al.*, 1990). Over trajectory analyses of several days or more winds average  $1\text{--}2 \text{ m s}^{-1}$  (Kirchhoff *et al.*, 1990; Greco *et al.*, 1990). Calms are often recorded (Ratisbona, 1976). As a region moves beneath the trade wind inversion, convection is suppressed and a dry season ensues (Riehl, 1950; Paegle, 1987). The tropics are nonetheless quite moist, and convective events mix the boundary layer every 3 to 5 days (Ratisbona, 1976; Jacob and Wofsy, 1988; Chatfield and Delany, 1990). Recent campaigns have observed winds in the boundary layer ranging from 2 to  $10 \text{ m s}^{-1}$  (Andreae *et al.*, 1988; Garstang *et al.*, 1988). Crutzen *et al.* (1985) computed three day back trajectories for the Amazon dry season with average velocities of  $7 \text{ m s}^{-1}$  at 850 mbar. Andreae *et al.* (1988) display similar results.

We will assume here that daily convection and sluggish winds dominate in the wet season, while in dry periods several days elapse between storm events and winds are stronger. Full calculations of plume dimensions would require a detailed knowledge of the pollution fields generated by tropical cities. For example, complete information on the  $C_0$  in Fig. 5 would be needed. Although many studies of general Amazonian geochemistry, atmospheric chemistry and biology have originated in or near Manaus (Orsini *et al.*, 1982; Browell *et al.*, 1988; Simoneit *et al.*, 1990; Fearnside *et al.*, 1993), it is difficult to find information on air quality problems within the city itself. This is true for tropical and developing regions as a class relative to the first world. The wet season pollution data from Pickering *et al.* (1992b) which appeared in Table 1 are limited but provide a useful foundation. An aircraft intercept of the Manaus effluent at 50 km downwind yielded  $\text{NO}_x$  concentrations of 2 to 3 ppbv. At an average horizontal wind speed of  $2 \text{ m s}^{-1}$  the plume had aged for perhaps 7 h. The authors note that overcast is common in the trough and reduces horizontal spreading rates, so that our global average diffusion coefficient may be an overestimate in this case. The observed plume width in fact indicates a pure dilution factor of about two. Coupled to the photochemical and depositional loss rates we have derived, a  $C_0$  of 10 to 15 ppbv seems reasonable.

Manaus may well experience high pollution levels and so local surface nitrogen oxide concentration of 0.1–1.0 ppmv. These would not be inconsistent with the Pickering *et al.* extrapolation.

For initial concentrations between 10 and 15 ppbv and wet season meteorology, the upper curve set in Fig. 5 suggests that convective activity will disrupt a typical urban plume before chemical/deposition losses can lower NO<sub>x</sub> concentrations to the threshold. A corollary is that most large plumes in the equatorial trough will have free tropospheric effects upon ozone. The effluent areas, however, will tend to be restricted. Over a day at a horizontal wind speed of 2 ms<sup>-1</sup> the total length may be 200 km, and even for the global eddy diffusion constant width increases only to 100 km. Total plume areas containing pollutant concentrations sufficient for free tropospheric effects will be of the order of several thousand square kilometers.

The areal extent of the plumes under windier conditions is difficult to evaluate. During the dry season, several days to a week may be available for dilution and internal removal to act on the pollutants. It is clear from Fig. 5 that the chemistry and deposition processes are likely to lower NO<sub>x</sub> to the 300 pptv level before convection occurs. The fast trade wind type easterlies will tend to lengthen plumes but will also reduce the residence time of air parcels over a city and hence lower C<sub>0</sub> (Pasquill, 1974). If the Manaus wet season concentration is taken as an upper limit, there is at least the potential for areas containing more than the threshold level to be several times greater than their wet season counterparts. Plumes many hundreds of kilometers long are conceivable, and it seems likely that a significant seasonality exists in the coverages. To aid in visualizing these arguments, distance scales can be added to Fig. 5. As conservative estimates of velocities for the surface easterlies, the global average values 1 ms<sup>-1</sup> and 3–5 ms<sup>-1</sup> are assumed here for the trough and for tropical regions lying beneath the trade wind inversion (Riehl, 1950; Shukla, 1987). The main horizontal axis labeled in units of time thus also represents distance in meters during the wet season. The second horizontal axis has been converted to distance in meters at 3 ms<sup>-1</sup>.

