Distribution and budget of O₃ in the troposphere calculated with a chemistry general circulation model

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Abstract. We present results of global tropospheric chemistry simulations with the coupled chemistry/atmospheric general circulation model ECHAM. Ultimately, the model will be used to study climate changes induced by anthropogenic influences on the chemistry of the atmosphere; meteorological parameters that are important for the chemistry, such as temperature, humidity, air motions, cloud and rain characteristics, and mixing processes are calculated on-line. The chemical part of the model describes background tropospheric CH₄-CO-NO_x-HO_x photochemistry. Emissions of NO and CO, surface concentrations of CH₄, and stratospheric concentrations of O₃ and NO_y are prescribed as boundary conditions. Calculations of the tropospheric O₃ budget indicate that seasonal variabilities of the photochemical production and of injection from the stratosphere are represented realistically, although some aspects of the model still need improvement. Comparisons of calculated O₃ surface concentrations and O₃ profiles with available measurements show that the model reproduces O₃ distributions in remote tropical and midlatitudinal sites. Also, the model matches typical profiles connected with deep convection in the Intertropical Convergence Zone (ITCZ). However, the model tends to underestimate O₃ concentrations at the poles and in relatively polluted regions. These underestimates are caused by the poor representation of tropopause foldings in midlatitudes, which form a significant source of tropospheric O₃ from the stratosphere, too weak transport to the poles, and the neglect of higher hydrocarbon chemistry. Also, mixing of polluted continental boundary layer air into the free troposphere may be underestimated. We discuss how these model deficiencies will be improved in the future.

1. Introduction

During recent decades it has been recognized that anthropogenic activities have had an increasing influence on the chemical composition of the atmosphere especially since the Industrial Revolution. A key component in the chemistry of the atmosphere and climate is ozone (O₃), of which the global budget is significantly influenced by anthropogenic emissions [World Meteorological Organization (WMO), 1992]. The dramatic decrease of the stratospheric O₃ concentrations between approximately 100 and 30 hPa at the South Pole during the austral spring and global stratospheric O₃ depletion have now been unequivocally related to anthropogenic emissions of chlorofluorocarbons (CFCs) [WMO, 1992]. On the other hand, anthropogenic emissions of NO_x by fossil fuel burning in industrial areas and by biomass burning in Africa and South America lead to enhanced photochemical production of ozone in the troposphere [WMO, 1992].

From a climatological viewpoint, the importance of ozone for the atmosphere is twofold. Firstly, ozone acts as a greenhouse gas. It absorbs terrestrial infrared radiation and hence its increase can cause a warming of the atmosphere [Ramanathan *et al.*, 1987; Lacis *et al.*, 1990; Fishman *et al.*, 1979]. Recently, Lelieveld and Van Dorland [1995] estimated that the global mean radiative forcing of climate by increasing tropospheric ozone in the past 1.5 century may be up to 0.5 W m⁻², which is about one third of the radiative forcing by increasing

CO₂. Secondly, O₃ is the most important source of OH radicals [Levy, 1971]. OH reacts with most atmospheric pollutants, and hence determines to a large extent the removal and lifetime of pollutants that are not efficiently removed by other processes; important examples are carbon monoxide (CO) and the greenhouse gas methane (CH₄).

The radiative activity of O₃ and production of OH from O₃ depends strongly on the distribution and ambient concentrations of O₃ in the troposphere [Crutzen, 1988; Lacis *et al.*, 1990; Thompson, 1992]. In order to accurately assess the role of tropospheric O₃ in the chemistry of the atmosphere and climate, a thorough understanding of all processes influencing its distribution and their interactions is necessary. Global three-dimensional atmospheric chemistry models are important tools in studies of the budget and distribution of O₃ in the troposphere. In the recent past these studies have been conducted mainly with global tracer transport/chemistry models which include, sometimes comprehensive, chemical schemes and prescribe the meteorology. Meteorological data may be derived from observations (e.g., Crutzen and Zimmermann [1991], using monthly averaged meteorology), or from European Center of Medium-Range Weather Forecasts (ECMWF) analyses [e.g., Heimann *et al.*, 1990], or are previously calculated by a general circulation model (GCM) (e.g., models described by Levy *et al.* [1985], Penner *et al.* [1991], and Kasibhatla *et al.* [1993], with a time resolution of about 6 hours).

In this work we present results of a simulation of global tropospheric chemistry using a coupled chemistry GCM. The GCM used in this study is European Center Hamburg Model (ECHAM), a climate model developed at the Max-Planck-

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Institute for Meteorology in Hamburg, Germany [Roeckner *et al.*, 1992]. All meteorological data needed to evaluate chemical tracer concentrations in the atmosphere are calculated on-line by ECHAM with a time resolution of 40 min. As a result of the meteorology calculations, more CPU time is required than with an off-line model with the same spatial resolution and chemistry. In our model the calculations associated with chemical species (i.e., the processes described in section 2 and transport in the atmosphere) need approximately the same amount of CPU time as the meteorology calculations. However, the use of an off-line model requires substantial CPU time and memory to read and store data for the calculation of transport and the complex interactions between meteorological and chemical processes, whereas a large amount of data may be needed to cover different model resolutions. Further, a chemistry GCM interactively calculates concentrations of radiatively active species such as O₃ that directly drive the radiation scheme and the GCM meteorology. When fully developed and tested, a coupled chemistry GCM is a powerful tool in the study of the intricate interactions between atmospheric chemistry and global climate.

As a first step in the development of such a model, we have coupled a tropospheric chemistry scheme to ECHAM. This paper describes the simulated tropospheric budget and distributions of O₃, using output from the last 2 years of a 3 year simulation. In section 2 we present a brief description of the model, the parameterization of rain-out and wash-out of soluble species (described in detail in the appendix), emissions of NO and CO, and other boundary conditions. Section 3 contains a detailed comparison of simulated O₃ concentrations with measurements both at the surface and at higher altitudes in the troposphere. Further, simulated nitrate deposition data and CO concentrations are compared to measurements. In section 4, the simulated budget terms and spatial and temporal distribution for tropospheric O₃ are examined. Attention will also be given to CO and CH₄ budgets.

