

# Global simulation of tropospheric O<sub>3</sub>-NO<sub>x</sub>-hydrocarbon chemistry

## 1. Model formulation

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**Abstract.** We describe a global three-dimensional model for tropospheric O<sub>3</sub>-NO<sub>x</sub>-hydrocarbon chemistry with synoptic-scale resolution. A suite of 15 chemical tracers, including O<sub>3</sub>, NO<sub>x</sub>, PAN, HNO<sub>3</sub>, CO, H<sub>2</sub>O<sub>2</sub>, and various hydrocarbons, is simulated in the model. For computational expediency, chemical production and loss of tracers are parameterized as polynomial functions to fit the results of a detailed O<sub>3</sub>-NO<sub>x</sub>-hydrocarbon mechanism. The model includes state-of-the-art inventories of anthropogenic emissions and process-based formulations of natural emissions and deposition that are tied to the model meteorology. Improvements are made to existing schemes for computing biogenic emissions of isoprene and NO. Our best estimates of global emissions include among others 42 Tg N yr<sup>-1</sup> for NO<sub>x</sub> (21 Tg N yr<sup>-1</sup> from fossil fuel combustion, 12 Tg N yr<sup>-1</sup> from biomass burning, 6 Tg N yr<sup>-1</sup> from soils, and 3 Tg N yr<sup>-1</sup> from lightning), and 37 Tg C yr<sup>-1</sup> for acetone (1 Tg C yr<sup>-1</sup> from industry, 9 Tg C yr<sup>-1</sup> from biomass burning, 15 Tg C yr<sup>-1</sup> from vegetation, and 12 Tg C yr<sup>-1</sup> from oxidation of propane and higher alkanes).

## 1. Introduction

Ozone in the troposphere is supplied by transport from the stratosphere, and is produced within the troposphere during the oxidation of hydrocarbons and CO catalyzed by NO<sub>x</sub> (NO + NO<sub>2</sub>) and HO<sub>x</sub> (OH + peroxy radicals). It is removed by photolysis, chemical reactions, and deposition to the surface. Increasing anthropogenic emissions of NO<sub>x</sub>, hydrocarbons, and CO over the past century have caused appreciable increases of tropospheric ozone over industrial continents and probably over the globe [Crutzen and Zimmermann, 1991; Martinerie et al., 1995; World Meteorological Organization (WMO), 1995]. This increase has important implications for regional air quality, global atmospheric chemistry, and climate change [Thompson et al., 1990; WMO, 1995].

Our understanding of the factors controlling tropospheric ozone is still limited. The difficulty is due in part to the complexity of the chemistry and in part to the wide range in the lifetimes for ozone and its precursors (hours to weeks). Global models of tropospheric ozone need to resolve the coupling between chemistry and transport on synoptic scales [Stordal et al., 1995]. The first global three-dimensional simulation of tropospheric ozone was presented by Levy et al. [1985]; it included transport from the stratosphere and deposition at the surface but no chemistry in the troposphere. Crutzen and Zimmermann [1991] and Roelofs and Lelieveld [1995] reported global ozone simulations including NO<sub>x</sub>-CO-CH<sub>4</sub> chemistry in the troposphere but not accounting for the more complicated

nonmethane hydrocarbon (NMHC) chemistry. Müller and Brasseur [1995] included NMHCs in a global ozone model using monthly mean winds.

Our model attempts to improve on earlier efforts by (1) incorporating a detailed but computationally expedient representation of tropospheric chemistry including NMHCs, (2) resolving synoptic-scale transport using meteorological data from a general circulation model (GCM), and (3) including process-based descriptions of emissions and deposition formulated to be consistent with the model meteorology. This paper describes the model. A detailed evaluation of model results with observations of ozone and its precursors is presented by Wang et al. [this issue(a)], and the factors controlling tropospheric ozone are investigated using this model [Wang et al., this issue(b)].

## 2. Model Framework

The model utilizes meteorological data archived from a GCM developed at the Goddard Institute for Space Studies (GISS) [Hansen et al., 1983]. It has a resolution of 4° latitude by 5° longitude, with seven vertical layers in a  $\sigma$  coordinate extending from the surface to 150 mbar. The seven layers are centered approximately at 960, 895, 790, 635, 470, 320, and 200 mbar. The GCM contains two additional vertical layers above 150 mbar, which we use only for the specification of upper boundary flux conditions as discussed in section 5. The GCM data archive includes 4-hour averages of winds, total cloud optical depths, precipitation at the surface, mixed layer heights, and column frequencies of wet and dry convection, and 5-day averages of temperature, humidity, and vertical distributions of cloud optical depth, precipitation, and convective mass fluxes. Cloud reflectivities at 800, 500, and 200 mbar are derived from the vertical distribution of cloud optical depth following Spivakovsky et al. [1990a]. A more detailed description of the meteorological variables can be found in the work

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of Prather *et al.* [1987], Jacob *et al.* [1993], and Chin *et al.* [1996]. The model has been used previously to simulate chemical tracers of atmospheric transport [Prather *et al.*, 1987; Jacob *et al.*, 1987; Jacob and Prather, 1990; Balkanski and Jacob, 1990; Balkanski *et al.*, 1992, 1993; Koch *et al.*, 1996], tropospheric OH [Spivakovsky *et al.*, 1990a], sulfate [Chin *et al.*, 1996], and ozone over North America [Jacob *et al.*, 1993; Chin *et al.*, 1994; Horowitz *et al.*, 1998; Liang *et al.*, 1998].

For this study, we used observed climatology to apply some corrections to the GCM meteorological fields. Monthly scaling factors were applied to the specific humidity in each grid box to match monthly mean data for 1986–1989 from the European Center for Medium-Range Weather Forecasts (ECMWF) model with a resolution of 1.5° longitude x 1.5° latitude x 14 vertical layers [Tränberth, 1992]. Surface air temperature and precipitation over land were scaled similarly to match the monthly 0.5°x0.5° climatology by Leemans and Cramer [1992]. Since diel temperature variability is lacking in our GCM data archive, we assumed that surface air temperature over land varies as a sinusoidal function that peaks in midafternoon with a diel amplitude for clear sky of 2 K in the tropics and 5 K in the extratropics [cf. Conway and Liston, 1990], decreasing linearly with overhead cloud cover. The daytime mixing heights over the tropical continents in the GCM are too low [Chin *et al.*, 1996], and we extend them to 2.5 km in daytime [Browell *et al.*, 1988; Jacob and Wofsy, 1988].

We transport 15 chemical tracers in the model to describe O<sub>3</sub>-NO<sub>x</sub>-CO-hydrocarbon chemistry (Table 1). Transporting O<sub>x</sub> and NO<sub>x</sub> as chemical families reduces the need for tracking many rapidly interchanging gases [Jacob *et al.*, 1989]. Jacob *et al.* [1993] included N<sub>2</sub>O<sub>5</sub> and HNO<sub>4</sub> as part of the NO<sub>x</sub> family in their simulation of summertime ozone over North America; separate transport of N<sub>2</sub>O<sub>5</sub> and HNO<sub>4</sub> is necessary here owing to their long lifetimes at low temperatures in winter and in the upper troposphere. Alkanes (≥C<sub>4</sub>) and alkenes (≥C<sub>3</sub>) are grouped as two lumped families ALK4 and ALKE, taking

**Table 1.** Chemical Tracers in the Model

Tracer	Composition
O <sub>x</sub>	O <sub>3</sub> + O + NO <sub>2</sub> + HNO <sub>4</sub> + 2 x NO <sub>3</sub> + 3 x N <sub>2</sub> O <sub>5</sub> + PANs
NO <sub>x</sub>	NO + NO <sub>2</sub> + NO <sub>3</sub> + HNO <sub>2</sub>
N <sub>2</sub> O <sub>5</sub>	
HNO <sub>4</sub>	
PANs	peroxyacetyl nitrates
Butylnitrate	lumped alkyl nitrates <sup>a</sup>
HNO <sub>3</sub>	
CO	
Ethane	
ALK4	lumped ≥C <sub>4</sub> alkanes <sup>a</sup>
ALKE	lumped ≥C <sub>3</sub> alkenes <sup>a</sup>
Isoprene	
Acetone	
KET	lumped ≥C <sub>4</sub> ketones <sup>a</sup>
H <sub>2</sub> O <sub>2</sub>	

Propane is included in the model as an equivalent emission of acetone with a yield of 80% [Singh *et al.*, 1994]. Methane concentration is specified as 1.7 ppmv.

