# Global simulation of tropospheric ozone using the University of Maryland Chemical Transport Model (UMD-CTM): 1. Model description and evaluation

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Received 21 October 2003; revised 6 February 2004; accepted 5 March 2004; published 1 May 2004.

[1] We have developed the three-dimensional global University of Maryland Chemical Transport Model (UMD-CTM), which can operate on a uniform horizontal grid or operate with a stretched-grid feature that allows transport and chemistry to be computed with mesoscale resolution in a region of interest. The model is suitable for computing photochemical air quality over a specific region, as well as addressing interregional and intercontinental transport issues. The model contains options for a uniform grid or a stretched-grid advection scheme and contains a fast chemical solver and schemes for convective transport, eddy diffusion, emissions, dry deposition, wet scavenging, and stratospheric influx. The model was run on a uniform grid for a full year, and results were evaluated with a variety of surface, airborne, balloon-borne, and satellite observations from many regions of the world. The evaluation was quantified by means of an evaluation index, which compares the model versus observation differences with the variance in the measurements. For most species no systematic biases were found in the results. Results of a simulation with the stretched-grid version of the model are reported in part 2 of this series of papers [Park et al., 2004]. INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution-urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere-composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere-constituent transport and chemistry; 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions; KEYWORDS: ozone, chemical transport model, model evaluation

**Citation:** Park, R. J., K. E. Pickering, D. J. Allen, G. L. Stenchikov, and M. S. Fox-Rabinovitz (2004), Global simulation of tropospheric ozone using the University of Maryland Chemical Transport Model (UMD-CTM): 1. Model description and evaluation, *J. Geophys. Res.*, *109*, D09301, doi:10.1029/2003JD004266.

# 1. Introduction

[2] While satellite observations of tropospheric trace gases are becoming more common (e.g., CO, CH<sub>4</sub>, NO<sub>2</sub>, SO<sub>2</sub>, HCHO, O<sub>3</sub>), global chemical transport models (CTMs) remain the only means of defining the full global distributions in time and space of numerous trace gases and aerosols. Such models are also necessary for assessing the effects of future emission scenarios on atmospheric constituent concentrations. Of particular importance is the ability

of a CTM to track the intercontinental transport of polluted air masses. Typically such models operate on grids with no better than 2-degree horizontal resolution. However, for accurate estimation of pollutant export from a continent, urban plumes need to be simulated in sufficient detail such that ozone production is reasonably represented. Ozone is one of the gases with a sufficiently long lifetime in the free troposphere that it may be transported from one continent to another. Urban plume representation requires mesoscale horizontal model resolution and relatively fine vertical resolution in the lower troposphere. However, mesoscale resolution globally, although now computationally possible, is not a practical and efficient use of computer resources. One of the solutions to this dilemma is variable-grid modeling in which fine resolution is used over an area of interest and a coarser grid is used outside of this region.

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[3] We have developed the University of Maryland Chemical Transport Model (UMD-CTM) with the option of using a standard uniform grid or a non-uniform (stretched) grid. The stretched-grid option is particularly useful for simulation of the transport of regional pollution to the global scale. The model has been assembled using algorithms developed in our group and by others. The evolution of this model can be traced to the initial use of the Lin and Rood [1996] advection scheme by Allen et al. [1996] for tropospheric transport. This advection scheme is used in the uniform-grid version of the model. The stretched-grid version uses a more general (i.e., nonuniform-grid version) of this scheme [Allen et al., 2000]. The UMD-CTM chemistry and physics algorithms were tested in a singlecolumn chemistry and radiation transport model by Park et al. [2001] and then extended to the three-dimensional (3-D) model. The uniform-grid model is similar to that described by Bey et al. [2001] in that it uses the same advection and deep convection schemes and is driven by the same input meteorology. However, the chemistry and physics (e.g., turbulent mixing, dry deposition, wet scavenging) schemes are different, and, of course, the stretched-grid option is a feature particular to the UMD-CTM.

[4] In this paper we introduce and describe in detail the uniform- and stretched-grid versions of the UMD-CTM. We also present the results of a 1-year global simulation on the uniform grid. A variety of model evaluations are described using surface, airborne, and satellite observations. For example, we compare the tropospheric ozone column amounts from the model with those from two TOMS (Total Ozone Mapping Spectrometer) tropospheric ozone algorithms. We introduce an Evaluation Index (EI) to make the comparisons between model and measurements quantitative. In part 2 [Park et al., 2004] we examine the effects of regional downscaling of transport and chemistry using the stretched-grid approach. In particular, we examine the effects of deep convection and mesoscale weather systems on trace gas mixing ratios and on tropospheric ozone production over and downwind of the central United States.

# 2. Model Description

# 2.1. Model Framework

[5] Two different frameworks for the UMD-CTM have been developed for tropospheric ozone photochemistry. One is on a uniform grid and the other is on the variable (or stretched) grid. Both frameworks use the same physical and chemical schemes but with different horizontal gridding.

[6] The uniform-grid UMD-CTM is driven by standard gridded assimilated meteorological data from the Goddard Earth Observing System Data Assimilation System (GEOS-DAS) [Schubert et al., 1993]. The model can be run with any of the different versions of the GEOS assimilation. For the application reported in this paper we have driven the model with the 20-layer  $2^{\circ} \times 2.5^{\circ}$  GEOS-1 assimilated data (regridded to  $4^{\circ} \times 5^{\circ}$ ) which extends from the surface to 10 hPa. In this simulation the lowest model levels are centered at approximately 50, 250, 600, 1100, and 1700 m above the local surface. The input variables used for the UMD-CTM calculations are surface pressure, surface type (land, ocean, or ice), temperature, u and v components of the wind, specific humidity, tropopause pressure, and

tropopause temperature at 0, 6, 12 and 18 UT, three-hour averaged vertical diffusion coefficient, surface albedo, and convective precipitation, and six-hour averaged cloud mass flux, convective cloud detrainment, cloud optical depth and 3-D total cloud fraction.

[7] The UMD-CTM calculates horizontal and vertical transport, turbulent mixing and chemical transformations of constituents in the troposphere. A chemical solver calculates concentrations of 57 chemical species, 48 of which are transported. The chemical solver and scheme used for the UMD-CTM are described below. The convection and diffusion routines used are described in detail elsewhere [*Allen et al.*, 1996; *Park et al.*, 2001]. Here, briefly, moist convective transport is parameterized using archived cloud mass flux and detrainment fields from the GEOS-DAS. The boundary layer turbulent mixing is computed by solving the diffusion equation with vertical eddy transfer coefficients.

[8] The Stretched Grid UMD-CTM is driven by the assimilated meteorology from the GEOS Stretched Grid Data Assimilation System (GEOS SG-DAS) [Fox-Rabinovitz et al., 2002], which contains the Stretched Grid-GCM (SG-GCM) [Fox-Rabinovitz et al., 1997, 2001]. The physics and dynamics of the SG-GCM are equivalent with those of the uniform-grid GEOS-3 GCM (R. M. Atlas, File Specification for GEOS-DAS Gridded Output, 2000, available at http://gmao.gsfc.nasa.gov) which has horizontal resolution of  $1^{\circ} \times 1^{\circ}$  with 48 vertical layers in a sigma coordinate system from the surface to 0.01 hPa. The SG-GCM uses the same number of grid points  $(360 \times 181 \times 48)$  as the GEOS-3 GCM, but with a stretched horizontal grid. In the SG-GCM dynamic calculations such as horizontal transport are done on the stretched grid but the model physics calculations are performed on the uniform  $1^{\circ} \times 1^{\circ}$  grid and then interpolated horizontally to the stretched grid. A hybrid sigma-pressure coordinate in the vertical is used in the stretched-grid UMD-CTM to decrease noise in the transport calculations in the upper troposphere and lower stratosphere. In this configuration the vertical grid has 17 sigma layers below 242 hPa and 8 constant pressure layers above 242 hPa. The lowest model levels are centered at approximately 10, 50, 100, 200, 400, 600, 900, 1200, and 1700 m above the local surface in the uniform- and stretched-grid simulations using GEOS-3 data, thereby providing better vertical resolution in the boundary layer than in the simulations using GEOS-1.