#### DISCUSSION

Several kinds of uncertainty influence the calculations in the present work. For example, we have made numerous approximations in order to facilitate the photochemistry modeling. The assumptions are common ones, however. The surrogate hydrocarbon system for reducing the number of species and reactions in a mechanism entails significant sacrifices in kinetic detail (Liu *et al.*, 1987; Chatfield and Delany, 1990; Elliott *et al.*, 1993b, 1995a). Alternatives such as structural lumping require specialized calibration (Falls and Seinfeld, 1978; Whitten *et al.*, 1980; Jacobson, 1994) and so are not used in computations of

global chemistry. Multiple scattering is highly parameterized within our photolysis rates, but full radiative transfer is often decoupled from photochemistry (Luther and Wuebbles, 1976; Isaksen *et al.*, 1977; Trainer *et al.*, 1987; Kinnison *et al.*, 1989; Jacob *et al.*, 1993a,b). Although our physical description of convective storms is low in resolution and depends for detrainment profiles on measurements and multi-dimensional simulations (Elliott *et al.*, 1995b), it stands up well in comparison with more complete studies (Pickering *et al.*, 1989, 1990, 1991, 1992a,b). The usefulness of the localized columnar chemistry calculations is limited to periods of hours to days because in the real atmosphere shear separates air parcels on longer time scales (Pickering *et al.*, 1989, 1990; Chatfield and Delany, 1990).

The arguments made regarding plume dimension are less well developed than our chemistry calculations. There is considerable play in the city size y<sub>0</sub>, and horizontal dilution exhibits a first power dependence on the parameter (Sillman *et al.*, 1990a,b). Furthermore, the tropics lie outside the latitudes for which Gaussian models have been validated (Gifford, 1982, 1995), so that selection of a diffusion coefficient is arbitrary to some extent. Our understanding of tropical urban effluent geometries could be improved by moving from the plume approach to three-dimensional chemical computations. We are currently working in this direction. Kinetics routines which we developed for general circulation model applications (Kao *et al.*, 1990; Elliott *et al.*, 1993a,b; Jacobson and Turco, 1994; Shen *et al.*, 1995; Elliott *et al.*, 1995a,b) are being inserted into the Regional Atmospheric Modeling System (RAMS; Pielke *et al.*, 1992; Bossert and Cotton, 1994a,b). The coupled code will be non-hydrostatic and possess nested grid capabilities so that resolution of the fine scale should be possible early in the evolution of a plume. Photochemical changes will be monitored in detail along the dispersion course, reducing the guesswork involved in constructing removal rates. Regional programs will be crucial to the study of greenhouse gas transformations which are sub-grid in scale relative to climate model meshes (Houghton *et al.*, 1990; IPCC, 1992; Graedel *et al.*, 1994).

The major uncertainties in plume characteristics lie in and around the cities themselves. Tropical urban air quality is not often treated in the literature, and probably has not been studied in the detail required to establish initial concentrations for our areal calculations. Since cities such as Manaus lie at the edges of or within the largest terrestrial sources of organics, there may be global scale motivations for characterizing their local atmospheric chemistry (Crutzen, 1987, 1988). The need for more information is underscored by estimates that tropical human populations are among the fastest growing on earth (Oak, 1986).

Our work suggests that equatorial urban effluent areas bounded by the NO<sub>x</sub> threshold could be quite extensive in the dry season. When conditions are



appropriate for long plumes, a few large cities might saturate a tropical forest area with respect to ozone effects aloft. Strong free tropospheric ozone production has been documented over the low latitude Atlantic Ocean both in soundings and satellite data (Logan and Kirchoff, 1986; Fishman *et al.*, 1986, 1990, 1991; Fishman and Larsen, 1987). The phenomenon has been linked to biomass burning release of  $\text{NO}_x$  (Chatfield and Delany, 1990; Pickering *et al.*, 1992a). However, rapid deforestation is accompanying human population growth within the tropics (Fearnside, 1987; French, 1994). We would speculate that the urban effluent dispersion described here will in some part supplant burning as a source of ozone to the free troposphere. Because ozone is a pollutant, oxidant and greenhouse gas, there may be some justification for centralizing the tropical population base.

#### SUMMARY

The terrestrial tropics constitute a major potential source of ozone because they are rich in surface hydrocarbon emissions (Graedel, 1994). As human populations rise in developing countries at low latitudes nitrogen oxide emissions will contact the organics and catalyze the ozone production (Crutzen, 1988). Convective storms will often intersect tropical urban plumes and the resulting vertical dilution will lead to enhancements in column ozone production (Liu *et al.*, 1987; Pickering *et al.*, 1992b). Furthermore, isolation from the surface will increase time constants for removal and involve fast upper level winds in the distribution process (Chatfield and Delany, 1990; Lelieveld and Crutzen, 1994).