<sup>a</sup>Lumping of individual compounds is done on a per carbon basis.

advantage of the similar O<sub>x</sub> and HO<sub>x</sub> yields of different NMHCs on a per carbon basis [Jacob *et al.*, 1989]. The chemistry of the ALK4 tracer is assumed to be that of a butane-pentane mixture [Lurmann *et al.*, 1986], while the chemistry of the ALKE tracer is assumed to be that of propene. Isoprene emitted by vegetation is transported separately from the other alkenes.

Ethane is treated as a separate tracer because of its importance for peroxyacetyl nitrate (PAN) formation in the remote atmosphere [Kanakidou *et al.*, 1991]. Propane emission is included in the model as an equivalent source of acetone with a yield of 80% [Singh *et al.*, 1994]. Acetone and higher ketones (lumped as KET) are included as two additional tracers because of their importance for PAN and HO<sub>x</sub> production in the upper troposphere [Singh *et al.*, 1995]. The chemistry of KET is assumed to be that of methylethyl ketone. A constant methane concentration is specified at 1.7 parts per million by volume (ppmv) throughout the model domain. Aldehydes and other short-lived species not included in Table 1 are assumed to be in chemical steady state during the day and either in steady state or inert (depending on the species) at night. Ethylene, terpenes, and aromatic compounds are neglected; sensitivity simulations indicate that they play little role in global or regional atmospheric chemistry.

The model solves the three-dimensional continuity equation for 15 tracers (Table 1) using operator splitting between transport and chemistry over 4-hour time steps. The chemical operator applied to tracer *i* (*i* = 1, ..., *n*; *n* = 15) includes contributions from chemical reactions, emissions, and dry deposition:

$$\frac{\partial m_i}{\partial t} = E_i + P_i \{m_j\} - (k_{d,i} + k_{c,i} \{m_j\}) m_i \quad (1)$$

where *m<sub>i</sub>* is the concentration of species *i*, *E<sub>i</sub>* is the emission rate, *P<sub>i</sub>* is the chemical production rate, and *k<sub>d,i</sub>* and *k<sub>c,i</sub>* are the first-order loss rate constants for dry deposition and chemical loss, respectively. Values for *P<sub>i</sub>* and *k<sub>c,i</sub>* are obtained by solution to the chemical mechanism described in section 3, and are fitted for rapid computation to polynomial functions of the tracer concentrations {*m<sub>j</sub>*} [*j* = 1, ..., *n*] and of meteorological variables (see the appendix). The system of *n* coupled differential equations (1) is integrated over the 4-hour time step using a Runge-Kutta fourth-order method with 4-hour average values of *E<sub>i</sub>*, *k<sub>d,i</sub>*, and photolysis rate constants. The linear projection of equation (1) used in the standard Runge-Kutta method renders the scheme unstable for tracers with lifetimes shorter than the integration time step. In our model the projection is computed instead using the analytical (exponential decay) solution to equation (1), which ensures the stability and improves the accuracy of the integration [Elliott *et al.*, 1993]. Another difficulty arises in computing chemistry in the lower troposphere because PANs, N<sub>2</sub>O<sub>5</sub>, and HNO<sub>4</sub> may interchange rapidly with NO<sub>x</sub>; when the lifetimes of these species are shorter than 2 hours, we group them with NO<sub>x</sub>, solve equation (1) for the family, and repartition the family after integration on the basis of chemical steady state.

The removal of soluble tracers HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> by wet deposition is calculated separately from the chemical operator following the scheme of Balkanski *et al.* [1993]. This scheme includes scavenging in convective updrafts and rainout and washout by nonconvective large-scale precipitation.

### 3. Chemistry

The Harvard chemical mechanism used in the model is based on recent compilations including those of *DeMore et al.* [1994] for inorganic and methane chemistry, *Atkinson et al.* [1992] for NMHC chemistry, and *Paulson and Seinfeld* [1992] for the oxidation of isoprene. The termolecular rate constant for the OH + NO<sub>2</sub> reaction is from *Donahue et al.* [1997]. The quantum yields of O<sup>1</sup>D from ozone photolysis at 312-320 nm are from *Michelsen et al.* [1994], leading to an O<sup>1</sup>D production rate in the tropical troposphere 20-40% higher than the recommendation of *DeMore et al.* [1994]. Photolysis of acetone is computed with updated quantum yields and absorption cross sections from *McKeen et al.* [1997]. The UV radiation intensities are computed with a six-stream radiative transfer code for the Rayleigh scattering atmosphere including cloud reflection and aerosol absorption [*Logan et al.*, 1981]; the aerosol optical depth for absorption is 0.1 at 310 nm varying inversely with wavelength. Climatological ozone columns are specified as a function of latitude and month [*Spivakovsky et al.*, 1990a]. The Harvard chemical mechanism has been compared in two recent studies with other mechanisms used in atmospheric chemistry models [*Olson et al.*, 1996; *Friedl*, 1997].

Hydrolysis of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> on aerosol surfaces is computed in the model as the collision rate of N<sub>2</sub>O<sub>5</sub> with sulfate aerosol particles [*Dentener and Crutzen*, 1993] assuming a reaction probability of 0.1 [*DeMore et al.*, 1994]. Global three-dimensional distributions of monthly averaged mass concentrations of sulfate aerosols are specified from the model simulation of *Chin et al.* [1996], which used the same GCM. The aerosol surface area is estimated from the sulfate mass concentrations by assuming that particles have a dry radius of 0.1 μm and are present in the atmosphere as aqueous (NH<sub>4</sub>)HSO<sub>4</sub> solutions [*Dentener and Crutzen*, 1993]. The molar fraction of water in an aerosol depends on relative humidity following Raoult's law [*Seinfeld*, 1986]. Aerosols are assumed to remain in a metastable liquid state below the deliquescence point of (NH<sub>4</sub>)HSO<sub>4</sub> [*Tang and Munkelwitz*, 1994]. Aqueous phase HO<sub>x</sub> chemistry in clouds is not included in the model since its effects on O<sub>x</sub> and NO<sub>x</sub> appear to be insignificant [*Liang and Jacob*, 1997].

### 4. Emissions

The model includes emissions from fuel combustion and industrial activities (NO<sub>x</sub>, CO, NMHCs), biomass burning (NO<sub>x</sub>, CO, NMHCs), vegetation (NMHCs), soils (NO<sub>x</sub>), and lightning (NO<sub>x</sub>). Table 2 gives the global emission inventories for the different tracers, and Figure 1 shows the distributions of NO<sub>x</sub> emissions from fossil fuel combustion, biomass burning, lightning, and soils.