#### 2.2. Transport

[9] The uniform grid CTM employs the *Lin and Rood* [1996] multidimensional and semi-Lagrangian extension of the piecewise parabolic method (PPM) [*Colella and Woodward*, 1984; *Carpenter et al.*, 1990] for grid-scale advection calculations as has been implemented by *Allen et al.* [1996]. We used the transport routine developed by *Allen et al.* [2000] for transport calculations on the stretched-grid. We parallelized this routine for use on a shared-memory parallel machine to increase the speed of model calculations. Figure 1 shows the stretched grid used for the model application in part 2 of this series of papers [*Park et al.*, 2004]. Here a fine-grid region with horizontal resolution of  $0.5^{\circ} \times 0.5^{\circ}$  is placed over the central United States. Outside of this region the resolution gradually



**Figure 1.** Example of stretched-grid from UMD-CTM, along with surface pressure (hPa) from 15 June 1985.

degrades to  $\sim 3.8^{\circ}$  on the opposite side of the globe. Vertical velocity and mass flux are computed from the convergence of the horizontal winds in both the uniform- and stretched-grid versions of the model.

#### 2.3. Emissions

[10] Emission inventories used for the UMD-CTM include those for  $NO_x$ , CO, and hydrocarbons from various sources (Table 1). Consideration is given to fossil fuel combustion and industrial activities, biomass burning, vegetation, soils, and lightning. Aircraft emissions are not included in the current version of the model.

### 2.3.1. Surface Emissions

[11] Compilation of surface emissions was done using three different emission inventories: the Global Emissions Inventory Activity (GEIA) [*Benkovitz et al.*, 1996], the Emission Database for Global Atmospheric Research (EDGAR) [*Olivier et al.*, 1994], and the biomass burning emission inventory of *Galanter et al.* [2000].

[12] The NO<sub>x</sub> inventories for anthropogenic and biogenic sources (soil) are based on seasonally varying  $1^{\circ} \times 1^{\circ}$  GEIA inventories. We included monthly NO<sub>x</sub> emissions from the biomass burning inventory of *Galanter et al.* [2000], who provided data for the year 1999. Biomass burning emissions include six types of sources: forest, savanna, fuelwood, agricultural residues, domestic crop residues, and dried animal waste on a  $1^{\circ} \times 1^{\circ}$  horizontal grid. We distributed low-level NO<sub>x</sub> emissions (mostly transportation and biomass burning) in the lowest model layer with 90% as NO and 10% as NO<sub>2</sub> (following *Wang et al.* [1998a] and *Environmental Protection Agency (EPA)* [1989]), and injected the stack emission of NO<sub>x</sub> from the anthropogenic source into the second lowest model layer.

[13] Global CO emissions include 385 Tg CO  $yr^{-1}$  from fossil fuel combustion and industrial activities, and 747 Tg CO yr<sup>-1</sup> from biomass burning. CO from fossil fuel combustion is based on the EDGAR inventory that includes annual global emissions of atmospheric species for the base year 1990 with  $1^{\circ} \times 1^{\circ}$  grid resolution. We applied the seasonal trend of the GEIA fossil fuel NO<sub>x</sub> emission to the EDGAR CO emission from the same type of source. We increased the original EDGAR CO emission (296 Tg CO  $yr^{-1}$ ) by 30% globally based on the findings from *Prados* [2000]. The results from her tracer CO simulations using the EDGAR CO inventory underestimate CO over the eastern United States and western Atlantic. Very recent studies [Allen et al., 2004; Palmer et al., 2003; Arellano et al., 2004] conclude that Asian fossil fuel emissions are underestimated in current inventories by nearly a factor of two. This increase will explain most of the underestimates of CO that Prados saw. We plan to include the Asian emission enhancement in future applications of the UMD-CTM, rather than the 30% global increase. Monthly CO emissions

Species	Source Type	Global	Northern Hemisphere	Southern Hemisphere
$NO_x [Tg N yr^{-1}]$	Fossil fuel combustion	21.0	19.9	1.1
	Biomass burning	7.8	4.5	3.3
	Soil	5.5	3.6	1.9
	Total	34.2	28.0	6.3
CO $[Tg yr^{-1}]$	Fossil fuel combustion	384.8	360.2	24.6
	Biomass burning	746.7	490.2	256.5
	Total	1131.5	850.4	281.1
Ethane [Tg C $yr^{-1}$ ]	Industry	3.14	2.98	0.16
	Biomass burning	3.43	2.52	0.91
	Total	6.57	5.50	1.07
Propane [Tg C yr <sup>-1</sup> ]	Industry	4.99	4.69	0.30
	Biomass burning	1.24	0.94	0.30
	Total	6.23	5.63	0.60
Ethene [Tg C yr <sup>-1</sup> ]	Industry	1.95	1.78	0.17
	Biomass burning	6.84	5.00	1.84
	Total	8.79	6.78	2.01
Propene [Tg C yr <sup>-1</sup> ]	Industry	0.82	0.75	0.07
	Biomass burning	3.26	2.37	0.89
	Total	4.08	3.12	0.96
Acetone [Tg C yr <sup>-1</sup> ]	Industry	1.1	1.0	0.1
	Biomass burning	12.5	8.2	4.3
	Vegetation	15.0	7.5	7.5
	Total	28.6	16.7	11.9
Isoprene [Tg C $yr^{-1}$ ]	Vegetation	503.	247.1	255.9

 Table 1. Global Budget of Emissions



Figure 2. Global lightning  $NO_x$  as a function of month calculated with GEOS-1 DAS used as input for the year of 1985.

from biomass burning from six types of sources are adopted from inventories compiled by *Galanter et al.* [2000].

[14] The emission inventories of hydrocarbons ( $C_2H_6$ ,  $C_3H_8$ ,  $C_2H_4$ , and  $C_3H_6$ ) are also based on EDGAR inventories. Annual emissions of each hydrocarbon from the biomass burning source have been given temporal variations the same as the temporal variation of CO emission from biomass burning. Hydrocarbon emissions from industry are assumed to vary with time in the same manner as NO<sub>x</sub> emissions from industry. Acetone is believed to be important for the budget of HO<sub>x</sub> [*Jaeglé et al.*, 1997; *Jacob et al.*, 2002] and PAN [*Singh et al.*, 1995] in the upper troposphere. We used the same method as *Wang et al.* [1998a] to estimate acetone inventories from industry, biomass burning, and vegetation. The global acetone emission (28.6 Tg C yr<sup>-1</sup>) includes 1.06 Tg C yr<sup>-1</sup> from industry, 12.5 Tg C yr<sup>-1</sup> from biomass burning, and 15 Tg C yr<sup>-1</sup> from vegetation.