2. Model Description

2.1. General Circulation Model ECHAM

The tropospheric chemistry simulations are carried out with the ECHAM spectral general circulation model, which is based on the ECMWF numerical weather prediction model [Roeckner *et al.*, 1992]. Vorticity, divergence, temperature, surface pressure, humidity, and cloud water are prognostic variables. Radiation, large-scale, and convective cloud formation and precipitation are calculated by the model, as well as explicit boundary layer mixing processes. Land surface processes are described by a five-layer heat conductivity soil model and by a hydrological model to determine evaporation and runoff. Sea surface temperatures are prescribed. In the T21 mode, which is used in this study, the horizontal resolution is approximately $5.6^\circ \times 5.6^\circ$ and the time resolution is 2400 s. The model uses 19 vertical layers in a hybrid σ - p -coordinate system, from the surface to 10 hPa. Average pressure levels relevant for the troposphere are 990, 970, 950, 900, 840, 760, 670, 580, 490, 400, 320, 250, 190, 140, and 100 hPa, referring to approximate midlayer altitudes of 0.03, 0.14, 0.38, 0.78, 1.4, 2.1, 3.1, 4.2, 5.6, 7.0, 8.6, 10.2, 11.9, 13.8, and 15.9 km above the surface.

In this work, version 3.2 of the ECHAM model is used. An important difference with the previous version 2 (used for tracer transport studies in Feichter *et al.* [1991] and Brost *et al.* [1991]) is the implementation of a semi-Lagrangian advection

scheme for tracer transport [Rasch and Williamson, 1990; Feichter *et al.* [1995]. Changes have also been made in the physical schemes for vertical diffusion and convection [Roeckner *et al.*, 1992; Tiedtke, 1989].

ECHAM distinguishes between large-scale and convective clouds. The large-scale cloud scheme is based on the work of Sundquist [1978] and Roeckner *et al.* [1991], and calculates condensation of water vapor, evaporation of cloud water, formation of precipitation by coalescence of cloud droplets and sedimentation of ice crystals, and the evaporation of precipitation in unsaturated air. Convective clouds in ECHAM are parameterized by the mass flux scheme of Tiedtke [1989]. The scheme distinguishes between penetrative convection, shallow convection and midlevel convection. Convective clouds are represented by a bulk model and include updraft and downdraft mass fluxes.

A detailed description of the model and an analysis of the simulated climate can be found in work by Roeckner *et al.* [1992], Lohmann *et al.* [1993], and Boer *et al.* [1992]. Certain flaws in the simulated climate and meteorology are known which may significantly affect the simulation of atmospheric O₃. Haskins *et al.* [1995] found an underestimation of coastal stratus, which is possibly caused by an inadequate parameterization of the boundary layer. The lack of cloudiness is most significant in the southeastern Pacific, but occurs also in the North Atlantic, North Pacific, and the ocean surrounding Antarctica and will affect the photochemistry in this areas to some extent. Roeckner *et al.* [1992] mention that the tropical upper troposphere is too warm by a few degrees. This will enhance the simulated humidity and therefore the concentration of OH in this area. Also, precipitation is too strong during the summer over South Africa and Australia and off the west coast of Central America. The rainfall over India is underestimated during the summer monsoon season. Precipitation affects, through wet deposition of HNO₃, the concentration and distribution of NO_x and, in turn, the formation of O₃ in remote regions. Finally, transport of chemical species may be affected by small errors in circulations, storm tracks, and the location and spatial extent of high and low pressure areas.

2.2. Chemistry

The tropospheric chemistry code describes the background CH₄-CO-NO_x-HO_x photochemistry. The gas phase chemical reactions making up this scheme have been published elsewhere [e.g., Crutzen and Gidel, 1983]. For the reaction of O(¹D) with H₂O, resulting in the production of OH-radicals, the water vapor mixing ratios calculated by ECHAM are used. The formation of HNO₃ through reaction of N₂O₅ on aerosols is included, using pseudo first-order reaction rates calculated by Dentener and Crutzen [1993] on the basis of sulfate and seasalt mixing ratios, aerosol size distributions, and relative humidity data. A description of the nighttime removal of N₂O₅ on cloud droplets and ice is included as well. All other reaction coefficients are taken from DeMore *et al.* [1992].

The method for calculation of photolysis rates was developed by Brühl and Crutzen [1988], and takes into account multiple scattering by air molecules, aerosol particles and clouds, using the delta-two-stream method of Zdunkowski *et al.* [1982]. From the parameters that are needed for the evaluation of the photolysis rates, the meteorological parameters (temperature, pressure, water vapor concentrations, cloud optical thickness, and cloud height) are calculated by the climate model, and the O₃ columns follow from the chemistry calcu-

lations (stratospheric O₃ columns are prescribed, see section 2.5). It should be noted that at this stage of the model development prescribed instead of calculated O₃ concentrations are used for the GCM radiation calculations.

The gas phase chemical scheme is solved using an Eulerian Backward Iterative (EBI) method [Hertel *et al.*, 1993]. Although the EBI scheme uses 2–3 times more computer time than the often applied Quasi Steady State Approximation, it is numerically more stable, which proved to be important in association with strong variabilities in calculated cloud parameters and NO_x concentrations in emission areas during rapid changes in meteorological conditions. Comparison of the EBI scheme with a Gear code demonstrated its accuracy under a wide range of atmospheric and chemical conditions.

Transport of the following tracers is calculated explicitly: odd-nitrogen (NO + NO₂ + NO₃ + 2*N₂O₅ + HNO₄), O₃, CO, CH₄, HNO₃, H₂O₂, and CH₃O₂H. Additional reaction products are not transported in view of their short chemical lifetime compared to the time constant of transport.

2.3. Emissions

The total emission of NO considered in the model is 40 Tg N yr⁻¹, attributed to industrial activities (20 Tg N yr⁻¹), lightning (4), soil microbiological processes (10) and biomass burning (6). The magnitude and the seasonal and global distributions of NO emissions are the same as used by Dentener and Crutzen [1993], although in the present study, the emissions from soils are not adjusted to account for NO_x “trapping” by vegetation. In future, we plan to evaluate lightning and soil emissions consistent with ECHAM calculated parameters.

The total emission of CO is 1900 Tg yr⁻¹, distributed over energy use (450 Tg yr⁻¹), biomass burning (700), vegetation (100), formation from natural (280) and anthropogenic (300) higher hydrocarbons, oceans (40), and wildfires (30). These values were adopted from a model study by Lelieveld and Van Dorland [1995]. However, we have increased the emissions from biomass burning, which are now closer to the estimate of Logan *et al.* [1981] and well within the range given by Seiler and Conrad [1987]. The CO emissions applied in our model are consistent with IPCC [1994].