#### 4.1. Fuel Combustion and Industrial Activities

A global NO<sub>x</sub> emission inventory (21 Tg N yr<sup>-1</sup>) from fossil fuel combustion has been compiled by the Global Emission Inventory Activity [*Benkovitz et al.*, 1996] with a 1°x1° resolution. We use the companion inventory compiled by M. T. Scholtz, K. A. Davidson, E. C. Voldner, and A. Li that gives inventories for four seasons (C. M. Benkovitz, personal communication, 1997) (Figure 1). We distribute these NO<sub>x</sub> emissions evenly in the model mixed layer, with 10% as NO<sub>2</sub>

**Table 2.** Emission Inventories in the Model

	Global	Northern Hemisphere	Southern Hemisphere
<b>NO<sub>x</sub></b>			
Fossil fuel combustion	21	20	1.2
Biomass burning	11.6	6.5	5.1
Soil	6.0	4.2	1.8
Lightning	3.0	1.7	1.3
Aircraft	0.51	0.47	0.04
Stratosphere <sup>a</sup>	0.10	0.06	0.04
Total	42	33	9.4
<b>CO</b>			
Fossil and wood fuel combustion, industry	520	480	40
Biomass burning	520	290	230
CH <sub>4</sub> oxidation <sup>b</sup>	800	460	340
NMHC oxidation <sup>b</sup>	290	170	120
Total	2130	1400	730
<b>Ethane</b>			
Industry	6.3	5.7	0.6
Biomass burning	2.5	1.4	1.1
Total	8.8	7.1	1.7
<b>Propane<sup>c</sup></b>			
Industry	6.8	6.1	0.7
Biomass burning	1.0	0.92	0.08
Total	7.8	7.0	0.8
<b>≥C<sub>4</sub> alkanes</b>			
Industry	30	27	3
<b>≥C<sub>3</sub> alkenes</b>			
Industry	10.4	9	1.4
Biomass burning <sup>d</sup>	12.6	7	5.6
Total	23	16	7
<b>Isoprene</b>			
Vegetation	597	297	300
<b>Acetone</b>			
Industry	1.0	0.9	0.1
Biomass burning	8.9	5.0	3.9
Vegetation	15	7.5	7.5
Oxidation of propane	6.2	5.3	0.9
Oxidation of higher alkanes <sup>b</sup>	6.2	5.5	0.7
Total	37	24	13

Units are Tg N yr<sup>-1</sup> for NO<sub>x</sub>, Tg CO yr<sup>-1</sup> for CO, and Tg C yr<sup>-1</sup> for NMHCs.

<sup>a</sup>Downward transport of NO<sub>x</sub> across the tropopause. This transport also supplies 0.38 Tg N yr<sup>-1</sup> of HNO<sub>3</sub> globally.

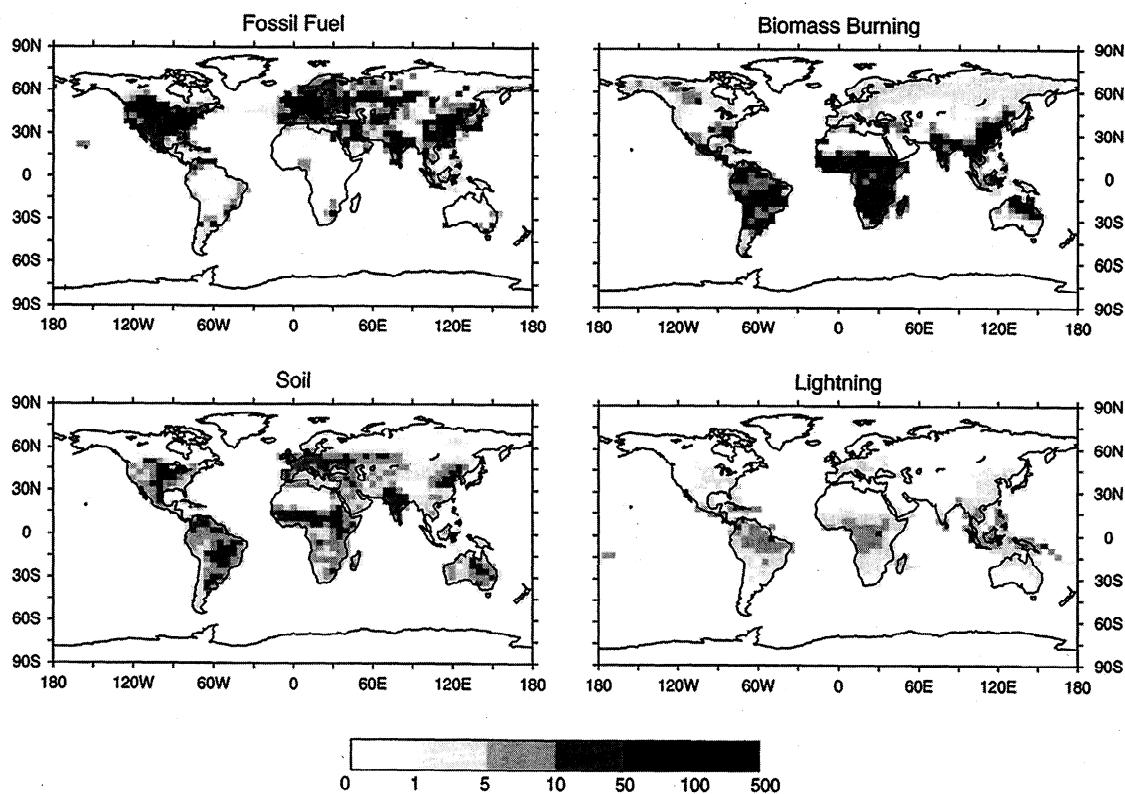
<sup>b</sup>Computed within the model.

<sup>c</sup>Included in the model as a direct emission of acetone; the yield of acetone from oxidation of propane is specified as 80% [*Singh et al.*, 1994].

<sup>d</sup>Including 6 Tg C yr<sup>-1</sup> of ≥C<sub>2</sub> aldehydes.

[*Environmental Protection Agency (EPA)*, 1989]. For NO emissions from subsonic aircraft, we adopted the 1992 monthly mean emission inventory compiled by *Baughcum et al.* [1996] and *Metwally* [1995]; the inventory has a resolution of 1°x1°x1 km, and the global source is 0.51 Tg N yr<sup>-1</sup>.

Our global CO emission inventory includes 390 Tg CO yr<sup>-1</sup> from fossil fuel combustion and industrial activities and 130 Tg CO yr<sup>-1</sup> from wood fuel burning. The inventory has a resolution of 1°x1° and is seasonal. Statistics for fossil fuel combustion and industrial processes were taken from an electronic database compiled by the United Nations (U.N.), which includes data for each fuel (e.g., coal, lignite, gasoline, diesel, residual fuel oil) in 32 consumption categories (e.g., power



**Figure 1.** Annual mean emissions of NO<sub>x</sub> ( $10^9$  atoms N cm<sup>-2</sup> s<sup>-1</sup>) from fossil fuel combustion, biomass burning, soils, and lightning.

plants, road transportation, household). Data for countries not included in the U.N. database were supplemented with fuel statistics from the Organization for Economic Development and Cooperation if available; regional averages for fuel consumption patterns were used otherwise. Emission factors (the amount of CO produced per unit of fuel consumed) were taken from compendium AP-42 of the *Environmental Protection Agency* [1985, 1993] and from the European CORINAIR inventory [Samaras and Zierock, 1989]. Estimates for consumption of biomass fuels (wood, charcoal, dung, and agricultural residues) were based on published literature and on consultations with experts in energy consumption in developing countries. Emissions were derived by country and were spatially disaggregated using a  $1^\circ \times 1^\circ$  population map [Benkovitz et al., 1996]. Exceptions are over the United States and Canada where recent estimates for national emissions of CO for 1985 [EPA, 1994] were scaled to the spatial distribution of CO emissions for 1985 from the National Acid Precipitation Assessment Program (NAPAP) [EPA, 1989]. Detailed descriptions of the inventory will be published separately.

We adopted the country-by-country inventory of Piccot et al. [1992] for emissions of paraffins ( $45 \text{ Tg C yr}^{-1}$ ) and olefins ( $18 \text{ Tg C yr}^{-1}$ ) from fossil fuel combustion and industrial activities. The emissions within each country were distributed on the basis of population density using a  $1^\circ \times 1^\circ$  population map [Benkovitz et al., 1996]. The Piccot et al. [1992] inventory gives no information on the speciation of paraffins and olefins; a speciation of emissions for the United States is, however, available from NAPAP [Middleton et al., 1990]. The NAPAP data apportion total paraffin emissions over the United States on a per carbon basis as 6% ethane, 2% propane, 20% butanes,

68% ( $\geq C_5$ ) alkanes, 2% acetone, and 2% higher ketones; olefin emissions are apportioned as 42% ethylene (not accounted for in the model) and 58% higher alkenes. There is evidence that the NAPAP inventory underestimates considerably the emissions of ethane and propane [Rudolph, 1995; Goldan et al., 1995a]. Fresh pollution plumes sampled at Harvard Forest, Massachusetts, have typical ethane : propane : butanes (molar) concentration ratios of 1.4:1:1 in winter [Goldstein et al., 1995], and winter urban air in Colorado has a propane to butanes molar ratio of about 1:1 [Goldan et al., 1995a]. On the basis of the Harvard Forest data, we modify the NAPAP apportionment of paraffins on a per carbon basis to be 14% ethane, 15% propane, 66.5% ( $\geq C_4$ ) alkanes, 2.3% acetone, and 2.2% higher ketones. Assuming the NMHC speciation for the United States to be globally representative, we deduce global emission rates of  $6.3 \text{ Tg C yr}^{-1}$  of ethane,  $6.8 \text{ Tg C yr}^{-1}$  of propane,  $30 \text{ Tg C yr}^{-1}$  of ( $\geq C_4$ ) alkanes,  $1.0 \text{ Tg C yr}^{-1}$  of acetone,  $1.0 \text{ Tg C yr}^{-1}$  of higher ketones, and  $10.4 \text{ Tg C yr}^{-1}$  of ( $\geq C_3$ ) alkenes.