[15] Isoprene is the most important biogenic hydrocarbon for tropospheric ozone chemistry. We used the temporal and geographical variation of isoprene emissions from Guenther et al. [1995] with a total amount of 503 Tg C yr<sup>-1</sup>. However, there is a large uncertainty associated with annual isoprene emissions due to the large number of variables influencing these emissions (species type, temperature, solar radiation, etc.). Spivakovsky et al. [2000] used a quite reduced amount of isoprene emission (380 Tg C  $yr^{-1}$ ) in order to closely calculate OH concentrations against the best estimate from OH measurements. Other 3-D global models have used a wide range of isoprene emission estimates (220 to 597 Tg C yr<sup>-1</sup>). Terpenes are also emitted from biogenic sources and weakly contribute to tropospheric ozone chemistry [Wang et al., 1998a]. We obtained the terpene inventory from GEIA and used it as a source of CO. Oxidation of 1 mole of monoterpene is assumed to yield 0.8 mole CO [Allen et al., 1996]. Precalculated CO emissions from the oxidation of terpenes are added into the total of surface CO emissions.

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

[16] The UMD-CTM uses a lightning  $NO_x$  generation algorithm developed by *Allen and Pickering* [2002] who parameterized the lightning flash rates with a polynomial

approximation based on GEOS-DAS convective mass fluxes on the  $2^{\circ} \times 2.5^{\circ}$  horizontal grid. Figure 2 shows the global monthly lightning NO<sub>x</sub> calculated using GEOS-1 DAS meteorology for the year of 1985. A strong seasonal variation in calculated lightning NO<sub>x</sub> is shown mainly due to the strong convective activity that is maximized during the summer in the Northern Hemisphere. The annual lightning NO<sub>x</sub> emission is 5.9 Tg N yr<sup>-1</sup> which is close to the recommended value of 6.5 Tg N yr<sup>-1</sup> of *Bradshaw et al.* [2000].

#### 2.3.3. Influx From the Stratosphere

[17] Because the model calculations mainly focus on tropospheric chemistry, the species having stratospheric sources such as ozone,  $NO_x$ , and  $HNO_3$  should be specified or parameterized in the model stratosphere. We used the synthetic ozone scheme (Synoz) [*McLinden et al.*, 2000] in the model for the representation of stratospheric ozone and for the calculations of influx of ozone and  $NO_y$  species to the troposphere. Previous model calculations showed that GEOS-1 DAS horizontal winds cause an excessive amount of large-scale transport of mass from the stratosphere into the troposphere [*Liu et al.*, 2001; *Bey et al.*, 2001]. The tropopause is defined in the model as the lowest layer where the temperature lapse rate falls below 2 K km<sup>-1</sup>.

[18] Using Synoz, a passive ozone-like tracer is released into the stratosphere at a rate equivalent to that of the prescribed cross-tropopause ozone flux observed:  $3.7 \times 10^{10}$  cm<sup>-2</sup> s<sup>-1</sup> or 479 Tg yr<sup>-1</sup> [*McLinden et al.*, 2000]. Use of Synoz ensures that the total cross-tropopause flux of ozone can be matched to observational constraints and that it is controlled in terms of seasonality and location by the model circulation.

[19] The influx of NO<sub>y</sub> from the stratosphere is calculated using the NO<sub>y</sub>/O<sub>3</sub> ratio. We use a value for this ratio of 0.004 (the same assumption used by *Wang et al.* [1998a]), which is at the high end of values observed at midlatitude [*Murphy et al.*, 1993]. We assume that stratospheric NO<sub>y</sub> consists of 25% NO<sub>x</sub> and the remainder HNO<sub>3</sub> [*McElroy et al.*, 1992].

#### 2.4. Chemistry

[20] We use the SMVGEAR II as the gas phase chemical solver [*Jacobson*, 1995]. A simplified chemical scheme was developed using our Single Column Chemical Transport and Radiation Model (SCCTM) [*Park et al.*, 2001] to expedite the speed of calculations but maintaining accurate tropospheric ozone chemistry. We performed several sensitivity calculations using the SCCTM to minimize the difference between computed mixing ratios with the full and simplified chemical reaction schemes. The modified chemical scheme has 57 chemical species and 130 kinetic reactions with 19 photochemical reactions [*Park*, 2001]. A constant methane mixing ratio of 1.7 ppmv was specified globally in the model.

[21] Computations of solar irradiance at each model grid and at every model time step demand enormous computational resources. Therefore an interpolation-based look-up table is used for calculating photolysis rates in the UMD-CTM. The profiles of photolysis rates for 19 reactions are pre-calculated using the radiation model described elsewhere [*Park et al.*, 2001] and are tabulated at 10 different solar zenith angles (from  $0^{\circ}$  to  $89^{\circ}$  with  $10^{\circ}$  intervals), at

 Table 2.
 NOy Lifetime Against Wet Scavenging as a Function of Altitude in UMD-CTM

Pressure	Lifetime, Day
1000	5.00
800	5.00
600	5.00
500	7.40
400	13.86
300	30.40
200	41.65
100	54.00

5 different total column ozone amounts (200, 250, 300, 325, and 350DU), and at 5 different surface albedos (0.0, 0.07, 0.3, 0.5, and 0.8). All photolysis rates are calculated assuming clear sky conditions in the atmosphere. US standard atmospheric profiles are used for this calculation. The precalculated tables are read once in the model and used for interpolating photolysis rates according to the solar zenith angle, the monthly TOMS total  $O_3$  observation, and GEOS-DAS surface albedo of every model gridbox at each model time step. Perturbation of photolysis rates due to clouds are parameterized using the method of *Chang et al.* [1987].

[22] We include the heterogeneous reaction of  $N_2O_5$  on aerosol particles using the parameterization from *Müller* and Brasseur [1995]. The first-order loss rate is parameterized with

$$\beta_{het} = 10^{-4} \times \left(1 - e^{-2RH}\right) \left(\sigma^2 + [SO_4]/[SO_4]^*\right) \tag{1}$$

where  $\sigma$  is the vertical coordinate(sigma values), RH is the relative humidity, [SO<sub>4</sub>] is the sulfate concentration (monthly average, in molecules cm<sup>-3</sup>) calculated by *Chin et al.* [2000], and [SO<sub>4</sub>]\* is a reference sulfate density, typical of moderately polluted surface air, set to 3 × 10<sup>9</sup> molecules cm<sup>-3</sup>. Sigma is computed for each model grid point in the portion of the grid with pressure as the vertical coordinate.

#### 2.5. Dry Deposition and Wet Scavenging

[23] Losses due to dry deposition are calculated using the deposition flux that is parameterized as the product of the concentration and the deposition velocity. The deposition velocity is a function of a species-independent aerodynamic resistance and a species-dependent surface resistance [*Wesley*, 1989]. Several researchers have calculated deposition velocity interactively with a numerical model. Here, we used constant deposition velocities (no diurnal or seasonal variation) as a function of surface types (tropical and nontropical forests, savanna, bare ground, water, ice, and snow) from *Brasseur et al.* [1998]. We assume that dry deposition takes place only in the lowest model layer.