In the present work we have applied a photochemical model of storm systems (Elliott *et al.*, 1995a, b) to simulate the tropospheric ozone production which follows convective overturn of tropical urban pollutants. Vertical profiles of post-storm ozone change were computed for various stages in the mixing of a city plume with an ambient forest boundary layer. We find that free tropospheric effects remain significant to about 300 pptv of  $\text{NO}_x$  in the effluent. Gaussian techniques indicate that dispersion to these levels may have a seasonal dependence (Gifford, 1982; Ratisbona, 1976). In the wet season frequent convection interrupts the spreading just before deposition and chemical losses have lowered the nitrogen oxides to the threshold. Intact plumes usually increase ozone production if lifted into the free troposphere. Light winds associated with the equatorial trough, however, limit the absolute extent of coverage. Light winds associated with the equatorial trough, however, limit the absolute extent of coverage. In the dry season chemistry and surface removal bring  $\text{NO}_x$  to 300 pptv before convection can disrupt the plume. Areas covered could reach several times the wet season values, but cannot be determined precisely because information on initial pollutant concentrations is not at hand.

#### REFERENCES

- Andreae M. O., Browell E. V., Garstang M., Gregory G. L., Harriss R. C., Hill G. F., Jacob D. J., Periera M. C., Sachse G. W., Setzer A. W., Silva Dias P. L., Talbot R. W., Torres A. L. and Wofsy S. C. (1988) Biomass burning emissions and associated haze layers over Amazonia. *J. geophys. Res.* **93**, 1509–1527.
- Atkinson R. and Lloyd A. C. (1984) Evaluation of kinetic and mechanistic data for modelling photochemical smog. *J. phys. chem. Ref. Data* **13**, 315–398.
- Barr S. and Gifford F. A. (1987) The random force theory applied to regional scale tropospheric diffusion. *Atmospheric Environment* **21**, 1737–1741.
- Blake D. S. and Rowland F. S. (1986a) Global atmospheric concentrations and source strength of ethane. *Nature* **321**, 231–233.
- Blake D. S. and Rowland F. S. (1986b) Worldwide increase in tropospheric methane, 1978–1983. *J. atmos. Chem.* **4**, 43–62.
- Blake D. S. and Rowland F. S. (1988) Continuing worldwide increase in tropospheric methane, 1978–1987. *Science* **239**, 1129–1131.
- Bossert J. E. and Cotton W. R. (1994a) Regional scale flows in mountainous terrain. Part I: a numerical and observational comparison. *Mon. Weath. Rev.* **122**, 1449–1471.
- Bossert J. E. and Cotton W. R. (1994b) Regional scale flows in mountainous terrain. Part II: simplified numerical experiments. *Mon. Weath. Rev.* **122**, 1472–1489.
- Bower J. S., Broughton G. G. J., Dando M. T., Lees A. J., Stevenson K. J., Lampert J. E., Sweeney B. P., Parker V. J., Driver G. S., Waddon C. J. and Wood A. J. (1991) Urban  $\text{NO}_2$  concentrations in the U.K. in 1987. *Atmospheric Environment* **25B**, 267–283.
- Browell E. V., Gregory G. L. and Harriss R. C. (1988) Tropospheric ozone and aerosol distributions across the Amazon basin. *J. geophys. Res.* **93**, 1431–1451.
- Bruhl C. and Crutzen P. J. (1988) Scenarios of possible changes in atmospheric temperature and ozone concentration due to man's activities, estimated with a one-dimensional coupled photochemical climate model. *Climate Dynamics* **2**, 173–203.
- Campbell G. W., Stedman J. R. and Stevenson K. (1994) A survey of nitrogen dioxide concentrations in the United Kingdom using diffusion tubes, July–December 1991. *Atmospheric Environment* **28**, 477–486.
- Chameides W. and Walker J. C. G. (1973) A photochemical theory of tropospheric ozone. *J. geophys. Res.* **78**, 8751–8760.
- Chatfield R. B. and Delany A. C. (1990) Convection links biomass burning to increased tropical ozone: however, models will tend to overpredict  $\text{O}_3$ . *J. geophys. Res.* **95**, 18,473–18,488.
- Costen R. C., Tennille G. N. and Levine J. S. (1988) Cloud pumping in a one-dimensional photochemical model. *J. geophys. Res.* **93**, 15,941–15,954.
- Crutzen P. J. (1973) A discussion of the chemistry of some minor constituents in the stratosphere and troposphere. *Pure appl. Geophys.* **106**, 1385–1399.
- Crutzen P. J. (1987) Role of the tropics in atmospheric chemistry. In *The Geophysiology of Amazonia: Vegetation and Climate Interactions* (edited by Dickinson R. E.), pp. 107–132. Wiley, New York.
- Crutzen P. J. (1988) Tropospheric ozone: an overview. In *Tropospheric Ozone* (edited by Isaksen I. S. A.), pp. 3–32. Reidel, Dordrecht.
- Crutzen P. J., Delany A. C., Greenberg J., Haagenson P., Heidt L., Lueb R., Pollock W., Seiler W., Wartburg A. and Zimmerman P. (1985) Tropospheric chemical composition measurements in Brazil during the dry season. *J. atmos. Chem.* **2**, 233–256.