#### 4.2. Biomass Burning

Our global biomass burning emission inventory for CO has a  $1^\circ \times 1^\circ$  spatial resolution and monthly temporal resolution. The global source totals  $510 \text{ Tg CO yr}^{-1}$ . The inventory incorporates estimates of forest wildfires (primarily at middle and high latitudes), tropical deforestation, slash/burn agriculture, savanna burning, and burning of agricultural waste. The methodology used is similar to that described by Hao et al. [1990] for tropical deforestation, Logan et al. [1981] for slash/burn agriculture, and Menaut et al. [1991] for savanna burning. Biomass burning, usually based on national information, was spa-

tially disaggregated within a country using the land use map of Matthews [1983]. The timing of biomass fires relies on wild-fire statistics at middle and high latitudes, on satellite monitoring of fires in Brazil (available electronically from INPE, Brazil) and Africa [e.g., Cahoon *et al.*, 1992], and on monthly rainfall data, with the fires occurring toward the end of the dry season if other information is lacking. A complete description of the biomass burning inventory will be in another publication currently in preparation by J. A. Logan.

Biomass burning emissions for other tracers are estimated by applying mean observed tracer emission ratios relative to CO. We use a global average NO<sub>x</sub> to CO molar emission ratio of 4.5% estimated by Andreae *et al.* [1996], which yields a global biomass burning source of 11.6 Tg N yr<sup>-1</sup> (Figure 1). This source is comparable to the previous estimates of 12 Tg N yr<sup>-1</sup> by Logan [1983] and 12.5 Tg N yr<sup>-1</sup> by Dignon and Penner [1991] but 36% higher than the estimate of 8.5 Tg N yr<sup>-1</sup> by Levy *et al.* [1991], who appear to have assumed a lower NO<sub>x</sub> to CO emission ratio.

Emission ratios of hydrocarbons to CO have been reported by a number of authors. We adopted average molar ratios of 0.55% for ethane to CO and 0.15% for propane to CO on the basis of measurements of fire plumes in North America [Laursen *et al.*, 1992; Nance *et al.*, 1993]. These ratios are in the range of values reported by Lobert *et al.* [1991] and Hurst *et al.* [1994]. The ethane to CO emission ratio is higher than the 0.4% measured by Bonsang *et al.* [1995] over the Ivory Coast. These references also indicate low emissions of (≥ C<sub>4</sub>) alkanes from fires. We adopted a (≥ C<sub>3</sub>) alkenes to CO molar ratio of 0.79% based on a propene to CO molar ratio of 0.49% [Lobert *et al.*, 1991; Laursen *et al.*, 1992; Nance *et al.*, 1993; Hurst *et al.*, 1994] and a butene to CO emission ratio of 0.3% [Lobert *et al.*, 1991]. Molar emission ratios of 1.3% for acetone to CO, 3.1% for (≥ C<sub>4</sub>) ketones to CO, and 1.1% for C<sub>2-3</sub> aldehydes to CO were taken from Mano [1995] as cited by Andreae *et al.* [1996]. We choose to emit the C<sub>2-3</sub> aldehydes as (≥ C<sub>3</sub>) alkenes on a per carbon basis since they have similar lifetimes and PAN yields [Atkinson *et al.*, 1992]. In summary, the hydrocarbon emissions from biomass burning in our model are 2.4 Tg C yr<sup>-1</sup> of ethane, 1.0 Tg C yr<sup>-1</sup> of propane, 8.9 Tg C yr<sup>-1</sup> of acetone, 27 Tg C yr<sup>-1</sup> of higher ketones, and 12 Tg yr<sup>-1</sup> of (≥ C<sub>3</sub>) alkenes. The large source of ketones is based on a single study and hence is subject to large uncertainty.

### 4.3. Vegetation

Large amounts of hydrocarbons are emitted from the terrestrial biosphere. Biogenic emissions from the oceans are estimated to be 2 orders of magnitude smaller [Guenther *et al.*, 1995]. Isoprene is the most important biogenic NMHC for O<sub>3</sub> production; terpenes are comparatively unimportant [Fehsenfeld *et al.*, 1992; Cantrell *et al.*, 1995]. We include in our model sources of isoprene and acetone from terrestrial vegetation.

We formulate isoprene emissions as a function of vegetation type, leaf area index (LAI, defined as square cm leaf area per square cm of surface), temperature, and solar radiation, using an algorithm developed by Guenther *et al.* [1995] with a few modifications described below. The global surface-type map is from Oslen [1992]; it has a spatial resolution of 0.5°x0.5° and distinguishes among 56 ecosystems. Guenther *et al.* [1995] assigned to each of the 56 ecosystems a base isoprene emission flux per unit leaf area (φ<sub>0</sub>) at 30°C and for a

photosynthetically active radiation (PAR) flux of 1000 μmol m<sup>-2</sup> s<sup>-1</sup>. We adopted their φ<sub>0</sub> values. The integrated isoprene emission flux Φ from a vegetation canopy is given by

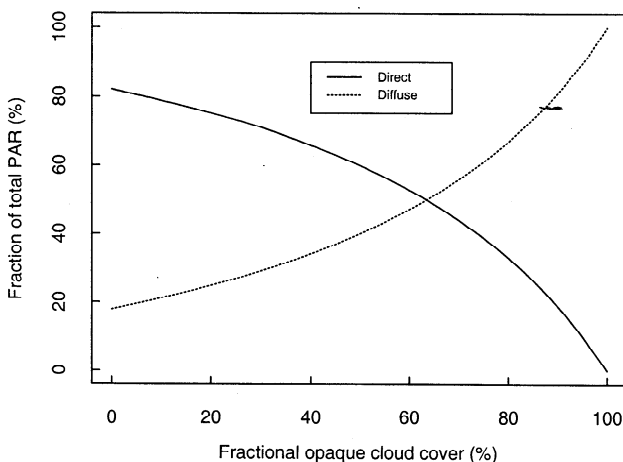
$$\Phi = \phi_0 \cdot \text{LAI}_{\text{eff}} \cdot f(T) \quad (2)$$

$$\text{LAI}_{\text{eff}} = \int_0^{\text{LAI}} g(\text{PAR}) dL \quad (3)$$

where  $f(T)$  is a correction function for surface air temperature  $T$ ,  $g(\text{PAR})$  is a correction function for the local photosynthetically active radiation (PAR) incident on the leaf, LAI is the leaf area index of the canopy, and LAI<sub>eff</sub> is the effective leaf area index corrected for light attenuation (and hence reduced isoprene emission) inside the canopy. The functions  $f(T)$  and  $g(\text{PAR})$  are taken from Guenther *et al.* [1995].

The LAI values for each 0.5°x0.5° grid square of the Olson [1992] map are calculated monthly as a function of ecosystem type, net primary productivity (NPP), and global vegetation index (GVI). The NPP is calculated from monthly mean climatologies of surface temperature and precipitation. The computations of LAI and NPP follow the algorithms by Guenther *et al.* [1995] with two exceptions. First, we use monthly mean GVIs from the 0.5°x0.5°, 5-year EDC-NESDIS [1992] data set (Guenther *et al.* [1995] used the data for 1990 only). Second, we do not allow LAIs to exceed the mean growing season values for different ecosystems reported by Lieth [1975] and Box [1981]. The Guenther *et al.* [1995] algorithm calculates mean growing season LAIs that are much higher than those observed for certain ecosystems, for example, 11 and 6.3 for tropical rain forest and savanna, respectively; observed values reported by Lieth [1975] and Box [1981] for these ecosystems are 8 and 4, respectively. Our correction to LAIs has, however, only a small effect on the isoprene emission fluxes owing to attenuation of PAR inside the optically thick canopy.