[24] Losses due to wet scavenging are assumed to occur continually as a first-order loss process dependent on altitude and surface type (land, water, ice) [*Allen et al.*, 2000]. The NO<sub>y</sub> lifetimes used for model calculations are shown in Table 2. The NO<sub>y</sub> lifetimes used in lower altitudes, however, are different from those of *Allen et al.* [2000] because the UMD-CTM already accounts for the loss of concentration due to dry deposition separately, whereas Allen et al. accounted for loss of concentration by dry and wet deposition together. We assume that the largest fraction of NO<sub>y</sub> consists of HNO<sub>3</sub> and apply these lifetimes to HNO<sub>3</sub>. The lifetimes of other soluble gases such as  $H_2O_2$  and HCHO are taken from *Warneck* [1988]. On an episodic basis during periods of convective precipitation, the lifetime of HNO<sub>3</sub> is assumed to be 1 day at sigma levels where the temperature is greater then 258 K (i.e., where clouds are mostly liquid water), and the lifetimes for other species are scaled down accordingly. Future versions of the UMD-CTM will parameterize wet scavenging as in *Chin et al.* [2000], using additional precipitation-related variables from the GEOS assimilation.

#### 3. Model Evaluation

[25] Ideally, when running a CTM driven with assimilated meteorology, one would like to compare model output with observations from the same year as for which the model simulation was conducted. However, there are insufficient observations globally to achieve this goal for any entire year. Therefore we compare model output from selected regions with surface and profile measurements from the same regions regardless of the year of the measurements. In these comparisons we use the limited climatologies that are available for ozone [Oltmans, 1993; Logan, 1999], for CO [Novelli et al., 1992], and for other species [Emmons et al., 1997, 2000]. Figure 3 presents the selected regions where profiles were examined. The regions were taken from *Emmons et al.* [2000] and are identified in Table 3. Although they cover only a small area of the globe, they are useful for providing a reasonable picture of the global distributions of chemical species. In addition, it is valuable to compare many regions at one time for each species, which can allow identification of systematic differences between the model results and observations [Emmons et al., 2000].

[26] In order to make the evaluation quantitative, we introduce an Evaluation Index (EI) defined as follows:

$$EI = \Sigma (M_i - O_i)^2 / \Sigma S_i^2$$
<sup>(2)</sup>

where  $M_i$  is the model calculation of a certain species,  $O_i$  is the observation of the same species, and  $S_i$  is the standard deviation of the observations. The summation in the numerator can either be performed over the means for altitude



**Figure 3.** Map showing regions where calculations were compared with observed data composites. Regions are identified in Table 3.

Table 3. Regions for Vertical Profile Data-Model Comparisons

Compaign	Pagion	Pagion Nama	Latitude	Longitude
Campaign	Region	Region Name	Kange, deg	Kange, deg
ABLE-2A	1	Brazil_E	-10, 0	300, 315
CITE-2	2	Pacific	30, 45	225, 235
CITE-2	3	Calif	35, 45	235, 250
ABLE-2B	1	Brazil_E	-10, 0	300, 315
ABLE-3A	4	Alaska	55, 75	190, 205
CITE-3	5	Natal	-15, 5	325, 335
ABLE-3B	6	Ontario	45, 60	270, 280
ABLE-3B	7	US Coast E	35, 45	280, 290
ABLE-3B	8	Labrador	50, 55	300, 315
PEMWEST-A	9	Pacific N	15, 35	180, 210
PEMWEST-A	10	Japan Coast E	25, 40	135, 150
PEMWEST-A	11	China Coast E	20, 30	115, 130
PEMWEST-A	12	Philippine Sea	5, 20	135, 150
TRACE-A	13	Africa Coast W	-25, -5	0, 10
TRACE-A	14	Atlantic S	-20, 0	340, 350
TRACE-A	15	Brazil E	-15, 5	310, 320
TRACE-A	16	Brazil Coast E	-35, -25	310, 320
TRACE-A	17	Africa S	-25, 5	15, 35
PEMWEST-B	10	Japan Coast E	25, 40	135, 150
PEMWEST-B	11	China Coast E	20, 30	115, 130
PEMWEST-B	12	Philippine Sea	5, 20	135, 150
PEMTROPICS-A	18	Tahiti	-20, 0	200, 230
PEMTROPICS-A	19	Easter Island	-40, -20	240, 260
PEMTROPICS-A	20	- Fiji	-30, -10	170, 190
PEMTROPICS-A	21	Guayaquil	-15, 10	265, 285

layers in the case of profile data or over monthly means in the case of surface data or long-term ozonesonde observations. For the evaluations made through comparisons with profile data, the EI is computed over the full altitude range of the observed profile. The model data were averaged over the region and month corresponding to those of the profile measurements. The standard deviations of observations can be taken over all individual measurements in a given altitude layer or over monthly means from a range of years at a surface station. Lower values of the index represent better model performance. Values of the index should not be compared between data types (e.g., aircraft, surface, sonde) because of the variations in the index calculation methods.

[27] Because the EI as defined in equation (2) can result in a relatively low value even though the model produces an annual cycle very different from that of the observations, we also compute an alternative form of the EI as follows:

$$EI^* = \Sigma ((M_i - B) - O_i)^2 / \Sigma S_i^2$$
(3)

where B is the annual mean model bias relative to the observations:

$$B = \Sigma (M_i - O_i)/12 \tag{4}$$

[28] For this evaluation we ran the model at  $4^{\circ} \times 5^{\circ}$  uniform-grid horizontal resolution with 20 sigma vertical layers for expediency of the calculation. The UMD-CTM global simulations have been performed for the year of 1985 using GEOS-1 DAS data.

#### 3.1. Zonal Mean OH

[29] Figure 4 shows the zonal mean OH concentrations calculated for January, April, July and October 1985. The seasonal variations of OH concentrations are shown, reflecting the variations of sunlight and water vapor which produce OH through the reaction of  $O(^{1}D) + H_{2}O[Levy, 1971]$ .

[30] The calculated zonal mean OH concentrations are evaluated by comparing with the global climatological distribution of tropospheric OH from *Spivakovsky et al.* [2000] who computed it using observed distributions of O<sub>3</sub>,



**Figure 4.** Calculated zonal mean OH concentrations  $(10^5 \text{ molecules cm}^{-3})$  for January, April, July, and October.



CO Observation vs. Model at the surface

**Figure 5.** Comparison of observed and calculated monthly mean CO mixing ratios at surface sites. Solid lines and diamonds are observed values [*Novelli et al.*, 1992, 1994] and vertical bars show the full variability of the monthly means from the various years. Dotted lines and open triangles are model calculations.

H<sub>2</sub>O, NO<sub>t</sub> (NO<sub>2</sub> + NO +  $2N_2O_5$  + NO<sub>3</sub> + HNO<sub>2</sub> + HNO<sub>4</sub>), CO, hydrocarbons, temperature, and cloud optical depth. The latitudinal and seasonal variations in OH from the UMD-CTM simulations are in good agreement with Spivakovsky et al. calculations but the peak concentrations of OH for April and July are larger in the UMD-CTM by 20–25%. However, differences were mostly within ±10% in the midlatitudes (30–45°) of both hemispheres.

[31] The global mean OH concentration is also evaluated by comparison with measurements of the anthropogenic compound methylchloroform (CH<sub>3</sub>CCl<sub>3</sub>), which is removed principally by OH oxidation [*Prinn et al.*, 1987]. *Prinn et al.* [2001] derived a CH<sub>3</sub>CCl<sub>3</sub> lifetime of  $4.9^{+0.6}_{-0.5}$  years with respect to the whole atmosphere. In comparison, the UMD- CTM simulations produce a lifetime of 4.7 years for  $CH_3CCl_3$  with respect to the whole atmosphere considering oceanic losses as well as stratospheric losses. Against OH oxidation below 200 hPa we calculate a  $CH_3CCl_3$  lifetime of 5.6 years. Therefore the integrated effects of OH oxidation in the model closely resemble those of the real atmosphere.