Emissions of CH₄ are not represented in the model. Instead, we prescribe CH₄ surface concentrations of 1772 ppm in the northern and 1680 in the southern hemisphere. These values are taken from Lowe *et al.* [1994] who used the measurements reported by Steele *et al.* [1987]. Because the lifetime of CH₄ is relatively long, approximately 10 years, explicit modeling of CH₄ emissions would require a spin-up simulation of several years. The fact that seasonal and latitudinal variations in CH₄ concentrations are neglected with the present approach is only of minor importance for the budgets and the distributions of tropospheric CO and O₃ compared to other uncertainties in the model.

2.4. Deposition Processes

The model considers dry deposition of O₃, NO, NO₂, NO₃, N₂O₅, HNO₃, and H₂O₂. The deposition velocities v_d for the chemical species are listed in Table 1 and are adopted from Dentener and Crutzen [1993]. Dry deposition velocities for NO₃ and N₂O₅ are the same as for HNO₃.

Since O₃ is the focus of this study, and the dry deposition velocity of O₃ is known to exhibit large variations over land connected, for example, with vegetation type, soil type, and radiation [e.g., Galbally and Roy, 1980], the calculation of dry

Table 1. Dry Deposition Velocities

Species	Land	Water/Ice
NO	0.04	...
NO ₂	0.25	0.10
HNO ₃	2.00	0.80
O ₃	0.40	0.05
H ₂ O ₂	0.50	0.50

Measurements are in centimeters per second.

deposition based upon a constant velocity is rather inaccurate and will affect O₃ concentrations in the continental boundary layer significantly. A new dry deposition formulation, based on model calculated parameters and detailed vegetation properties, resulting in variable dry deposition velocities, has been developed and tested and is discussed in an accompanying paper [Ganzeveld and Lelieveld, 1995]. The results of that study show that the monthly averaged surface O₃ concentration in continental boundary layers changes between -25 to +15% when compared to the constant deposition velocity approach. In the free troposphere and in remote oceanic sites, however, the change in O₃ concentrations is a few percent or less.

Dry deposition of CO, representing about 10% of the total sink of CO [Logan *et al.*, 1981], is not included in our model yet. Accounting for CO dry deposition will decrease modeled CO concentrations and therefore increase OH concentrations. This effect will be most significant in the continental boundary layers, and only small in the free troposphere and in remote areas. The resulting change in HO₂ production by the reaction of OH with CO will affect the chemical production and destruction of O₃, but on a global scale, the effect is only small.

The model considers wet deposition of H₂O₂ and HNO₃. The calculation of in-cloud scavenging, below-cloud scavenging and release into the atmosphere after evaporation of precipitation uses the cloud (micro-)physical parameters calculated by ECHAM. Treatment of dry and wet deposition processes in the model is described in detail in the appendix.

Apart from HNO₃ and H₂O₂, other species such as CH₂O, CH₃O₂H, and HNO₄ are subject to wet deposition. However, the influence of these processes on the budget and distribution of O₃ is considered to be only marginal regarding the occurrence and specific lifetimes of these species.

2.5. Stratospheric O₃ and NO_x

The exchange of air between the stratosphere and the troposphere in the model is determined by the simulated dynamics. The simulated tropospheric O₃ source resulting from cross-tropopause transport is directly associated with the simulated exchange of air. Stratospheric O₃ concentrations have to be realistic since the stratospheric source contributes significantly to the tropospheric O₃ budget. However, the tropospheric chemistry scheme does not fully account for O₃ production/destruction in the stratosphere. Stratospheric ozone concentrations are therefore taken from a two-dimensional troposphere-stratosphere chemical model [Brühl and Crutzen, 1988]. A disadvantage of this method is the implicit assumption that ozone concentrations in the stratosphere do not vary with longitude. Therefore, in the lower stratosphere, that is, 1–2 model layers above the tropopause, O₃ is not fixed but depends on transport, while for concentration changes due to chemical reactions, the tropospheric chemistry scheme is used. The tropopause is defined as the uppermost layer of the troposphere

for which the variation of potential temperature with height is smaller than the empirical threshold value of 0.0028 K m^{-1} .

In order to obtain realistic NO_x and HNO₃ concentrations, we derive total NO_y concentrations in the lower stratosphere from the NO_y-O₃ ratio. Measurements of the ratio at altitudes above a potential temperature of 430 K range from 0.0022 to 0.0035 between 60°S and 20°S, from 0.0014 to 0.0034 between 20°S and 20°N, and from 0.0026 to 0.005 between 20°N and 70°N [Murphy *et al.*, 1993]. In our model we adopted a value of 0.002 for the latitude bands between 20°S and 20°N, and 0.004 from the 20° to 60° latitude bands, while transport controls NO_y in high latitudes.

3. Comparison With Measurements

3.1. Ozone

Figure 1 shows calculated monthly averaged O₃ concentrations and standard deviations for O₃ for different sites over a range of latitudes in the NH and SH. Open squares denote measurement results from background stations, adopted from Oltmans and Levy [1994]. The period of observation differs from site to site, varying from 1 to almost 20 years. The calculated data relate to the surface layer, except for Niwot Ridge, Izaña, and Mauna Loa where layers closest to the height of the measurement site are chosen. The lengths of the vertical bars represent 2 times the standard deviation. They express the model variability, and may be compared to the ninetieth percentile ranges given by Oltmans and Levy [1994] (omitted in Figure 1 for clarity).