We calculate the vertical profile of PAR inside the canopy using the canopy radiation transfer model of Norman [1982], as in the work of Guenther *et al.* [1995]. The total (direct and diffusive) PAR at a canopy top is calculated on the basis of the solar zenith angle  $\theta$  and the opaque cloud fraction  $C$ . The can-

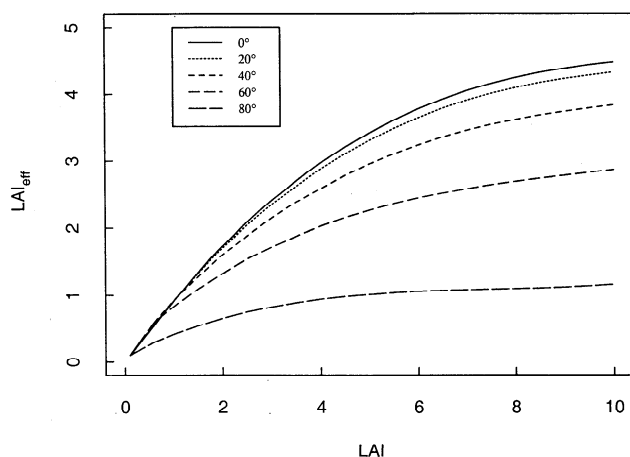


**Figure 2.** Partitioning of PAR between direct and diffuse components at the canopy top as a function of opaque cloud cover, computed using the radiative transfer model of Norton [1996] for a solar zenith angle of 30°.

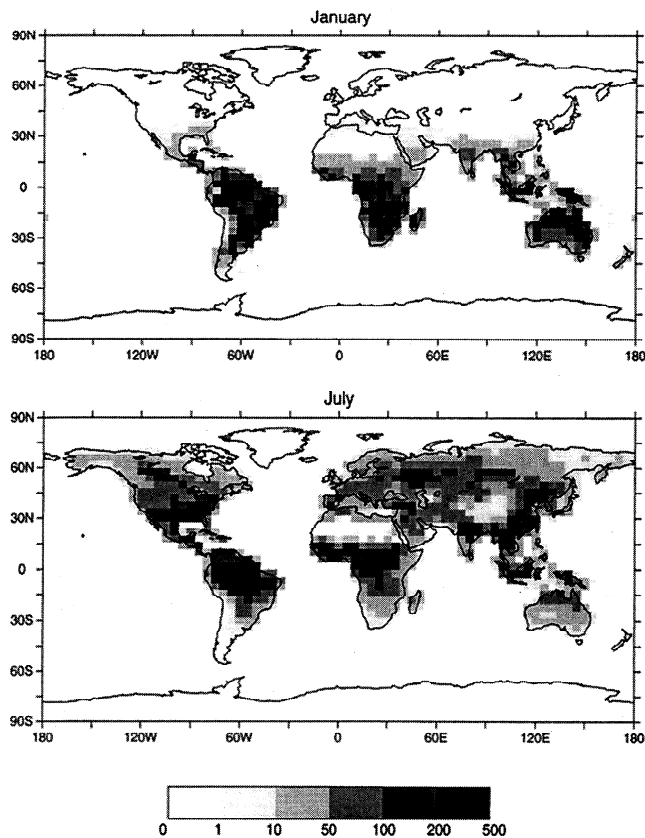
opy radiative model of *Norman* [1982] calculates attenuation rates separately for direct and diffuse PAR and partitions leaf areas into shaded and sunlit fractions depending on overhead LAI and solar zenith angle; sunlit leaves receive both direct and diffuse PAR, while shaded leaves receive diffuse PAR only. *Guenther et al.* [1995] simplified the radiative transfer calculation by resolving the canopy into less than five vertical layers, and they employed an empirical formula to account for the effects of clouds on direct and diffuse PAR at the canopy top. In our work, we solve the radiative transfer equation inside the canopy more accurately, and we calculate diffuse and direct PAR at the canopy top as a function of solar zenith angle and overhead opaque cloud cover using a one-dimensional radiative transfer model for the atmosphere [*Norton, 1996*] (Figure 2). To speed up the computation in the three-dimensional model, we parameterized the effective leaf area index  $LAI_{eff}$  (equation (3)) as a polynomial function of LAI,  $\theta$ , and C using the singular value decomposition method [*Press et al., 1992*]. Figure 3 shows the dependence of  $LAI_{eff}$  on LAI for different solar zenith angles. The leveling-off of  $LAI_{eff}$  with increasing LAI reflects the attenuation of PAR inside the canopy and the accompanying decrease of isoprene emission by leaves.

The global distribution of isoprene emissions in our model (Figure 4) agrees qualitatively with *Guenther et al.* [1995], but our total isoprene emission of 597 Tg C yr<sup>-1</sup> is 20% higher. We attribute the difference largely to the inclusion of diel temperature variations in our model (section 2), which leads to higher daytime temperatures. Changes in temperatures on synoptic time scales in the GCM also contribute to higher isoprene emission in our model. Temperature variability increases isoprene emissions because of the near-exponential dependence of emissions on temperature up to 40°C.

Acetone also has a strong biogenic source, both from direct emissions and the oxidation of short-lived natural hydrocarbons [*Singh et al., 1994; Goldan et al., 1995b*]. *Singh et al.* [1994] estimated a global acetone source of 5 to 8 Tg C yr<sup>-1</sup> from direct biogenic emission and up to 6 Tg C yr<sup>-1</sup> from oxidation of biogenic hydrocarbons. We include in our model a total (direct and secondary) biogenic source for acetone of 15 Tg C yr<sup>-1</sup> adjusted to match observed acetone concentrations



**Figure 3.** Effective leaf area index  $LAI_{eff}$  for canopy emission of isoprene (equation (3)) as a function of LAI for different solar zenith angles and for clear sky.



**Figure 4.** Monthly mean isoprene emission fluxes ( $10^{10}$  atoms C cm<sup>-2</sup> s<sup>-1</sup>) computed in the model for January and July.

[*Wang et al., this issue(a)*]. The temporal and spatial distribution of this acetone source is assumed identical to that of isoprene.

#### 4.4. Soil NO<sub>x</sub> Emissions

Nitrogen oxides are emitted by soil microbes during nitrification and denitrification processes. Following *Yienger and Levy* [1995], we compute NO emission fluxes as a function of vegetation type (from the *Olson* [1992] map), temperature, precipitation history, fertilizer usage if any, and a canopy reduction factor  $\eta$ . Parameter  $\eta$  is the fraction of soil-emitted NO<sub>x</sub> that is deposited within the canopy before it is exported to the atmosphere; it reflects the oxidation of NO to NO<sub>2</sub> in the canopy air followed by uptake of NO<sub>2</sub> by vegetation [*Jacob and Bakwin, 1991*]. *Jacob and Bakwin* [1991] estimated  $\eta = 70\%$  for the Amazon Forest based on concurrent measurements of soil emission fluxes and vertical profiles of NO and ozone concentrations inside the canopy. This result was extended by *Yienger and Levy* [1995] to other ecosystems by assuming an arbitrary function of LAI and stomatal area index (the product of LAI and the ratio of stomatal area to leaf area). We attempt here to formulate  $\eta$  on a more physical basis.