- Csanady G. T. (1973) *Turbulent Diffusion in the Environment*. Reidel, Dordrecht.
- Demore W. B., Sander S. P., Golden D. M., Molina M. J., Hampson R. F., Kurylo M. J., Howard C. J. and Ravishankara A. R. (1990) Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 9, Jet Propulsion Laboratory Publ. 90-1, Pasadena, California.
- Dodge M. C. (1989) A comparison of three photochemical oxidant mechanisms. *J. geophys. Res.* **94**, 5121–5136.
- Dos Santos J. M. (1987) Climate, natural vegetation, and soils in Amazonia: an overview. In *The Geophysiology of Amazonia: Vegetation and Climate Interactions* (edited by Dickinson R. E.), pp. 25–36. Wiley, New York.
- Elliott S., Turco R. P. and Jacobson M. Z. (1993a) Test on combined projection and forward differencing integration for stiff photochemical family systems at long time step. *Computers and Chemistry* **17**, 91–102.
- Elliott S., Kao C. Y. J., Turco R. P. and Zhao X. P. (1993b) Kinetics Programs for Simulation of Tropospheric Photochemistry on the Global Scale. Los Alamos National Laboratory Technical Report LA-12539-MS, 72 pp.
- Elliott S., Turco R. P., Zhao X. P., Kao C. Y. J. and Shen M. (1995a) Photochemical numerics for global scale modeling: fidelity and GCM testing. *J. appl. Met.* **34**, 694–718.
- Elliott S., Kao C. Y. J., Shen M., Turco R. P. and Jacobson M. Z. (1995b) A streamlined family photochemistry package reproduces major nonlinearities in the tropospheric ozone system. *Computers and Chemistry* (in press).
- Falls A. H. and Seinfeld J. H. (1978) Continued development of a kinetic mechanism for photochemical smog. *Envir. Sci. Technol.* **12**, 1398–1406.
- Fearnside P. M. (1987) Causes of deforestation in the Brazilian Amazon. In *The Geophysiology of Amazonia: Vegetation and Climate Interactions* (edited by Dickinson R. E.), pp. 37–62. Wiley, New York.
- Fearnside P. M., Leal N. and Fernandez F. M. (1993) Rain forest burning and the global carbon budget: biomass, combustion efficiency, and charcoal formation in the Brazilian Amazon. *J. geophys. Res.* **98**, 16,733–16,743.
- Feichter J. and Crutzen P. J. (1990) Parameterization of vertical tracer transport due to deep cumulus convection in a global transport model and its evaluation with <sup>222</sup>Rn measurements. *Tellus* **42B**, 100–117.
- Finlayson-Pitts B. J. and Pitts J. N. (1986) *Atmospheric Chemistry: Fundamentals and Experimental Techniques*. Wiley, New York.
- Fishman J. and Crutzen P. J. (1978) The origin of ozone in the troposphere. *Nature* **274**, 855–858.
- Fishman J. and Larsen J. C. (1987) Distribution of total ozone and stratospheric ozone in the tropics: implications for the distribution of tropospheric ozone. *J. geophys. Res.* **92**, 6627–6634.
- Fishman J., Minnis P. and Reichle J. G. Jr. (1986) Use of satellite data to study tropospheric ozone in the tropics. *J. geophys. Res.* **91**, 14,451–14,465.
- Fishman J., Watson C. E., Larsen J. C. and Logan J. A. (1990) Distribution of tropospheric ozone determined from satellite data. *J. geophys. Res.* **95**, 3599–3617.
- Fishman J., Fakhruzzaman K., Cros B. and Nganga D. (1991) Identification of widespread pollution in the southern hemisphere deduced from satellite analysis. *Science* **252**, 1693–1696.
- Fitzjarrald D. R., Moore K. E., Cabral O. M. R., Sclar J., Manzi A. O. and de Abreu Sá L. D. (1990) Daytime turbulent exchange between the Amazon forest and the atmosphere. *J. geophys. Res.* **95**, 16,825–16,838.
- French H. (1994) Making environmental treaties work. *Sci. Am.* 94–97.
- Garstang M., Scala J., Greco S., Harriss R., Beck S., Browell E., Sachse G., Gregory G., Hill G., Simpson J., Tao W. K. and Torres A. (1988) Trace gas exchanges and convective transports over the Amazonian rain forest. *J. geophys. Res.* **93**, 1528–1550.