At Barrow, at the Arctic Ocean coast in Alaska, the model strongly underestimates O₃ concentrations, especially during autumn and winter. The observed spring minimum is possibly due to photochemical O₃ destruction associated with atmospheric Br [Barrie *et al.*, 1988], which is not represented in the model. The model predicts a spring maximum which is in fact measured directly above the boundary layer. A salient feature in most other background NH locations is the occurrence of a spring maximum and a summer minimum, associated with the relatively large downflux of O₃ from the stratosphere in the spring and relatively efficient O₃ destruction in the ocean troposphere in the summer, and is captured very well by the model. Absolute O₃ concentrations in Reykjavik (Iceland) and Mace Head (west coast of Ireland) are too low in the model, especially in winter and spring. At Mace Head, the modeled standard deviation increases from winter to summer as the site is increasingly influenced by European pollution photochemistry. At Niwot Ridge (Colorado), the photochemical O₃ production during late spring and in the summer appears to be relatively strong in the model, resulting in a calculated summer maximum for O₃ rather than a spring maximum due to stratosphere-troposphere exchange as indicated by the measurements. Probably the model grid used for the comparison does not represent the characteristics of the measurement site. The calculated concentrations are too low for this location, which may partly be caused by the absence of higher hydrocarbon chemistry in our model. On the basis of a comparison between model calculations and O₃ observations Liu *et al.* [1987] concluded that the chemistry of higher hydrocarbons is of particular importance for photochemical O₃ production in Niwot Ridge.

The Bermuda grid square calculations yield too low O₃ during winter and spring and too high O₃ during summer. The model grid which represents the Bermuda site is influenced significantly by pollution from the North American continent.

The neighbouring grid eastward is less influenced by pollution and fits the measured concentration pattern better, especially during summer and autumn. The spring to summer O₃ maximum in Izaña is not reproduced by the model. At Mauna Loa (Hawaii), the spring O₃ maximum from stratospheric influence is reproduced well. Standard deviations are relatively high in Mauna Loa and Izaña, both in the measurements and in the model calculations. According to Oltmans and Levy [1994], this is related to wind regimes characteristic for mountainous areas, yielding highest ozone levels at night associated with a downslope flow. Our coarse grid model does not reproduce these relatively small-scale features, since both sites are located in ocean grids and the model has limited orographic detail. For Mauna Loa, the high standard deviations that are calculated may be associated with the variability in convective transports. In Izaña, anthropogenic emissions from the continent are likely to play a role in the model; sometimes European pollution is transported southward to Africa and is mixed into the airmasses that are transported to Izaña.

Modeled O₃ concentrations for the clean tropical site Barbados are characterized by an O₃ maximum in winter and a minimum in summer, related to the net photochemical O₃ destruction intensity during both seasons. The model fits the measured concentrations well, although they are somewhat low during winter. Here, the standard deviations are low throughout the year, similar to the measurements. The annual O₃ concentration profile for Samoa, in the southern hemisphere, resembles that for Barbados, but maximum and minimum are shifted 6 months, in line with the seasonal variations. Samoa and the other southern hemisphere sites are characterized by a winter maximum and a summer minimum. Although this is represented well by the model, the simulated maximum occurs 1 or 2 months later than the measured one for mid- and high-latitude sites, probably connected with particularly inefficient transport in the model of O₃ southward during winter. Furthermore, O₃ concentrations are generally underestimated in the southern hemisphere. The extent of this underestimation increases toward the South Pole, which will be discussed later. As can be seen in the measurements as well, the standard deviation is much lower in the southern hemisphere than at the northern hemisphere, reflecting the remoteness of the sites.

Figure 2 shows a comparison between measured and modeled O₃ concentration profiles for eight sites located in the northern and southern hemisphere. Measured profiles are taken from Figures 1 and 2 in Oltmans *et al.* [1989]. Data for the northern hemisphere winter and summer season were not included in this reference; these are adopted from Table 1 in Komhyr *et al.* [1989] and have a lower vertical resolution. All concentration profiles are based on electrochemical concentration cell (ECC) ozonesonde observations. Standard deviations produced by the model are not shown, because they are too small to account for the differences between calculated and modeled profiles.

The profiles show that we generally underpredict O₃ mixing ratios throughout the troposphere. For the two northernmost sites, Edmonton and Resolute (Canada), the strongest underestimation of modeled O₃ around the tropopause (located between 200 and 300 hPa) occurs during spring, suggesting a too low stratospheric O₃ injection into the troposphere at these latitudes. Stratospheric O₃ injection at the midlatitudes is associated with cut-off lows and tropopause foldings. These are not simulated properly due to the relatively coarse grid resolution applied in this study, as will be discussed in more detail

Figure 1. Measured and calculated monthly average O₃ mixing ratios, including model standard deviations, at the surface (parts per billion by volume). Open squares denote the measurements [Olmans and Levy, 1994].

in section 4. For Boulder (Colorado), concentrations around the tropopause are simulated quite well, but the surface and midtroposphere concentrations are underpredicted.

The modeled profiles at Resolute, Edmonton, and Boulder display a strong vertical concentration gradient near the surface. Unfortunately, the vertical resolution is too low to detect

a similar gradient in the measurements. We note that such vertical O₃ gradients over the continents are a general characteristic of the model, connected with the boundary layer representation. Concentrations decrease toward the surface as a result of dry deposition, which removes O₃ from the surface layer. Differences may be as high as 5 ppb from one layer to the

Figure 2. Measured and calculated seasonally averaged O_3 mixing ratios (parts per billion by volume) as a function of height (hectopascal). Open squares denote the measurements [Komhyr et al., 1989; Oltmans et al., 1989].

Figure 2. (continued)

next for seasonally averaged O₃ concentrations. This may indicate that the boundary layer turbulent mixing in the model is too slow for species with significant surface destruction or emission. This could also contribute to the underestimation of O₃; stronger upward mixing of NO_x would increase the net O₃ production per NO_x molecule, and therefore O₃ concentrations at higher altitudes. Associated mixing of free tropospheric air into the boundary layer would also result in higher surface O₃ concentrations.

For Hilo (Hawaii), simulated O₃ concentrations are too high near the tropopause in the winter and spring when compared to the measurements. Possibly, the influence of the subtropical subsidence carrying O₃-rich air downward is too strong. In the measured concentration profiles in Hilo, midtropospheric maxima in March, April, and May (MAM) and September, October, and November (SON) are found. The Hilo profiles resemble those measured at Samoa, although here, the midtropospheric maxima are most pronounced in SON and December, January, and February (DJF). Probably the particular shape of the profiles is related to deep convective transport, through which O₃-poor air is transported rapidly from the surface to the upper troposphere, while compensating mesoscale motions carry relatively O₃-rich air downward from the upper troposphere [Lelieveld and Crutzen, 1994]. The comparison between model and measurements indicates that the strength of the convective motions in the upper troposphere may be overestimated in the autumn and winter at Samoa.