Following *Jacob and Bakwin* [1991], we express  $\eta$  as follows:

$$\eta = \frac{k_d}{k_v + k_d} \quad (4)$$

where  $k_d$  and  $k_v$  are the deposition and ventilation rate constants for NO<sub>x</sub> in the canopy air, respectively; ventilation refers

to the export of air from the canopy by turbulence. We compute  $k_d$  as

$$k_d = \frac{1}{R_c \cdot \Delta Z} \quad (5)$$

where  $R_c$  is the canopy surface resistance for deposition of NO<sub>x</sub> and  $\Delta Z$  is the canopy depth. Values of  $R_c$  are calculated in the model as part of the dry deposition algorithm described in section 6, assuming a NO<sub>2</sub> to NO<sub>x</sub> concentration ratio of 0.7 inside the canopy [Jacob and Bakwin, 1991]. We compute the canopy ventilation rate constant  $k_v$  by assuming that it is proportional to the mean wind speed  $\bar{v}$  inside the canopy:

$$k_v = \frac{\alpha \bar{v}}{\Delta Z} \quad (6)$$

where  $\alpha$  is a dimensionless coefficient. Based on the micrometeorological model calculations reported by Shaw [1982], we parameterize  $\bar{v}$  as:

$$\bar{v} = \min\left(\frac{V}{\gamma \sqrt{\text{LAI}}}, V\right) \quad (7)$$

where  $V$  is the above-canopy wind speed and  $\gamma$  is a nondimensional extinction coefficient which characterizes the rate at which wind speed decreases with depth in the canopy. Values of  $\gamma$  are 1, 2, and 4 for grass, shrub, and forest ecosystems, respectively [Shaw, 1982]. The coefficient  $\alpha$  ( $2.8 \times 10^{-2}$  and  $5.6 \times 10^{-3}$  for day and night, respectively) is adjusted to yield a canopy ventilation time of 1 hour during daytime and 5 hours at night for the Amazon Forest in April, as reported by Jacob and Bakwin [1991] (LAI = 7,  $\Delta Z$  = 30 m, and  $V$  = 3 m s<sup>-1</sup> [Fitzjarrald et al., 1990]).

We estimate in this manner a canopy reduction factor  $\eta$  = 70% for the Amazon Forest in April, as obtained by Jacob and Bakwin [1991]. However, our computed global average  $\eta$  is only 20%. Compared with the Amazon Forest, most ecosystems have smaller values of LAI and  $\gamma$ , stronger winds above the canopy, and higher canopy surface resistances for NO<sub>2</sub> deposition. Our global mean  $\eta$  is considerably less than the estimate of 50% by Yienger and Levy [1995]. Our global above-canopy emission of NO<sub>x</sub> from soils is 6 Tg N yr<sup>-1</sup> (Figure 1), only 10% higher than that of Yienger and Levy [1995], likely reflecting differences in the meteorological fields used for surface temperature and precipitation.

#### 4.5. Lightning NO<sub>x</sub>

Estimates of NO<sub>x</sub> production from high-temperature fixation of N<sub>2</sub> by lightning are highly uncertain [Lawrence et al., 1995; Price et al., 1997a, b; Bradshaw et al., 1998]. Following the scheme of Price and Rind [1992], we compute frequencies of lightning flashes in our model based on the heights of local convective cloud tops from the GISS GCM. Price and Rind [1994] showed previously that the lightning frequencies derived in this manner from the GCM are in good agreement with satellite observations. We compute the intra-cloud (IC) to cloud-ground (CG) lightning flash ratio for a given grid square:

$$\frac{\text{IC}}{\text{CG}} = 2.7 F^{0.5} \quad (8)$$

where  $F$  is lightning frequency in flashes per minute [Rutledge et al., 1992]. The resulting global mean IC/CG flash ratio in our model is 7.7. The NO<sub>x</sub> yield of a CG lightning flash is

assumed to be 3 times that of an IC lightning flash because of higher flash energy [Liaw et al., 1990, and references therein]. We assume further that the amount of NO<sub>x</sub> produced by a lightning flash is proportional to the channel length. We determine the CG lightning channel length in the model as the distance from the surface to the negative charge layer (NCL) where temperature is -10°C [Williams, 1985] and the IC channel length as the distance from the NCL to the convective cloud top. We thus obtain a global IC/CG NO<sub>x</sub> emission ratio of 3.3. The vertical distribution of the lightning NO<sub>x</sub> source is specified from cloud outflow simulations by K. E. Pickering (reported by Friedl [1997]) using a mesoscale cloud-ensemble model for tropical continental, tropical marine, and midlatitude continental convective systems. The resulting distribution is "C" shaped with 40-75% of lightning NO<sub>x</sub> released in the top 3 km of convection and 1-20% released in the lowest 1 km above the surface depending on the type of convective system.

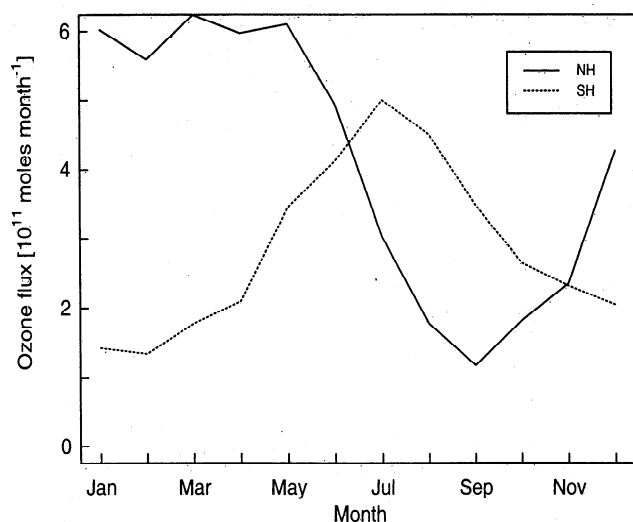
Our formulation of the lightning NO<sub>x</sub> source, as described thus far, constrains the distribution of the source but not its magnitude. Penner et al. [1991] and Levy et al. [1996] have pointed out that measurements of NO, when interpreted with global three-dimensional model simulations, offer some constraints on the source strength. Following their approach, we adjusted the global source of NO from lightning in our model to match observations of NO from Drummond et al. [1988] and Smyth et al. [1996] in the upper troposphere over the northern equatorial Atlantic, where lightning influence on NO concentrations is particularly strong. Our resulting best estimate of the lightning NO<sub>x</sub> source in the model is 3 Tg N yr<sup>-1</sup> (Figure 1), the same as previously estimated by Levy et al. [1996] and Penner et al. [1991], who used different observations as constraints. There are, however, large uncertainties in these estimates as they are contingent on accurate model simulation of transport and chemistry of NO<sub>x</sub> in the upper troposphere.

### 5. Transport of O<sub>3</sub> and Reactive Nitrogen From the Stratosphere

Flux upper boundary conditions are applied to the model at 150 mbar to represent the transport of O<sub>3</sub>, NO<sub>x</sub>, and HNO<sub>3</sub> from the stratosphere to the troposphere. At extratropical latitudes, the tropopause is lower than 150 mbar [Holton et al., 1995], and we take this difference into account in the analysis of model results in the companion papers.

The vertical resolution of the GISS GCM is too coarse for simulation of stratosphere-troposphere exchange [Spivakovsky and Balkanski, 1994]. We therefore constrain the cross-tropopause mass fluxes in our model using airflow climatology derived from observations [Holton et al., 1995; Appenzeller et al., 1996]. Appenzeller et al. [1996] showed that the cross-tropopause air mass flux has a May-June peak in the northern hemisphere but an austral winter peak in the southern hemisphere. We specify the relative seasonal variation of the cross-tropopause flux of ozone in each hemisphere as the product of the monthly cross-tropopause air mass fluxes given by Appenzeller et al. [1996] and the monthly climatological ozone concentrations at 100 mbar at midlatitudes (J. A. Logan, An analysis of ozonesonde data, 1, Its application in testing models of tropospheric chemistry, manuscript in preparation, 1998). We choose to retain the spatial distribution of the cross-tropopause ozone flux derived from the GISS GCM transport; 80-90% of the flux in each hemisphere is between 20° and 60°





**Figure 5.** Monthly mean downward fluxes of ozone across the tropopause specified in the model for the northern (NH) and southern hemispheres (SH).

latitude, the remainder is at higher latitudes, and downward transport in the tropics is negligible, consistent with current knowledge [Holton *et al.*, 1995]. The relative seasonal and spatial distribution of the cross-tropopause ozone flux is then scaled to a global mean cross-tropopause flux in the model so as to match ozonesonde observations at middle and high latitudes in the winter northern hemisphere.