- Gifford F. A. (1961) Use of routine meteorological observations for estimating atmospheric dispersion. *Nucl. Safety* **2**, 47–51.
- Gifford F. A. (1975) Atmospheric dispersion models environmental pollution applications. In *Lectures on Air Pollution and Environmental Impact Analysis* (edited by Haugen D. A.), pp. 35–38. Am. Met. Soc., Boston.
- Gifford F. A. (1977) Tropospheric relative diffusion observations. *J. appl. Met.* **16**, 311–313.
- Gifford F. A. (1982) Horizontal diffusion in the atmosphere: a Lagrangian dynamical theory. *Atmospheric Environment* **16**, 505–512.
- Gifford F. A. (1984) The random force theory: application to meso- and large-scale atmospheric diffusion. *Boundary Layer Met.* **30**, 159–175.
- Gifford F. A. (1995) Some recent long-range diffusion observations. *J. appl. Met.* (in press).
- Gladstone K. P., Niki H., Shepson P. B., Bottenheim J. W., Schiff H. I. and Sandhu H. S. (1991) Photochemical oxidant concentrations in two Canadian prairie cities: model evaluation. *Atmospheric Environment* **25B**, 243–254.
- Graedel T. E. (1994) Global emissions inventories to aid atmospheric modelers. *EOS* **75**(50), 585–591.
- Greco S., Swap R., Garstang M., Ulanski S., Shipman M., Harriss R. C., Talbot R., Andreae M. O. and Artaxo P. (1990) Rainfall and surface kinematic conditions over central Amazonia during ABLE 2B. *J. geophys. Res.* **95**, 17,001–17,014.
- Hahn C. J., Warren S. G., London J., Chervin R. M. and Jenne R. (1982) Atlas of simultaneous occurrence of different cloud types over the ocean. *NCAR/TN-201 + STR*, National Center for Atmospheric Research, Boulder, Colorado.
- Hanna S. R., Briggs G. A. and Hosker R. P. (1982) *Handbook on Atmospheric Diffusion*. Technical Information Center, U.S. Department of Energy.
- Hauglustaine D. A., Granier C., Brasseur G. P. and Megie G. (1994) The importance of atmospheric chemistry in the calculation of radiative forcing on the climate system. *J. geophys. Res.* **99**, 1173–1186.
- Hesstvedt E., Hov O. and Isaksen I. S. A. (1978) Quasi steady state approximations in air pollution modeling: comparison of two numerical schemes for oxidant prediction. *Int. J. Chem. Kinet.* **10**, 971–994.
- Houghton J. T., Jenkins G. J. and Ephraums J. J. (1990) *Climate Change: The IPCC Scientific Assessment*. Cambridge University Press, Cambridge.
- Instituto Brasileiro de Geografia (1971) *Mapa da Bacia Amazonica*.
- IPCC (1992) *Greenhouse Gases*. Cambridge University Press, Cambridge.
- Isaksen I. S. A., Midtbø K. N., Sunde J. and Crutzen P. J. (1977) A simplified method to include molecular scattering and reflection in calculations of photon fluxes and photodissociation rates. *Geophys. Norv.* **31**, 11–26.
- Isaksen I. S. A., Hov O. and Hesstvedt E. (1978a) Ozone generation over rural areas. *Envir. Sci. Technol.* **12**, 1279–1284.
- Isaksen I. S. A., Hesstvedt E. and Hov O. (1978b) A chemical model for urban plumes: Test for ozone and particulate sulfur formation in St. Louis urban plume. *Atmospheric Environment* **12**, 599–604.
- Jacob D. J. and Wofsy S. C. (1988) Photochemistry of biogenic emissions over the Amazon forest. *J. geophys. Res.* **93**, 1477–1486.
- Jacob D. J. and Wofsy S. C. (1990) Budgets of reactive nitrogen, hydrocarbons, and ozone over the Amazon forest during the wet season. *J. geophys. Res.* **95**, 16,737–16,754.
- Jacob D. J., Logan J. A., Gardner G. M., Yevich R. M., Spivakovsky C. M. and Wofsy S. C. (1993a) Factors regulating ozone over the United States and its export to the global atmosphere. *J. geophys. Res.* **98**, 14,817–14,826.