At Lauder (New Zealand), the profiles indicate that the tropopause height is simulated well. On the other hand, too low O₃ concentrations are calculated in the midtroposphere, especially in the winter and the spring. This may be associated with the inability of the model at T21 resolution to properly simulate tropopause foldings in midlatitudes, through which O₃ enters the troposphere, and partly with underestimation of transport from polluted areas. The modeled O₃ mixing ratios are too low throughout the troposphere at the South Pole, Syowa, and Cape Grim, due to underestimation of O₃ transport from low latitudes into the Antarctic. Further, the model fails to reproduce the relatively small-scale (~1 grid square) katabatic flow that dominates surface O₃ levels in Antarctica by transport from the stratosphere. This may improve in future by applying a higher resolution version of ECHAM.

In summary, the model captures the monthly average surface concentrations and seasonal profiles of O₃ relatively well. The model does not perform well for sites near or in the Arctic and Antarctic regions where calculated O₃ concentrations are systematically too low. This is partly due to underestimation of O₃ transport from the midlatitudes (also found in the ECHAM tracer transport test by Feichter *et al.* [1991]), and partly due to the large local influences of the stratosphere on surface concentrations, especially in the Antarctic.

3.2. Nitrate Deposition

In Table 2 we present a comparison of calculated and observed annual average nitrate wet and total deposition values. The measurement compilation is taken from Dentener and Crutzen [1994] where further references can be found. In some European sites, bulk samplers were used for the measurements; for these sites total (wet + dry) deposition values are more suitable for comparison with measured values. For some areas that are characterized by strong deposition gradients from one grid cell to the next, we show the range of values over the neighbouring grids. For most European and North and

Table 2. Measured and Calculated Yearly Nitrate Wet Deposition Rates

Site	Latitude/ Longitude, deg	Nitrate Wet Deposition		Total Deposition
		Measured	Simulated	Simulated
Far Oer*	61N 7W	247	37	47
Norway*	69N 25E	45	72	96
Sweden	57N 18E	345	240	289
Baltic*	58N 22E	283	240	289
NAO ship	57N 20W	40	39	47
Ireland	52N 10W	117	50	66
Portugal	42N 7W	25	40	59
Amsterdam Island	38S 78E	8	14	16
Samoa	14S 170W	16	8	9
Hawaii	20N 156W	17	7	8
Amazone Basin	5S 55W	110	130	246
San Carlos	2N 67W	175	188	342
Torres de Paine	52S 73W	5	7	12
Lake Calado	10S 50W	100	129	287
Puerto Rico	18N 67W	136	22	28
Costa Rica	10N 85W	50	72	83
C. Amazonia	3S 60W	70	154	310
Bermuda	32N 65W	70	242	329
			(67–375)	(95–829)
Florida	25N 80W	162	118	515
Massachusetts	42N 70W	271	353	671
			(161–376)	(268–873)
Nova Scotia	45N 63W	226	327	603
			(146–353)	(222–829)
New Brunswick	46N 67W	281	327	603
			(146–353)	(222–829)
Newfoundland	49N 59W	60	164	240
			(64–327)	(74–603)
Quebec	50N 67W	229	198	309
Poker Flat	67N 147W	11	11	14
Beijing	40N 116E	126	50	144
Guizhou	27N 106E	164	107	199
Hong Kong	22N 114E	226	143	348
Linan	30N 120E	398	206	475
Allababad	25N 82E	144	6	107
Jodphur	26N 73E	62	2	81
Minicoy Island	8N 73E	51	37	50
Nagpur	21N 79E	92	45	158
Pune	19N 74E	61	38	98
Port Blair	12N 93E	104	31	53
Ryori	39N 141E	174	80	97
Katherine	14S 132E	65	23	39
Cape Grim	41S 144E	30	8	24
Barrington Tops	32S 151E	94	21	68
Dorrigo	30S 152E	124	26	62
Coffs Harbour	30S 153E	96	26	62
Wagga Wagga	35S 147E	78	21	68
Newplymouth	39S 175E	54	14	16
Congo south	4S 12E	181	111	199
Congo north	5N 17E	407	116	274
			(11–364)	(115–464)
Nigeria	8N 8E	200	81	173
Cape Point	34S 18E	28	2	9
			(0.2–47)	(4–132)
Dye 3	65N 43W	56	11	12
South Pole	85S	1	0.2	0.3
			(0.2–0.7)	(0.3–0.9)

Measurements in milligrams Nitrogen per square meter per year.

*Sites where bulk samplers were used.

South American sites the modeled deposition agrees within ±50% with the measured values, which is satisfactory considering that the nitrate deposition is strongly dependent on very variable local NO_x sources, chemistry, and precipitation patterns.

The strong underestimation of modeled deposition values for Far Oer and Ireland is probably caused by too weak transport of NO_x and HNO₃ from more polluted regions. On the other hand, for Bermuda the model overpredicts nitrate deposition, which is probably caused by artificial transport from the American continent by the instantaneous mixing over large grid boxes in the model, as was already noted in the discussion of Figure 1. Nitrate deposition calculated for the adjacent oceanic grid cells (lower value of the range given in Table 2) agrees much better with the measurements. A similar argument applies to the simulation of nitrate deposition on Newfoundland.

For the Asian sites, simulated wet deposition is underestimated by up to 75%, and for some cases by more than an order of magnitude. This may partly be caused by an underestimation of precipitation in these regions, especially during the summer monsoon season in India for which the measured precipitation is about 4 times higher than the modeled precipitation [Roeckner *et al.*, 1992]. However, dry deposition of nitrate compensates for this; therefore simulated total deposition exceeds the measured wet deposition. The nitrate wet deposition measured at the Australian and Pacific sites (including Samoa and Hawaii) is systematically larger than the model results (by up to 75%), even when the total simulated deposition is considered. This suggests that transport of NO_x and HNO₃ from more polluted regions is underestimated. We find that yearly averaged concentrations of HNO₃ calculated for the North and South Pacific are too low by about a factor of 2 when compared to measurement values [Prospero and Savoie, 1989]. Further, peroxyacetylnitrate (PAN) acts as a reservoir species for NO_x but is not considered in the model. PAN can be transported over much larger distances than NO_x, thereby increasing NO_x concentrations at remote locations. However, the model results of Kasibhatla *et al.* [1993] show too low NO_x and HNO₃ concentrations over the eastern North Pacific even when taking PAN into account. The missing PAN chemistry may be a reason for the underestimation of the deposition at Dye 3 in the Arctic region; Singh *et al.* [1992] demonstrated that 50–70% of the NO_x present in the Arctic derives from PAN. For the African sites nitrate deposition is lower than indicated by measurements. Here, again, an underestimation of the precipitation amount may be the cause.