We obtain in this manner annual mean cross-tropopause ozone fluxes of  $5 \times 10^{12}$  mol yr<sup>-1</sup> and  $3.5 \times 10^{12}$  mol yr<sup>-1</sup> in the northern and southern hemispheres, respectively. Figure 5 shows the monthly mean fluxes in each hemisphere. Our values are at the lower end of those reviewed by Fishman [1985] and Warneck [1988], which range from  $5 \times 10^{12}$  to  $11 \times 10^{12}$  mol yr<sup>-1</sup> in the northern hemisphere and from  $3 \times 10^{12}$  to  $6 \times 10^{12}$  mol yr<sup>-1</sup> in the southern hemisphere. Our global flux of  $8.5 \times 10^{12}$  mol yr<sup>-1</sup> is 20% lower than the value of  $11 \times 10^{12}$  mol yr<sup>-1</sup> used in two recent tropospheric ozone models [Müller and Brasseur, 1995; Roelofs and Lelieveld, 1995].

Reactive nitrogen oxides produced from the oxidation of N<sub>2</sub>O in the stratosphere are also transported across the tropopause. The cross-tropopause flux boundary condition for total reactive nitrogen (NO<sub>y</sub>) is prescribed by scaling the estimated ozone fluxes with a NO<sub>y</sub>/O<sub>3</sub> concentration ratio of 0.4% observed in the lowermost stratosphere [Murphy *et al.*, 1993]. A flux of 0.48 Tg N yr<sup>-1</sup> of NO<sub>y</sub> is computed, similar to the estimate made by Ko *et al.* [1991] from mass balance considerations for N<sub>2</sub>O. The NO<sub>y</sub> transported across the tropopause is assumed to consist of NO<sub>x</sub> and HNO<sub>3</sub> with a molar ratio of 1:4 [McElroy *et al.*, 1992].

## 6. Dry Deposition

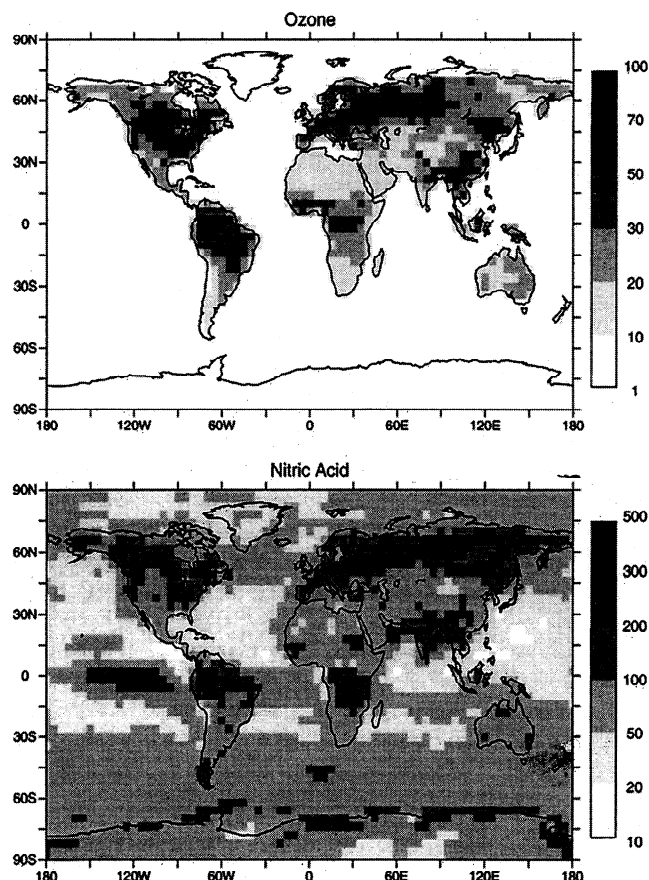
We use a resistance-in-series model [Wesely and Hicks, 1977] to compute dry deposition velocities of O<sub>3</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, PANs, and H<sub>2</sub>O<sub>2</sub>. The deposition velocity  $V_i$  for species  $i$  is computed as

$$V_i = \frac{1}{R_a + R_{b,i} + R_{c,i}} \quad (9)$$

where  $R_a$  is the aerodynamic resistance to transfer to the surface,  $R_{b,i}$  is the boundary resistance, and  $R_{c,i}$  is the canopy sur-

face resistance.  $R_a$  and  $R_{b,i}$  are calculated from the GCM meteorological variables [Jacob *et al.*, 1993]. Surface resistances  $R_{c,i}$  for different species and for different surface types are based largely on the canopy model of Wesely [1989] with some improvements, including explicit dependence of canopy stomatal resistances on LAI [Gao and Wesely, 1995] and on direct and diffuse PAR within the canopy [Baldochi *et al.*, 1987]. The same radiative transfer model for direct and diffuse PAR in the canopy is used as in the formulation of isoprene emissions (section 4). Surface resistances for deposition to tropical rain forest and tundra are taken from Jacob and Wofsy [1990] and Jacob *et al.* [1992], respectively. The surface resistance for deposition of NO<sub>2</sub> is taken to be the same as that of ozone [Erisman and Pul, 1994; Kramm *et al.*, 1995; Eugster and Hesterberg, 1996] and hence lower than specified by Wesely [1989]. Dry deposition of CO and hydrocarbons is negligibly small and not included in the model [Müller and Brasseur, 1995].

Figure 6 shows the simulated 24-hour average deposition velocities of ozone and HNO<sub>3</sub> in July. Deposition velocities of ozone are much lower over the oceans (<0.05 cm s<sup>-1</sup>) than over the continents (0.1–1 cm s<sup>-1</sup>) because of the poor solubility of ozone in water. Nitric acid has much higher deposition velocities (0.2–5 cm s<sup>-1</sup>), reflecting a lack of surface resistance. The high ozone deposition velocities over the Amazon Forest (1–1.8 cm s<sup>-1</sup> in daytime) are consistent with the observations of Fan *et al.* [1990]. We compared the seasonal variation of the ozone deposition velocity in the model to long-term observations by Munger *et al.* [1996] at Harvard Forest, Massachu-



**Figure 6.** Twenty-four-hour average deposition velocities (10<sup>-2</sup> cm s<sup>-1</sup>) for ozone and HNO<sub>3</sub> at 250 m above the surface in July.



setts. The simulated ozone deposition velocities at that location peak in summer (0.4–0.8 cm s<sup>-1</sup> in daytime, <0.2 cm s<sup>-1</sup> at night) and decrease in winter to less than 0.2 cm s<sup>-1</sup> for both day and night, in good agreement with the observed values.

## 7. Conclusions

We have described the formulation of a global three-dimensional model for tropospheric chemistry. The model transports 15 chemical tracers and includes a detailed O<sub>3</sub>-NO<sub>x</sub>-hydrocarbon mechanism. Integration of this mechanism is made computationally expedient through the use of parameterized polynomial functions for production and loss rates of tracers. A 1-year simulation on a 72x46x7 grid takes 22 CPU hours on an IBM RS6000 workstation (model 39H) with a single processor; 50% of the CPU time is spent on the chemical integration.

The model includes state-of-the-art inventories of anthropogenic emissions from fuel combustion, industrial activities, and biomass burning. The formulations for natural emissions and deposition are process based and are tied to the underlying model meteorology and observed climatologies. Isoprene emission from vegetation is computed using the algorithm of *Guenther et al.* [1995] with improved representations of LAI and canopy radiation transfer; our global isoprene source (597 Tg C yr<sup>-1</sup>) is 20% higher than that given by *Guenther et al.* [1995]. Emission of NO<sub>x</sub> from soils is computed using the scheme of *Yienger and Levy* [1995]; we improve their simple parameterization of the canopy reduction factor with a more physical model based on the work of *Jacob and Bakwin* [1991]. We obtain a global mean canopy reduction factor of 20%. Our global above-canopy NO<sub>x</sub> source of 6 Tg N yr<sup>-1</sup> is 10% higher than that given by *Yienger and Levy* [1995]. We estimate a global source of 3 Tg N yr<sup>-1</sup> of NO<sub>x</sub> by lightning, in good agreement with *Levy et al.* [1996] and *Penner et al.* [1991] and at the lower end of the 2–10 Tg N yr<sup>-1</sup> range reviewed by *Bradshaw et al.* [1998].