- Jacob D. J., Logan J. A., Yevich R. M., Gardner G. M., Spivakovsky C. M., Wofsy S. C., Munger J. W., Sillman S., Prather M. J., Rodgers M. O., Westberg H. and Zimmerman P. R. (1993b) Simulation of summertime ozone over North America. *J. geophys. Res.* **98**, 14,797–14,816.
- Jacobson M. Z. (1994) Developing, Coupling and Applying GATOR: a gas, aerosol, transport and radiation model to study urban and regional air pollution. Ph.D. dissertation, University of California at Los Angeles, 436.
- Jacobson M. Z. and Turco R. P. (1994) SMVGEAR: a sparse matrix, vectorized Gear code for atmospheric models. *Atmospheric Environment* **28**, 273–284.
- Kao C. Y. J., Glatzmaier G. A., Malone R. C. and Turco R. P. (1990) Global three dimensional simulations of ozone depletion under postwar conditions. *J. geophys. Res.* **95**, 22,495–22,512.
- Kinnison D., Johnston H. and Wuebbles D. J. (1989) Sensitivity study of global ozone to  $\text{NO}_x$  emissions from aircraft. In *Ozone in the Atmosphere* (edited by R. D. Bojkov and Fabian P.), pp. 289–294. A. Deepak, Hampton, Virginia.
- Kirchhoff V. W. J. H., da Silva I. M. O. and Browell E. V. (1990) Ozone measurements in Amazonia: dry season versus wet season. *J. geophys. Res.* **95**, 16,913–16,926.
- Lelieveld J. and Crutzen P. J. (1994) Role of deep cloud convection in the ozone budget of the troposphere. *Science* **264**, 1759–1761.
- Levy II J., Mahlman J. D., Moxim W. J. and Liu S. C. (1985) Tropospheric ozone: the role of transport. *J. geophys. Res.* **90**, 3753–3772.
- Lin X., Trainer M. and Liu S. C. (1988) On the nonlinearity of the tropospheric ozone production. *J. geophys. Res.* **93**, 15,879–15,888.
- Liu S. C., Trainer M., Fehsenfeld F. C., Parrish D. D., Williams E. J., Fahey D. W., Hübler G. and Murphy P. C. (1987) Ozone production in the rural troposphere and the implications for regional and global ozone distributions. *J. geophys. Res.* **92**, 4191–4207.
- Logan J. A. (1983) Nitrogen oxides in the troposphere: global and regional budgets. *J. geophys. Res.* **88**, 10,785–10,807.
- Logan J. A. and Kirchhoff V. W. J. H. (1986) Seasonal variations of tropospheric ozone at Natal, Brazil. *J. geophys. Res.* **91**, 7875–7881.
- Luther F. M. and Gelinas R. J. (1976) Effect of molecular multiple scattering and surface albedo on atmospheric photodissociation rates. *J. geophys. Res.* **81**, 1125–1132.
- Luther F. M. and Wuebbles D. J. (1976) Photodissociation rate calculations. UCRL-78911 Lawrence Livermore Laboratory.
- Madronich S. (1987) Photodissociation in the atmosphere 1. actinic flux and the effects of ground reflections and clouds. *J. geophys. Res.* **92**, 9740–9752.
- McElroy M. B. and Hunten D. M. (1966) A method of estimating the earth albedo for dayglow measurements. *J. geophys. Res.* **71**, 3635–3638.
- McKeen S. A., Hsie E.-Y. and Liu S. C. (1991a) A study of the dependence of rural ozone on ozone precursors in the eastern United States. *J. geophys. Res.* **96**, 15,377–15,394.
- McKeen S. A., Hsie E.-Y., Trainer M., Tallamraju R. and Liu S. C. (1991b) A regional model study of the ozone budget in the eastern United States. *J. geophys. Res.* **96**, 10,089–10,845.
- Milford J. B., Russell A. G. and McRae G. J. (1989) A new approach to photochemical pollution control: implications of spatial patterns in pollutant responses to reductions in nitrogen oxides and reactive organic gas emissions. *Envir. Sci. Technol.* **23**, 1290–1301.
- Molion L. C. B. (1987) On the dynamic climatology of Amazon Basin and associated rainproducing mechanisms. In *The Geophysiology of Amazonia: Vegetation and Climate Interactions* (edited by Dickinson R. E.), pp. 391–408. Wiley, New York.