3.3. Carbon Monoxide

Table 3 presents a comparison of annually averaged simulated and measured CO concentrations at sites between 71°N

Table 3. Measured and Calculated Yearly Averaged CO Concentrations

Site	Latitude/ Longitude, deg	Average Yearly CO	
		Measured	Simulated
Ascension Island	8S 142W	86.8	85.9
Barrow	71N 156W	152.7	143.8
Christmas Island	2N 157W	80.9	88.0
Guam	13N 144W	106.4	95.0
Cape Kumakahi	19N 155W	108.7	95.7
Mauna Loa	19N 155W	100.3	85.3
Niwot Ridge	40N 105W	121.2	128.6
Samoa	14S 170W	63.7	66.8

Concentrations in parts per billion by volume. Measurement result have been adopted from Novelli *et al.* [1992].

Table 4. Simulated Global Budget for O₃

	Season	30°– 90°N	0°– 30°N	0°– 30°S	30°– 90°S	Global
Net chemical formation	MAM	52	–44	7	–3	11
	JJA	97	8	12	–6	110
	SON	35	11	6	–21	31
	DJF	7	–17	36	–7	18
Year Total		190	–43	61	–37	170
Net transport into atmospheric compartment	MAM	15	109	35	19	178
	JJA	–15	59	55	38	137
	SON	–13	49	43	19	98
	DJF	39	99	2	23	163
Year Total		26	315	135	99	575
Dry deposition	MAM	55	76	44	16	191
	JJA	80	67	57	21	225
	SON	48	61	53	17	179
	DJF	27	70	41	8	145
Year Total		210	272	195	62	740
Average tropospheric content	MAM	72	81	58	35	246
	JJA	74	69	60	42	245
	SON	56	67	68	40	231
	DJF	52	73	63	32	221
Year Total		64	73	62	38	236

The net chemical formation, net transport, dry deposition (teragrams ozone (3 months)^{–1}; (teragrams ozone per year), and tropospheric content (teragrams ozone) are given. MAM is March, April, and May. JJA is June, July, and August. SON is September, October, and November. DJF is December, January, and February.

and 14°S. The measurement values are the “curve fitted” values listed in Table 3b by Novelli *et al.* [1992]. Apart from Niwot Ridge, which is from time to time significantly influenced by transport from anthropogenic sources, all sites listed are located in remote and thus relatively unpolluted regions, which are most important for the present model version to simulate correctly.

The agreement between modeled and measured concentrations is quite good. The largest underestimations (of the order of 10–15%) are found for the northern hemisphere Pacific sites Guam, Cape Kumakahi, and Mauna Loa. This may partly be related to the occurrence of a relatively strong north–south gradient in CO concentrations in these regions, due to an increasingly efficient destruction by OH toward the equator, whose resolution is not captured correctly by the model. However, distances from the most important source areas are large. As was noted in section 3.2 concerning HNO₃, an insufficient transport from the source areas is also a probable cause for the underestimated CO concentrations in remote locations.

4. Model Results

4.1. Budget and Distribution of O₃

Table 4 shows the tropospheric source and sink terms, and the tropospheric content of O₃, subdivided in four semi-hemispheres and four seasons (December, January, February (DJF); March, April, May (MAM); June, July, August (JJA); and September, October, November (SON)). Global and yearly average values are also given.

The transport terms in Table 4 reflect the net changes in tropospheric O₃ content in each compartment due to all transports, and are therefore the sum of the flux of O₃ through the tropopause and of horizontal transport from one grid to the adjacent ones. Assuming that interhemispheric transport for

O₃ is small compared to other source terms, the separate sums for the northern and the southern areas represent the net stratospheric source for each hemisphere. These values are 341 and 234 Tg O₃ yr⁻¹ for the northern and southern hemisphere, respectively. The total amount of O₃ transported across the tropopause, 575 Tg yr⁻¹, lies within the range calculated earlier by general circulation models, 512–768 Tg yr⁻¹, while downward fluxes are about 50% larger in the northern hemisphere compared to the southern hemisphere [Gidel and Shapiro, 1980; Mahlman *et al.*, 1980; Levy *et al.*, 1985]. The range of 200–870 Tg yr⁻¹ given by Murphy and Fahey [1994] reflects the present uncertainty regarding this source of tropospheric O₃. The down transport maximizes during winter and spring months in both hemispheres, coinciding with maximum lower stratospheric O₃ concentrations and frequencies of synoptic disturbances. However, the model resolution is too coarse to accurately simulate the relatively small-scale tropopause foldings in midlatitudes which are believed to constitute a major source of tropospheric O₃, as will be discussed later in this section. Model results for downward transport of stratospheric O₃ should therefore be conceived as preliminary.

The calculated global yearly O₃ dry deposition flux is 740 Tg yr⁻¹. For 30°–90°N, dry deposition of O₃ has its maximum in the summer, which is related to the maximum O₃ photochemical production in the boundary layer. In the northern hemisphere tropics, a slight maximum occurs during winter/spring, coinciding with considerable transport of stratospheric O₃ into the area during this period.

Net chemical production in the troposphere, 170 Tg yr⁻¹, is an additional source of O₃, which is to a large extent induced by anthropogenic emissions. On a global scale, the largest net chemical production of O₃ takes place in the northern hemisphere midlatitudes during summer, due to a combination of strong insolation and high anthropogenic NO_x emissions, while O₃ destruction through photolysis and subsequent reaction of O(¹D) with H₂O is less important compared to the tropics. Between 30° and 90°S net chemical destruction occurs throughout the year. In the tropics, photochemical production is strongly enhanced by NO_x emissions from biomass burning, which maximize in the dry season. However, in this period, also the influx of stratospheric O₃ maximizes (~30° latitude), leading to relatively large destruction of O₃. Hence the net photochemical production terms for the tropical winter and spring do not only reflect the strong influence of biomass burning emissions.