#### 3.2. Carbon Monoxide

[32] Figure 5 shows a comparison between the calculated and the observed CO mixing ratios at 20 selected NOAA/ CMDL sites [*Novelli et al.*, 1992, 1994] where the observations are available as means of multiyear records of CO surface mixing ratios. The monthly mean of observed surface-layer CO and variability over the period of record

 Table 4. Evaluation Index for Surface CO at CMDL Sites

Site	Evaluation Index (EI)	EI*
ZEP Ny-Alesund, Svalbard	4.7	4.4
MBC Mould Bay, N.W.T.	1.7	1.3
BRW Barrow, Alaska	6.1	1.4
ICE Heimaey, Vestmannaeyjar	3.6	1.8
CBA Cold Bay, Alaska	13.9	1.5
SHM Shemya Island, Alaska	7.5	1.1
LEF Park Falls, Wisconsin	4.2	2.2
CMO Cape Meares, Oregon	1.6	1.6
NWR Niwot Ridge, Colorado	11.5	1.3
UTA Wendover, Utah	5.5	2.9
BMW Southhampton, Bermuda	2.3	0.7
KEY Key Biscayne, Florida	1.3	1.2
MLO Mauna Loa, Hawaii	4.1	0.8
GMI Guam, Mariana Islands	5.1	0.3
CHR Christmas Island, Pacific Ocean	2.3	2.3
ASC Ascension Island, Atlantic Ocean	2.5	2.3
SMO Tutuila, American Samoa	2.1	1.2
EIC Easter Island, Pacific Ocean	6.1	2.7
CGO Cape Grim, Tasmania	14.2	1.6
PSA Palmer Station, Antarctica	7.7	0.8

(up to 10 years) are presented, as well as the monthly means of calculated CO for 1985 that have been interpolated horizontally to the locations of the measurement sites. Model calculations were also vertically interpolated to the altitude of the measurement site because model horizontal resolution is not fine enough to resolve small-scale variations of topography (e.g., Mauna Loa, Hawaii, elevation of 3.4 km).

[33] In most cases the agreement between model and observations is reasonable in terms of seasonal variation, such that the minimum occurs during the summer when the CO oxidation is greatest. At high latitude stations in the northern hemisphere, the model captured the seasonal variation as well as the mean values quite well except at Barrow, Alaska where the mean values from the model were too low in winter and spring. Model calculations fall short of the observations at the midlatitude stations in the northern hemisphere where industrial activities are the main contributor to the abundance of CO concentrations. In the southern hemisphere, the model reproduced the observations quite well, except at Christmas Island where the model mixing ratios were too low during the Northern Hemisphere summer and at Ascension Island where the CO mixing ratios peaked two months early. The calculated CO is in quite close agreement with the observations at Cape Meares, Oregon on west coast of U.S. but is low at interior U.S. (Wisconsin, Colorado, and Utah) and downwind (Bermuda) stations. These comparisons suggest that either U.S. CO emissions are too small or the OH sink is too large. Also note that the model simulation is using 1985 assimilated meteorology, whereas the observations are from a variety of years. The global total fossil fuel CO emissions used here are similar to that used by Bey et al. [2001], who also noted CO mixing ratio underestimates at CMDL stations. Another possible cause of our underestimates and those of Bey et al. is the effect of aerosol on OH concentrations. Martin et al. [2003] have recently noted that aerosols may reduce OH sufficiently to allow 5-15 ppbv more CO over much of the Northern Hemisphere than what is computed in models without aerosols.

[34] Table 4 contains the EI values computed for CO at CMDL stations. Particularly good model performance is demonstrated at Mould Bay, Cape Mears, and Key Bis-

cayne, each with EI values <2. Some North American sites (Barrow, Cold Bay, Shemya Island, Niwot Ridge) at which the model underestimated observed CO (as noted above) had particularly high values of the EI. High values were also noted at two Southern Hemisphere sites (Cape Grim and Palmer Station). The model overestimated CO at both of these locations. When the EI\* values (annual mean model bias removed) are examined, these high values at the underestimated and overestimated stations are much reduced. For example, at Niwot Ridge with EI = 11.5, the EI\* = 1.3, which is among the lower values for the CMDL stations. At Christmas Island, the model missed the observed August–September peak and the November–December minimum and received an EI\* score of 2.3, which is among the higher values (indicating a poor comparison).

[35] We compared profiles of CO calculated at many regions with aircraft measurements compiled by *Emmons* et al. [2000] who collected data from a number of aircraft campaigns and formed "data composites" for the available chemical species. Figure 6 shows the CO comparison at regions in the northern hemisphere that are mostly affected by fossil fuel combustion. The comparison was initiated by identifying the region and time period of the measurements that should be used to horizontally average the model calculations and to take the appropriate monthly mean of the calculated CO. The same averaging over the region and time period was applied for comparisons of other species described below. Table 5 presents the EI values for each of the regions. The observed CO is well reproduced in the model for most regions, although for a few regions (Alaska, Labrador, Ontario, and US\_Coast\_E) the calculations fall short of the observations. EI values are particularly high for the Alaska (5.0) and US Coast E (5.9) regions. Seasonal variations of CO outflow from eastern Asia are well captured in the model (several EI values less than or equal to 1). For example, for the China Coast E and Japan Coast E regions there are increases in CO mixing ratios in the lower and middle troposphere from the PEMWEST-A to the PEMWEST-B campaign because the PEMWEST-B campaign took place during February and March, which is a typical period of strong outflow from Asia to the North Pacific [Hoell et al., 1997]. Figure 7 presents CO comparisons for regions that are influenced by emissions from biomass burning and the EI values are in Table 5. In most of these regions the model shows very good agreement with the observations (9 out of 12 regions with EI less than or equal to 1). Elevated CO mixing ratios in the lower troposphere are noted in both calculations and observations at Natal (the NOAA/CMDL station) and during the TRACE-A campaign, representing the influence of biomass burning emissions. In general, the model performed better in regions dominated by biomass burning emissions (mean EI of 0.9) than it did in the fossil-fuel dominated regions (mean EI of 2.3). However, variability in the observations is greater in the biomass burning regions and tends to lower the EI values.

#### 3.3. Reactive Nitrogen

#### 3.3.1. Nitric Oxide

[36] Photolysis of NO<sub>2</sub> and reactions involving NO, CO, and hydrocarbons are a major source of ozone in the troposphere. Because of the high reactivity of NO and



**Figure 6.** Comparison of CO profiles for regions primarily influenced by emissions from fossil fuel combustion. Boxes and whiskers represent the central 50% and 90% of the observations with a vertical bar at the median, and a star at the mean. Model results, mean and standard deviation in the region, are shown by the solid and dotted lines.

NO<sub>2</sub>, NO<sub>x</sub> (NO + NO<sub>2</sub>) is often the rate-limiting precursor for ozone formation throughout most of the troposphere [*Liu et al.*, 1980, 1987]. As a result, the production of ozone is limited by the abundance of NO<sub>x</sub>. Therefore it is important to evaluate NO<sub>x</sub> results provided by models through comparison with available observations.