- Nicolet M., Meier R. R. and Anderson D. E. (1982) Radiation field in the troposphere and stratosphere-II. numerical analysis. *Planet Space Sci.* **30**, 935–983.
- Nimer E. (1979) *Climatologia do Brasil*. Instituto Brasileiro de Geografia, Rio de Janeiro.
- Oak R. R. (1986) Proceedings of the Technical Conference on Urban Climatology and its Applications with Special regard to Tropical Areas, WMO Report 752, World Climate Program, Geneva.
- Odman M. T., Kumar N. and Russell A. G. (1992) A comparison of fast chemical kinetic solvers for air quality modeling. *Atmospheric Environment* **26A**, 1783–1789.
- Orsini C. Q., Netto P. A. and Tabacniks M. H. (1982) Preliminary data on atmospheric aerosol of the Amazon basin. *Atmospheric Environment* **16**, 2177–2181.
- Paegle J. (1987) Interaction between convective and large scale motions over Amazonia. In *The Geophysiology of Amazonia: Vegetation and Climate Interactions* (edited by Dickinson R. E.), pp. 347–390. Wiley, New York.
- Pasquill F. (1971) Atmospheric diffusion of pollution. *Q. Jl. R. Met. Soc.* **97**, 369–395.
- Pasquill F. (1974) *Atmospheric Diffusion*. Wiley, New York.
- Paulson S. E. and Seinfeld J. H. (1992) Development and evaluation of a photooxidation mechanism for isoprene. *J. geophys. Res.* **97**, 20,703–20,715.
- Penner J. E., Atherton C. S., Dignon J., Ghan S. J. and Walton J. J. (1991) Tropospheric nitrogen: a three-dimensional study of sources, distributions and deposition. *J. geophys. Res.* **96**, 959–990.
- Pickering K. E., Luke W. and Dickerson R. R. (1989) Clear-sky profiles of trace gases as influenced by upstream convective activity. *J. geophys. Res.* **94**, 14,879–14,892.
- Pickering K. E., Thompson A. M., Dickerson R. R., Luke W. T., McNamara D. P., Greenberg J. P. and Zimmerman P. R. (1990) Model calculations of tropospheric ozone production potential following observed convective events. *J. geophys. Res.* **95**, 14,049–14,062.
- Pickering K. E., Thompson A. M., Scala J. R., Tao W. K., Dickerson R. R., Simpson J. and Garstang M. (1991) Photochemical ozone production in tropical squall line convection during NASA global tropospheric experiment/Amazon boundary layer experiment 2A. *J. geophys. Res.* **96**, 3099–3114.
- Pickering K. E., Thompson A. M., Scala J. R., Tao W. K. and Simpson J. (1992a) Ozone production potential following convective redistribution of biomass burning emissions. *J. Atmos. Chem.* **14**, 297–313.
- Pickering K. E., Thompson A. M., Scala J. R., Tao W. K., Dickerson R. R. and Simpson J. (1992b) Free tropospheric ozone production following entrainment of urban plumes into deep convection. *J. geophys. Res.* **97**, 17,985–18,000.
- Pickering K. E., Scala J. R., Thompson A. M., Tao W. K. and Simpson J. (1992c) A regional estimate of convective transport of CO from biomass burning. *Geophys. Res. Lett.* **19**, 289–292.
- Pickering K. E., Thompson A. M., Tao W. K. and Kucsera T. L. (1993) Upper tropospheric ozone production following mesoscale convection during STEP/EMEX. *J. geophys. Res.* **98**, 8737–8749.
- Pielke R. A. (1984) *Mesoscale Meteorological Modeling*. Academic Press, New York.
- Pielke R. A., Cotton W. R., Walko R. L., Tremback C. J., Lyons W. A., Grasso L. D., Nicholls M. E., Moran M. D., Wesley D. A., Lee T. J. and Copeland J. H. (1992) A comprehensive meteorological modeling system—RAMS. *Meteor. Atmos. Phys.* **49**, 69–91.
- Ramanathan V., Callis L., Cess R., Hansen J., Isaksen I. S. A., Kuhn W., Laci A., Luther F., Mahlman J., Reck R. and Schlesinger M. (1987) Climate chemical interactions and effects of changing atmospheric trace gases. *Rev. Geophys.* **25**, 1441–1482.