WMO [1995] lists integrated budget terms calculated with two three-dimensional models [Lelieveld and Van Dorland, 1995; Berntsen and Isaksen, 1994]. The calculated global tropospheric budgets are for the stratospheric O₃ source terms 528 and 846 Tg yr⁻¹, for dry deposition 953 and 1178 Tg yr⁻¹, and for net photochemical production 427 and 295 Tg yr⁻¹, respectively. Comparison with our calculated budget terms indicates fair agreement for the stratospheric O₃ source. However, our estimates of the net photochemical production and dry deposition are significantly lower. It is likely that our model, which has a relatively high vertical resolution near the surface, is less “diffusive” than the three-dimensional models included in WMO [1995]. This results in a relatively less efficient transport of NO_x from source regions, which decreases O₃ formation in remote regions. Differences in modeled surface deposition between models probably reflect differences in vertical transport connected with the representation of the boundary layer. Differences in O₃ stratospheric influx and dry

Table 5. Budget Terms for Photochemical O₃ Production and Destruction

	30°– 90°N	0°– 30°N	0°– 30°S	30°– 90°S	Global
<i>O₃ Formation</i>					
NO + HO ₂ → OH + NO ₂	503	957	867	93	2420
NO + CH ₃ O ₂ → NO ₂ + CH ₃ O	127	324	283	36	770
<i>O₃ Destruction</i>					
O(¹ D) + H ₂ O → 2OH	171	792	673	75	1711
O ₃ + HO ₂ → OH + 2O ₂	185	373	289	74	920
O ₃ + OH → HO ₂ + O ₂	69	156	125	19	368

The global net production of O₃ from the reactions listed in Table 5 is 191 Tg yr⁻¹. Additional net loss of 21 Tg yr⁻¹, that accounts for net chemical production listed in Table 4 (170 Tg yr⁻¹) is attributed to the reactions HNO₃ + OH (+16 Tg yr⁻¹), N₂O₅ decomposition (–27), NO₃ photolysis (–11). Budget terms are in teragrams ozone per year.

deposition terms will directly influence the net photochemical production since the total O₃ budget approximately balances over a year. We stress that the global net photochemical production is the relatively small residue of large production and destruction terms (Table 5), and may therefore not be a proper diagnostic for model calculated O₃ chemistry.

Figure 3 shows zonally averaged O₃ concentrations in the troposphere for four seasons. The convective region near the Intertropical Convergence Zone (ITCZ) at the equator is clearly discernable as a relatively O₃ low column of air from the surface up to the tropopause (~16 km). The O₃ lifetime is shortest (less than 1 week) in the tropical marine lower troposphere, associated with high insolation and humidity and resulting in low O₃ concentrations. Convection transports relatively O₃-poor air from the surface upward up to the tropical tropopause. In the subtropical subsidence areas downward transport of O₃-rich air prevails. The simulated zonal average O₃ distributions qualitatively resemble the latitude-altitude O₃ profiles shown by Smit *et al.* [1989], based on measurements by balloon soundings from a ship between 60°N and 40°S over the Atlantic Ocean. These show a distinct area of low O₃ at 0°–10°S extending from the surface up to the tropopause, and an area of O₃-rich air in the upper and midtroposphere at 30°–40°N. In our model, this area of O₃-rich air results for a significant part from the influx of stratospheric O₃ into the troposphere. In the northern hemisphere in DJF, the influx from the stratosphere appears as a relatively narrow (~20°) tongue (Figure 3a); O₃ enters the troposphere approximately at 30°N through the tropopause break between the high tropical tropopause and the lower midlatitude tropopause, the location of the subtropical jet stream. The O₃ largely remains between 30°N and the equator, where it is chemically destroyed. Tropopause folds at midlatitudes, associated with synoptical disturbances, causing O₃ influx from the stratosphere, are not resolved in the coarse grid version (T21) of our model. Therefore calculated free tropospheric O₃ concentrations are relatively low north of 40°N in DJF. In MAM the concentration of O₃ increases throughout the northern hemisphere troposphere. The influx from stratospheric O₃ is also large in this season, which combines with significant net photochemical production of O₃ in spring (Tables 4 and 5); this causes the relatively highest average O₃ concentrations at the surface throughout the year. In JJA, the influx of O₃ from the stratosphere in the northern hemisphere has decreased sharply. During this sea-

Figure 3. Calculated zonal mean O₃ mixing ratios (parts per billion by volume) for (a) December, January, and February (DJF); (b) March, April, and May (MAM); (c) June, July, and August (JJA); and (d) September, October, and November (SON).

son, convection causes efficient mixing of pollutant O₃ precursors from the boundary layer through the free troposphere, causing elevated O₃ concentrations aloft. Finally, surface and free tropospheric O₃ concentrations decrease again in SON when photochemical activity decreases in the northern hemisphere.

In the southern hemisphere, maximum net photochemical O₃ production takes place in DJF. Practically all NO sources are located between 0° and 30°S, a region characterized by strong convective motions that cause efficient mixing of pollutants, for example, from biomass burning emissions, into the mid and upper troposphere. This produces relatively high O₃ concentrations above the boundary layer. JJA and SON are characterized by relatively lower photochemical activity, but stronger input of O₃ from the stratosphere. Transport of O₃ and its precursors from tropical regions toward the South Pole is small, so that O₃ concentrations are low south of 60°S throughout the year, especially in summer when net photochemical destruction of O₃ is strongest in these NO_x-poor regions.

Figure 4 shows calculated surface O₃ concentrations for all seasons. Concentrations are seasonally and 24-hour averaged over the lowest layer of the model, that is, representing approximately 30 m above the surface. High photolysis rates, in combination with anthropogenic NO_x-emissions, cause rela-

tively high O₃ concentrations over land in the northern hemisphere during the summer (typical: 25–40 ppb). In the winter, concentrations are up to about 50% lower in the polluted surface layer.

Concentrations over the oceans are higher in the winter than in the summer due to lower photolysis rates and, therefore, less efficient destruction of O₃ in these NO_x-poor environments. The results in Figure 4 show the influence of O₃, produced over the polluted continents, on O₃ levels in marine locations in the northern hemisphere, particularly between 25° and 50°N. Although JJA concentrations over land are relatively high, the O₃ is efficiently destroyed after transport to NO_x-poor marine regions. In combination with the strong stratospheric O₃ source in winter and spring, a spring maximum occurs over the northern Atlantic Ocean, while O₃ concentrations minimize during summer. This typical seasonal cycle is confirmed by measurements as discussed in section 3. The effect of biomass burning emissions in the tropics and subtropics is clearly discernable from the simulated regional O₃ maxima over Africa and South America. O₃ levels are particularly high south of the equator when burning activity is strongest (in September and October).