[37] We chose to compare model-calculated and observed NO because NO observations are known to be more reliable than those of  $NO_x$  [*Bradshaw et al.*, 2000]. Observed and calculated NO only include daytime NO concentrations

(solar zenith angle less than 90°). Regions affected primarily by fossil fuel combustion are shown in Figure 8, and Figure 9 shows comparisons for regions mainly affected by emissions from biomass burning. EI values are given in Table 5. Calculated and measured NO are generally in good agreement (EI  $\leq 1$  for 10 of 12 regions dominated by industrial emissions and 8 of 12 regions dominated by biomass burning) and show an increase with altitude because the lifetime of NO<sub>x</sub> increases with altitude. Lightning NO<sub>x</sub> production and the influx from the stratosphere

 Table 5.
 Evaluation Index for GTE Comparisons

		-			
Campaign (Region Name)	СО	NO	HNO <sub>3</sub>	PAN	O <sub>3</sub>
ABLE-3A (Alaska)	5.0	0.1		0.9	1.5
ABLE-3B (Labrador)	2.4	3.7	1.0	11.3	4.9
ABLE-3B (Ontario)	2.5	0.5	0.8	2.6	0.3
ABLE-3B (US_Coast_E)	5.9	0.4	0.9	3.6	1.1
CITE-2 (Calif)	1.1	4.8	1.7	1.3	1.3
CITE-2 (Pacific)	2.4	0.4	0.5	3.2	0.5
PEMWEST-A (China_Coast_E)	2.2	0.1	22.0	17.0	1.4
PEMWEST-A (Japan Coast E)	0.4	0.7	1.1	26.4	2.3
PEMWEST-A (Pacific N)	3.8	0.6	12.6	41.6	1.9
PEMWEST-B (China Coast E)	1.0	0.2	2.2	0.6	2.7
PEMWEST-B (Japan_Coast_E)	0.4	0.6	0.4	2.0	0.3
PEMWEST-B (Philippine_Sea)	0.4	1.0	1.5	5.8	2.1
ABLE-2A (Brazil_E)	0.3	8.2			15.6
ABLE-2B (Brazil_E)	2.1	0.7		532.5	45.1
CITE-3 (Natal)	0.4	0.1			0.7
TRACE-A (Africa Coast W)	1.0	3.7	5.1	4.6	2.1
TRACE-A (Africa S)	0.2	1.0	0.7	0.8	0.7
TRACE-A (Atlantic S)	1.2	0.7	8.9	23.4	1.4
TRACE-A (Brazil Coast E)	0.6	2.0	3.4	1.0	16.4
TRACE-A (Brazil E)	0.3	0.3	4.2	2.4	0.5
PEMTROPICS-A (Easter Island)	2.8	0.7	13.5	38.0	2.8
PEMTROPICS-A (Fiji)	0.7	1.6	1.8	4.8	0.5
PEMTROPICS-A (Tahiti)	0.7	0.5	1.8	5.4	1.4
PEMTROPICS-A (Guayaquil)	0.5	0.4	5.5		3.4

contribute to the budget of  $NO_x$  in the upper troposphere. The model closely reproduced profiles of NO over the regions strongly affected by surface emissions (industrial and biomass burning) showing a typical C-shaped profile, as well as over the remote regions showing an increasing trend with altitude. In contrast to CO, the mean EI value for industrial regions (1.1) is lower than for the regions dominated by biomass burning (1.7).

#### 3.3.2. Nitric Acid

[38] Nitric acid is produced by the reactions of NO<sub>2</sub> with OH and by hydrolysis of N2O5 on aerosols and is removed by wet and dry deposition. Figure 10 shows comparisons between calculated and observed profiles of  $HNO_3$  for regions where the observations are available. EI values are presented in Table 5. Calculated and observed nitric acid are in generally good agreement in the lower and middle troposphere, although the model overestimates HNO<sub>3</sub> mixing ratios at the east and west coasts of the United States. EI values are generally low (mostly <2) near major emission source regions with the exception of China Coast E. Otherwise, the model performance was the poorest in remote regions where variability is generally small (e.g., Pacific N, Atlantic S, and Easter Island, with EI values between 8.9 and 13.5). The model overestimated  $HNO_3$  by a factor of 2-5 in the upper troposphere, especially for the TRACE-A campaign. Overestimation of nitric acid mixing ratios in the free troposphere is a common problem in global models [e.g., Brasseur et al., 1996; Emmons et al., 1997; Wang et al., 1998b; Hauglustaine et al., 1998; Bey et al., 2001]. The possible reasons for excessive HNO<sub>3</sub> are 1) the model does not differentiate between gas phase HNO<sub>3</sub> and particulate nitrate  $NO_3^-$ , while the observations are for gas phase  $HNO_3$  only, and 2) the scavenging from convective precipitation is underestimated [Wang et al., 1998b]. Horowitz et al. [2003] obtained good agreement between simulated and observed HNO<sub>3</sub>, and they found that HNO<sub>3</sub> is very sensitive to the wet deposition parameterization. These explanations and findings do not

fully explain the discrepancy appearing in the model results provided by the UMD-CTM. The simple wet scavenging routine implemented in the UMD-CTM reproduced fairly well the concentrations of soluble species including HNO<sub>3</sub> and  $H_2O_2$  (not shown) in the lower troposphere in the tropics where convective precipitation is frequent. In order to explain the HNO<sub>3</sub> discrepancy in the remote troposphere, several authors [*Chatfield*, 1994; *Fan et al.*, 1994; *Hauglustaine et al.*, 1996; *Jacob et al.*, 1996] proposed a third explanation: the rapid conversion of HNO<sub>3</sub> to NO<sub>x</sub> on aerosols. However, this proposed process would result in the overestimation of NO mixing ratios, which are currently in good agreement with observations in the UMD-CTM.

#### 3.3.3. Peroxyacetyl Nitrate

[39] Peroxyacetyl nitrate (PAN) is mainly formed in the boundary layer by the reaction of NO<sub>2</sub> with peroxyacetyl radicals originating from the oxidation of nonmethane hydrocarbons (NMHCs); its transport and thermal decomposition provide a source of NO<sub>x</sub> and ultimately a source of  $O_3$  in the remote troposphere. A comparison of observed and calculated profiles of PAN is shown in Figure 11. EI values are shown in Table 5. PAN mixing ratios are well simulated over Alaska (EI = 0.9) and a number of other North American regions. The model is consistent with the observations in the lower troposphere for regions affected by anthropogenic influence with the exception of the PEMWEST-B/Japan Coast E and PEMWEST-B/China Coast E regions. The model results for the ABLE3B/ US COAST E, PEMWEST-A/Japan Coast E, CITE2-California, and PEMWEST-A/China Coast E regions overestimate the measurements by a factor of 2-4 in the free troposphere. EI values are particularly high for two of these regions (PEMWEST-A/Japan Coast E and PEMWEST-A/ China Coast E). However, in these same regions the EI for PAN is much lower in PEMWEST-B (0.6 and 2.0, respectively). In regions affected by biomass burning the calculations show enhanced PAN mixing ratios, although model values appear much too high over Brazil E during the wet season ABLE2B campaign. The EI value for this region is the largest one computed (532.5) over all the species and regions evaluated. During this campaign the variability of observed PAN was very low, helping to drive the EI to a large value. The model overpredicted both PAN and NO for this region and time of year. However, the EI values over the Brazilian regions are much lower for the dry season TRACE-A campaign (1.0 and 2.4). Over the tropical ocean (Easter island, Fiji, and Tahiti) PAN mixing ratios are generally low both in the model and observations. The model, however, still overestimates the measurements in the middle and upper troposphere. The overestimation of modeled PAN in the upper troposphere suggests that the lifetime of calculated PAN could be too long in the middle and upper troposphere.