- Ratisbona L. (1976) The climate of Brazil. In *Climates of Central and South America* (edited by Schwerdtfeger W.). Elsevier, New York.
- Riehl H. (1950) On the role of the tropics in the general circulation of the atmosphere. *Tellus* **1950**, 1–17.
- Riehl H. and Malkus J. S. (1958) On the heat balance in the equatorial trough zone. *Geophysica* **6**, 503–538.
- Riehl H. and Simpson J. (1979) The heat balance of the equatorial trough zone revisited. *Contr. Atmos. Phys.* **52**, 287–305.
- Ruiz-Suarez J. C., Ruiz-Suarez J. G., Gay C., Castro T., Montero M., Eidels-Dubovoi S. and Muhlia A. (1991) Photolytic rates for NO<sub>2</sub>, O<sub>3</sub> and HCHO in the atmosphere of Mexico City. *Atmospheric Environment* **27A**, 427–430.
- Scala J., Garstand M., Tao W. K., Pickering K. E., Thompson A. M., Simpson J., Kirchoff V. W. J., Browell E. V., Sachse G. W., Torres A. L., Gregory G. L., Rasmussen R. A. and Khalil A. K. (1990) Cloud draft structure and trace gas transport. *J. geophys. Res.* **95**, 17,015–17,030.
- Seinfeld J. H. (1986) *Air Pollution*. Wiley, New York.
- Shen M., Turco R. P. and Paulson S. E. (1996) Role of isoprene in tropospheric photochemistry and ozone production. *J. geophys. Res.* (submitted).
- Shukla J. (1987) General circulation modeling and the tropics. In *The Geophysiology of Amazonia: Vegetation and Climate Interactions* (edited by Dickinson R. E.), pp. 409–462. Wiley, New York.
- Sillman S., Logan J. A. and Wofsy S. C. (1990a) A regional scale model for ozone in the United States with subgrid representation of urban and power plant plumes. *J. geophys. Res.* **95**, 5731–5748.
- Sillman S., Logan J. A. and Wofsy S. C. (1990b) The sensitivity of ozone to the nitrogen oxides and hydrocarbons in several regional ozone episodes. *J. geophys. Res.* **95**, 1837–1851.
- Simoneit B. R. T., Cardoso J. N. and Robinson N. (1990) An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. *Chemosphere* **21**, 1285–1297.
- Singh H. B. and Zimmerman P. (1992) Atmospheric distribution and sources of non-methane hydrocarbons. In *Gaseous Pollutants: Characterization and Cycling* (edited by Nriagu J. O.). Wiley, New York.
- Thompson A. M. (1984) The effect of clouds on photolysis rates and ozone formation in the unpolluted troposphere. *J. geophys. Res.* **89**, 1341–1349.
- Thompson A. M. (1992) The oxidizing capacity of the earth's atmosphere: probable past and future changes. *Science* **256**, 1157–1165.
- Trainer M., Hsie E. Y., McKeen S. A., Tallamraju R., Parrish D. D., Fehsenfeld F. C. and Liu S. C. (1987) Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site. *J. geophys. Res.* **92**, 11,879–11,894.
- Trier A. (1993) First Ibero-American conference on the atmospheric environment, CIAMAA91/IACAE91, Santiago De Chile 7–11 January 1991; an overview. *Atmospheric Environment* **27A**, 291–292.
- Turco R. P. (1985) The photochemistry of the stratosphere. In *The Photochemistry of Atmospheres* (edited by Levine J. S.). Academic Press, New York.
- Warren S. G., Hahn C. J., London J., Chervin R. M. and Jenne R. L. (1986) Global distribution of total cloud cover and cloud type amounts over land. NCAR/TN-273 + STR, National Center for Atmospheric Research, Boulder, Colorado.
- Whitten G. Z., Hogo H. and Killus J. P. (1980) The carbon bond mechanism: a condensed kinetic mechanism for photochemical smog. *Envir. Sci. Technol.* **14**, 690–700.
- Zimmerman P. R., Greenberg J. P. and Westberg C. E. (1988) Measurements of atmospheric hydrocarbons and biogenic emission fluxes in the Amazon boundary layer. *J. geophys. Res.* **93**, 1407–1416.