We took a simple approach in estimating the NO<sub>x</sub> emissions from biomass burning by applying an average NO<sub>x</sub> to CO emission ratio [*Andreae et al.*, 1996] to the CO emission inventory. The resulting NO<sub>x</sub> source is 11.6 Tg N yr<sup>-1</sup>, at the high end of 7–13 Tg N yr<sup>-1</sup> reported by the *WMO* [1995]. A better approach would be to use the observed correlation of NO<sub>x</sub> to CO<sub>2</sub> emission ratios with the N/C ratios of the fuels [*Lobert et al.*, 1991; *Hurst et al.*, 1994]. The N/C ratios for different fuel types are readily available from literature [cf. *Crutzen and Andreae*, 1990]. Emissions of CO<sub>2</sub> from biomass burning can be estimated from global inventories of biomass burned for different fuel types [cf. *Hao and Ward*, 1993].

There has been recent interest in acetone as a major source of HO<sub>x</sub> radicals in the upper troposphere [*Singh et al.*, 1995]. Our model includes acetone sources of 1.0 Tg C yr<sup>-1</sup> from industrial emission, 9 Tg C yr<sup>-1</sup> from biomass burning, 12 Tg C yr<sup>-1</sup> from the oxidation of propane and higher alkanes, and 15 Tg C yr<sup>-1</sup> from vegetation (including both direct emission and secondary production from biogenic hydrocarbons). The vegetation source was adjusted to reproduce aircraft observations of acetone concentrations over the tropical western Pacific and the South Atlantic, as is discussed further by *Wang et al.* [this issue(a)]. Our total acetone source of 37 Tg C yr<sup>-1</sup> is at the upper limit of the 25–37 Tg C yr<sup>-1</sup> range previously estimated by *Singh et al.* [1994].

## Appendix: Chemical Parameterization

Chemical production and loss rates of tracers are computed in the three-dimensional model as parameterized polynomial functions of the ensemble of independent variables defining the chemical environment of the model: tracer concentrations, water vapor, pressure, temperature, solar zenith angle, ozone column, surface albedo, and cloud reflectivities at 800, 500, and 200 mbar. These polynomial functions are used to calculate the following: (1) photolysis rate constants of O<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>4</sub>, HNO<sub>3</sub>, PAN, butylnitrate, acetone, methylethyl ketone, and H<sub>2</sub>O<sub>2</sub>; (2) OH and HO<sub>2</sub> concentrations; (3) partitioning of NO<sub>x</sub> as NO, NO<sub>2</sub>, NO<sub>3</sub>, and HNO<sub>2</sub>; (4) chemical production rates of O<sub>3</sub>, PANs, butylnitrate, CO, acetone, and methylethyl ketone; and (5) chemical loss rate of O<sub>3</sub>. They are constructed by least squares fitting to results from 10,000 photochemical point model calculations spanning the atmospheric ranges of the independent variables [*Spivakovsky et al.*, 1990b]. The point model uses an implicit finite difference kinetic solver and takes randomly selected input values of the independent variables over their respective atmospheric ranges. Radical species and hydrocarbon oxidation intermediates not transported as tracers are assumed to be in chemical steady state in the point model calculations.

The procedure for selecting terms in the polynomial functions is described by *Spivakovsky et al.* [1990b]. The photolysis rate functions include 300 to 400 terms, and the chemical functions include 700 to 900 terms; each term is a product of up to two independent variables with a combined polynomial order of up to 5. Two sets of parameterizations for the photolysis rate functions are constructed for the tropics and the extratropics, and eight sets of parameterizations for the chemical functions are constructed spanning different domains of pressure, temperature, and NO<sub>x</sub> concentrations (Table A1) to improve the quality of the least squares fit. Parameterizations including propene and isoprene are constructed only for the atmosphere below 600 mbar because of the short lifetimes of these species.

The quality of a parameterization is evaluated with the root-mean-square relative error (RMSRE):

$$\text{RMSRE} = \exp \left( \sqrt{\frac{1}{n} \sum_{k=1}^n \left( \log \left( \frac{Y_k}{\hat{Y}_k} \right) \right)^2} \right) - 1 \quad (10)$$

where  $n$  is the number of an independent set of point model calculations for the parameterization domain ( $n = 2000$ ),  $Y_k$  is the output from point model calculation  $k$ , and  $\hat{Y}_k$  is the corresponding value computed using the parameterization. The RMSREs range from 2 to 4% for the photolysis rate functions; 8 to 19% for OH concentrations; 4 to 25% for HO<sub>2</sub> concentrations; 2 to 15% for NO/NO<sub>x</sub>, NO<sub>2</sub>/NO<sub>x</sub>, and NO<sub>3</sub>/NO<sub>x</sub> concentration ratios; 9 to 33% for ozone production; 6 to 17% for ozone loss; 20 to 30% for PAN production; 9 to 16% for butylnitrate production; 8 to 40% for CO production; 7 to 17% for acetone production; and 14 to 48% for KET production. RMSREs are smaller for clean than for polluted chemical regimes. Since the RMSREs are computed for randomly chosen points, which include extreme situations not likely to exist in the atmosphere, errors in the three-dimensional model are expected to be smaller. We conducted additional tests of the parameterization functions using multiple-day box model simulations with diurnally varying photolysis rates for polluted

**Table A1.** Chemical Regimes for the Parameterization Functions

Parameterization Regime	T, K	P, mbar	NO <sub>x</sub> , pptv	CO, ppbv	ALK4, pptv	ALKE, pptv	Isoprene, pptv	Acetone, pptv	KET, pptv
A: low altitude, low NO <sub>x</sub> , with isoprene	230 - 320	600 - 1,020	0.1 - 400	10 - 400	10 - 20,000	10 - 10,000	10 - 20,000	10 - 10,000	10 - 5,000
B: low altitude, high NO <sub>x</sub> , with isoprene	230 - 320	600 - 1,020	400 - 20,000	10 - 400	10 - 20,000	10 - 10,000	10 - 20,000	10 - 10,000	10 - 5,000
C: low altitude, low NO <sub>x</sub> , no isoprene	230 - 320	600 - 1,020	0.1 - 400	10 - 400	1 - 20,000	0	0	10 - 10,000	10 - 5,000
D: low altitude, high NO <sub>x</sub> , no isoprene	230 - 320	600 - 1,020	400 - 20,000	10 - 400	1 - 20,000	0	0	10 - 10,000	10 - 5,000
E: low altitude, low NO <sub>x</sub> , low NMHCs	230 - 320	600 - 1,020	0.1 - 300	10 - 200	1 - 200	0	0	1 - 1,000	1 - 500
F: high altitude, low NO <sub>x</sub>	200 - 290	100 - 600	0.1 - 400	10 - 400	1 - 20,000	0	0	10 - 10,000	10 - 5,000
G: high altitude, high NO <sub>x</sub>	200 - 290	100 - 600	400 - 20,000	10 - 400	1 - 20,000	0	0	10 - 10,000	10 - 5,000
H: high altitude, low NO <sub>x</sub> , low NMHCs	200 - 290	100 - 600	0.1 - 300	10 - 200	1 - 200	0	0	1 - 1,000	1 - 500

The concentration ranges of O<sub>3</sub> (1-250 ppbv), CH<sub>4</sub> (0.5-2 ppmv), ethane (0.01-10 ppbv), and H<sub>2</sub>O<sub>2</sub> (0.01-10 ppbv) are the same for all parameterizations; ppmv, parts per million by volume; pptv, parts per trillion by volume. Regimes E and H are subsets of D and G, respectively, and are included to improve the accuracy of the calculation in the remote atmosphere.

and clean conditions and for the upper troposphere; we found good agreement in all cases with results from the implicit finite difference chemical solver (time step of 15 min).

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