#### 3.4. Ozone

#### 3.4.1. Surface Observations and Ozonesondes

[40] Model-computed ozone mixing ratios were compared with multiyear surface measurements from *Oltmans and Levy* [1994] (not shown) and 800, 500, and 300 hPa ozonesonde data from *Logan* [1999] (Figures 12–14). In general, major features are well captured by the model (as evidenced by the generally low EI values in Table 6). These



Figure 7. CO profiles for regions influenced by biomass burning, as in Figure 6.



Figure 8. NO profiles for regions influenced by fossil fuel combustion, as in Figure 6.



Figure 9. NO profiles for regions influenced by biomass burning, as in Figure 6.



Figure 10. HNO<sub>3</sub> profiles for the selected regions, as in Figure 6.



Figure 10. (continued)



Figure 11. PAN profiles for the selected regions, as in Figure 6.



Figure 11. (continued)



# Ozone Observation vs. Model at 800 mb

**Figure 12.** Comparison of the observed and the simulated ozone mixing ratios at 800 hPa for the ozonesonde sites. Solid line and diamonds are monthly mean of multiyear ozonesonde measurements and dashed lines and triangles are model results. Vertical bars are standard deviations in the observations. Data are from *Logan* [1999].



Ozone Observation vs. Model at 500 mb





**Figure 14.** Same as Figure 12 but at 300 hPa. For stations Alert, Resolute, Churchill, Edmonton, and Goose\_Bay, stratospheric data were filtered out from each individual sonde profile using given tropopause pressure. Solid lines and squares represent the filtered tropospheric data, and the unfiltered data are shown as solid lines and diamonds.

**Table 6.** Evaluation Index for Ozone for the Ozonesonde Sites<sup>a</sup>

Sites	800 hPa	500 hPa	300 hPa
Alert(83N, 62W)	1.9 (1.8)	0.3 (0.2)	0.2 (0.1)
Ny Alesund(79N, 12E)	1.2 (1.1)	1.2 (0.6)	0.6 (0.3)
Resolute(75N, 95W)	0.4 (0.4)	0.3 (0.3)	0.2 (0.2)
Sodankyla(67N, 27E)	1.2 (0.9)	0.7 (0.3)	0.3 (0.2)
Churchill(59N, 147W)	2.3 (0.9)	0.6 (0.3)	0.03 (0.03)
Edmonton(53N, 114W)	1.2 (1.1)	0.3 (0.3)	0.1 (0.1)
Goose_Bay(53N, 60W)	1.2 (1.2)	0.3 (0.3)	0.1 (0.1)
Lindenberg(52N, 99E)	3.1 (0.8)	1.3 (0.6)	0.1 (0.1)
Hohenpeissenberg(48N, 11E)	0.4(0.4)	0.4 (0.3)	0.1 (0.1)
Payerne(47N, 7E)	0.6 (0.4)	0.8 (0.4)	0.1 (0.1)
Biscarosse(44N, 1W)	0.5 (0.5)	0.4 (0.3)	0.1 (0.1)
Sapporo(43N, 141E)	1.0 (0.9)	0.3 (0.2)	0.2 (0.2)
Boulder(40N, 105W)	0.8 (0.3)	0.3 (0.3)	0.1 (0.1)
Cagliari(39N, 9E)	0.5 (0.3)	0.5 (0.2)	0.1 (0.1)
Wallops_Island(38N, 76W)	0.3 (0.3)	0.5 (0.5)	0.1 (0.1)
Tateno(36N, 140E)	1.1 (0.4)	0.2 (0.2)	0.2 (0.2)
Kagoshima(32N, 131E)	0.5 (0.5)	0.3 (0.3)	0.3 (0.1)
Naha(26N, 128E)	0.8 (0.5)	0.5 (0.1)	0.4 (0.1)
Hilo(20N, 155W)	0.6 (0.6)	0.6 (0.5)	0.3 (0.1)
Brazzaville(4S, 14E)	0.8 (0.8)	0.4 (0.3)	0.2 (0.2)
Natal(6S, 35W)	1.0 (0.5)	0.3 (0.2)	0.2 (0.1)
Ascension(8S, 15W)	1.1 (1.1)	0.2 (0.2)	0.5 (0.5)
Samoa(14S, 170W)	2.4 (0.4)	0.6 (0.5)	0.6 (0.1)
Pretoria(26S, 28E)	3.0 (0.3)	0.4 (0.2)	0.5 (0.3)
Asp_Laverton(38S, 145E)	0.7 (0.2)	1.2 (0.2)	0.4 (0.1)
Lauder(45S, 170E)	0.3 (0.1)	0.9 (0.1)	0.1 (0.02)
Marambio(64S, 57W)	1.2 (0.6)	0.2 (0.2)	0.3 (0.3)
Syowa(69S, 39E)	3.2 (0.6)	0.4 (0.4)	0.1 (0.1)

<sup>a</sup>Values in parentheses are the evaluation index (EI\*) adjusted for the annual mean model bias compared with the observations.

features include: (1) the broad midyear maximum in the Northern Hemisphere from the middle to the upper troposphere and the winter minimum, (2) the summer maximum over the polluted continents, and (3) the winter maximum and summer minimum in the lower troposphere at southern hemispheric middle and high latitudes and the spring maximum in the middle troposphere at southern midlatitudes. However, the model did not capture observed surface layer and 800 hPa springtime maxima [e.g., Logan, 1985, 1999] at remote mid- and high-latitude sites (Alert, Resolute, Churchill, Edmonton, and Goose Bay). Possible causes of these maxima are summarized in Monks [2000] and were a focus of the spring 2000 TOPSE (Tropospheric Ozone Production about the Spring Equinox) campaign [Atlas et al., 2003]. Analyses of measurements and model output indicate that seasonal variations in the stratosphere-troposphere exchange (STE) of ozone, in horizontal transport, and photochemistry contribute to these maxima [e.g., Wang et al., 1998c, 2003; Yienger et al., 1999; Lelieveld and Dentener, 2000; Allen et al., 2003; Browell et al., 2003; Dibb et al., 2003]. The relative contributions of seasonal variations in transport and chemistry vary greatly with altitude and location. The inability of the UMD-CTM to capture these maxima was not investigated in detail. However, an inadequate simulation of seasonal variations in crosstropopause  $O_3$  exchange contributes to the discrepancy. Fusco and Logan [2003] captured these maxima in a 1994 GEOS-CHEM [Bey et al., 2001] calculation driven by the GEOS-1 DAS. They also used Synoz but with a larger prescribed cross-tropopause ozone flux (570 vs. 479 Tg  $O_3$  yr<sup>-1</sup>). A relatively large flux may be necessary to capture these maxima because the seasonal cycle of  $O_3$  in the GEOS-CHEM when driven by GEOS DAS fields is

"significantly weaker than observed" [*Fusco and Logan*, 2003]. Interannual variability and differences in chemistry are additional possible explanations for the missed peaks.

[41] EI values vary considerably among the five mid-tohigh-latitude stations mentioned above. Despite missing the springtime maximum, Resolute shows a low EI of 0.4 at 800 hPa. However, the values of the index for 800 hPa are much larger at Churchill (2.3) and Alert (1.9). The EI\* values for these stations are little different than the EI values, except at Churchill where the model underestimated the ozone at 800 hPa most of the year. One other Northern Hemisphere station (Lindenberg) and two Southern Hemisphere stations (Pretoria and Syowa) showed large EI values ( $\geq$ 3), which resulted from either consistent overestimates or underestimates of ozone throughout the year. EI\* values for these stations are significantly lower than the EI scores since the seasonal cycles are reasonably well simulated. In general the model performed well in estimating lower tropospheric ozone. Over half of the stations have EI values  $\leq 1$  (i.e., the model error is less than or equal to the standard deviation of the measurements).

[42] High latitude ozone mixing ratios at 300 hPa are very sensitive to the location of the tropopause. Therefore we used individual station tropopause pressure data to identify stratospheric measurements for removal from the data sets for the Alert, Resolute, Churchill, Edmonton, and Goose Bay sites. All model values at 300 hPa were in the model troposphere. Figure 14 shows that the calculated ozone is in close agreement with the tropospheric data at 300 hPa. Model results at 500 and 300 hPa are in good agreement with observations in the tropics but higher than observations by a maximum of 20 ppbv in the midlatitudes (Asp\_Laverton at 500 hPa) of the Southern Hemisphere. El values decrease with increasing altitude as the variability of the observed ozone increases.

#### 3.4.2. Aircraft Campaigns

[43] Figure 15 shows vertical profile comparisons for regions primarily affected by fossil-fuel emissions and Figure 16 shows comparisons for regions affected by emission from biomass burning. EI values are given in Table 5. In many of these regions model results are generally in good agreement with the observed profiles (EI  $\leq$  1.5 in 13 of 24 regions). Model results, however, are lower than observed at Alaska, but the EI value is not large due to the large variability of the measurements. The model underestimated ozone in the lower troposphere at eastern Asia regions (China Coast E (EI = 2.7) and Japan Coast\_E) during the PEMWEST-B campaign (February-March), which coincides with the lack of a springtime ozone maximum in the model in this region shown in the comparison with ozonesonde data. The model reproduced well the profiles of ozone for regions affected by biomass burning emission, although it overestimates ozone for Brazil\_E (EI = 15.6 for ABLE2A and 45.1 for ABLE2B) and Brazil Coast E (EI = 16.4 for TRACE-A), which coincides with an overestimation of NO for these regions shown in Figure 9. However, observations of ozone at Brazil E during ABLE2A and ABLE2B are low compared with other measurements for nearby regions (e.g., TRACEA-Brazil\_E). The model performed much better in comparison with the TRACE-A-Brazil E data (EI = 0.5). Therefore it seems that the discrepancies could be caused by



Figure 15. O<sub>3</sub> profiles for regions influenced by fossil fuel emissions, as in Figure 6.



Figure 16. O<sub>3</sub> profiles for regions influenced by emission from biomass burning, as in Figure 6.



**Figure 17.** Tropical tropospheric ozone columns (TTO) averaged for SON 1985 (top) from the UMD-CTM simulation, (middle) from TOMS observations with the convective cloud differential (CCD) method [*Ziemke et al.*, 1998] and (bottom) with the modified residual (MR) method [*Thompson and Hudson*, 1999].

interannual variability of emissions and transport due to the different years of the observations and calculations.

# 3.4.3. TOMS Tropical Tropospheric Column Ozone

[44] Figure 17 compares UMD-CTM model results for the September, October, November (SON) period of 1985 with the 1985 global distribution of Tropical Tropospheric Ozone columns (TTO) for the same months from TOMS observations with the modified residual (MR) method [Thompson and Hudson, 1999] and the convective cloud differential (CCD) method [Ziemke et al., 1998], respectively. The model reproduces a minimum over the tropical Pacific on both sides of the dateline and a maximum over the tropical Atlantic, as observed by both techniques. Figure 18 shows the longitudinal distribution of meridional-average TTO for three latitude bands. During the SON period, the UMD-CTM calculations are nearly identical to one of the satellite retrievals or between the values from the two retrievals at most longitudes. The model underestimates the SON TTO values from the MR method over the tropical Atlantic (similar to the results of Peters et al. [2002]), but exceeds the CCD values in this region. The simulated TTO is generally higher than both TOMS TTOs over most longitudes during December through February (DJF) in the 5-12°N band and for the western longitudes in the 5°S to 5°N band. The model values are larger than the retrievals in these two bands in the March through May (MAM) period as well. In the June through August season,

the simulated TTO falls between two methods, being higher than CCD method but lower than MR method, similar to the SON season. The largest discrepancy between the model and TOMS occurs over northern Africa during DJF and MAM when the simulated TTO shows enhancements due to the biomass burning over that region, whereas this feature is not observed in TOMS TTO by either method. This discrepancy arises because ozone resulting from biomass burning in this region remains primarily in the lower troposphere where the sensitivity of TOMS is poor due to Rayleigh scattering [*Martin et al.*, 2002].

#### 4. Conclusions

[45] We have developed a new 3-D global chemical transport model (the UMD-CTM) for tropospheric chemistry which provides global and regional distributions of 57 chemical species. The model is driven by assimilated meteorology and has options for either uniform or stretched grid horizontal resolution. The chemical scheme focuses on tropospheric ozone chemistry and includes 130 kinetic and 19 photochemical reactions. The UMD-CTM accounts for large-scale advection, sub-grid processes such as deep



**Figure 18.** Meridional average of TTO over (left)  $12^{\circ}S-5^{\circ}S$ , (middle)  $5^{\circ}S-5^{\circ}N$ , and (right)  $5^{\circ}N-12^{\circ}N$  as a function of longitude for each season. The simulated and observed TTOs are regridded on a latitudinal grid with 1 degree resolution. Solid lines represent the simulated TTO and dotted and dashed lines are observed TTO from the CCD and MR methods, respectively.

convective mixing and turbulent mixing, wet and dry deposition, gas-phase, and heterogeneous chemical transformation, and surface emissions.

[46] The results presented in this paper are from a 1-year run of a uniform  $4^{\circ} \times 5^{\circ}$  grid version of the model. Results from the stretched-grid version of the UMD-CTM are discussed in part 2 [Park et al., 2004]. The results (CO, O<sub>3</sub>, and nitrogen compounds presented here) provided by the UMD-CTM were compared with several types of observations in a model evaluation. The model captured the seasonal variation of CO well, although it underestimated surface concentrations of CO at sites within and downwind of the United States. There was a tendency for the model to overestimate PAN and HNO<sub>3</sub> in the upper troposphere in over half of the regions in which measurement profiles were available. Comparisons with ozonesonde measurements show that major features analyzed by ozonesonde measurements are quite well captured by the UMD-CTM, except for the springtime ozone maximum at remote northern midlatitude sites in the lower troposphere. The springtime maximum was thought to be a result of stratospheric ozone influx [e.g., Levy et al., 1985; Oltmans and Levy, 1992; Moody et al., 1995]. However, recent 3-D global model studies [Wang et al., 1998c; Yienger et al., 1999; Lelieveld and Dentener, 2000; Allen et al., 2003] also suggest the importance of in-situ chemical production and transport in the troposphere. The lack of a lower tropospheric springtime maximum of ozone in the model may result from insufficient amplitude in the seasonal cycle of cross tropopause flux of ozone. Comparisons with data composites of aircraft measurement profiles reveal that the calculations are in good agreement with the observations from many different regions and time periods. The model is capable of capturing the influence of emissions from fossil fuel combustion as well as biomass burning. Although we used assimilated meteorology for the specific year 1985, the model results reflect the major climatological features that are found in the observations from a variety of years. In summary, we failed to find any universal systematic bias in the model calculations. The ability of the model to reproduce the observations allows us to use this model to further investigate the role of factors controlling global tropospheric chemistry. The results of this study also allow us to proceed with regional downscaling of transport and chemistry in the UMD-CTM [Park et al., 2004].

[47] Acknowledgments. This research was supported under a NASA Earth Observing System Interdisciplinary Science Investigation (NASA Grant NAG5-9672).

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