An interesting feature in Figure 4 is the O₃ surface low around the equator between about 150°E and 170°W, which moves south-north with season, coinciding with the movement

Figure 4. Calculated average surface O₃ mixing ratios (parts per billion by volume) for (a) December, January, and February (DJF); (b) March, April, and May (MAM); (c) June, July, and August (JJA); and (d) September, October, and November (SON).

of the ITCZ. The area is characterized by high sea surface temperatures and therefore strong evaporation, thus high water vapor concentrations, and strong convection and precipitation. These high levels of precipitation, removing nitrogen oxides from the atmosphere, and of water vapour, leading to efficient chemical destruction of O₃, result in low O₃ concentrations at the surface. Convection mixes the O₃ depleted air throughout the troposphere up to the tropopause, as noted earlier in the discussion of Figure 3. An area of low O₃ also occurs over the Indian Ocean south of the equator during DJF and MAM. In the Antarctic, modeled surface concentrations are lower throughout the year than the measured concentrations, as discussed in section 3.1.

4.2. Budgets of CH₄ and CO

The chemical destruction of CH₄ through reaction with OH, as predicted by the model (454 Tg yr⁻¹), gives an indication of the total source strength. Other CH₄ sinks are microbiological oxidation in soil surface layers with a strength of 30 ± 25 Tg CH₄ yr⁻¹ [Born *et al.*, 1990], and chemical destruction in the stratosphere that is approximately 45 Tg CH₄ yr⁻¹ [Cruzen and Schmailzl, 1983]. If we include an annual CH₄ increase of ~ 20 Tg yr⁻¹, we derive a total CH₄ source of ~ 550 Tg yr⁻¹, which is ~ 30 Tg yr⁻¹ higher than the previous estimate by Lelieveld *et al.* [1993]. We find a yearly average tropospheric content of 3980 Tg CH₄ which is somewhat lower than the 4130 Tg calculated by Lelieveld and Van Dorland [1995] who applied

explicit CH₄ emissions in their model. The difference (approximately 4%) is probably due to different vertical resolutions of the models, which result in small differences in calculated troposphere volumes. The lifetime of CH₄ as computed with our model, approximately 8.8 years, is relatively low compared to other estimates: e.g., Lelieveld *et al.* [1993] calculate $10 \text{ yr} \pm 10\%$. This indicates that our calculated OH concentrations may be relatively high, probably related to the temperature bias of the climate model in the upper tropical troposphere.

Table 6 gives an overview of the calculated global CO budget. Almost 75% of all CO is emitted in the tropics, to a large extent associated with biomass burning. However, as a result of significant CO transports from the 30° and 60°N region to the tropics and of the oxidation of CH₄ by OH which is most efficient in the tropics, an even larger amount is photochemically destroyed between 0° and 30°N than is emitted there. CO

Table 6. Tropospheric Budget of CO

	30°–90°N	0°–30°N	0°–30°S	30°–90°S	Global
Emission	474	638	766	22	1900
CH ₄ + OH	103	341	303	49	795
CO + OH	-426	-1105	-949	-163	-2644
Net chemistry	-323	-764	-646	-114	-1849
Content	100	115	101	62	377

Tropospheric budget is in teragrams carbon per year.

emissions between 30° and 90°S are only very small; a large fraction of CO that is photochemically destroyed in this area has been transported into the region from the tropics. The global budget in Table 6 leaves a deficit of 51 Tg CO; this amount is transported to the stratosphere where it is efficiently removed by reaction with OH. The results indicate an average CO lifetime of 2.5 months. Although the comparison of modeled and measured CO concentrations shows a good agreement (Table 3) and suggest that the total CO emission of 1900 Tg CO yr⁻¹ is a reasonably accurate estimate in this simulation, we note that a lower tropical OH concentration, together with a treatment in the model of CO dry deposition and explicit higher hydrocarbon emissions and chemistry will alter the modeled CO distribution to some extent. However, the strength and surface dependence of CO dry deposition and the size and distribution of CO and nonmethane hydrocarbons (NMHC) emissions are still highly uncertain, which renders estimation of the size and sign of possible changes difficult.

5. Conclusion

We have presented first results of tropospheric chemistry calculations with the chemistry general circulation model ECHAM. The chemical code describes the background CH₄-CO-NO_x-HO_x chemistry, explicit emissions of NO and CO, and dry and wet deposition processes.

In our analysis we have concentrated on the simulation of tropospheric O₃. Large seasonal variations in stratosphere-troposphere exchange of O₃ are calculated, showing a maximum during winter and spring. The total amount of O₃ transported across the tropopause, as well as the distribution between the northern and southern hemisphere, are in fair agreement with previous estimates based on (more detailed) modeling and observational studies. A strong seasonal variability is also found in the photochemical production and destruction of O₃, with maximum production in polluted NO_x-rich continental regions and maximum destruction in the NO_x-poor marine tropical troposphere.

To evaluate the distribution of O₃ in the troposphere, we have compared simulated and measured surface concentrations and profiles. Regarding surface concentrations, the model performs qualitatively well showing a realistic seasonal variability for most sites studied. The model captures the spring O₃ maximum and summer minimum measured in remote sites in the northern Atlantic Ocean. The model is able to quantitatively reproduce O₃ concentration patterns in remote tropical locations, but it underestimates O₃ in midlatitudes. Therefore the calculated total tropospheric O₃ burden of 236 Tg seems somewhat low in view of the general assertion that the troposphere contains ~10% of the total atmospheric O₃ column, which is ~30 Dobson unit (DU; ~300 Tg).

There appear to be three main reasons for this. First, practically all simulated down mixing of stratospheric ozone occurs at the tropopause breaks at approximately 30° latitude, where it is efficiently destroyed by photochemical reactions. The model grid resolution is too coarse to resolve tropopause foldings at midlatitudes, by which a significant amount of O₃ is expected to enter the troposphere, associated with synoptical disturbances. O₃ injected here has a much longer lifetime than in (sub)tropical regions, especially in winter and spring when the stratospheric source is large, and can therefore be transported over a larger region, including the polar regions. We plan to use the model with a higher resolution (T42 with a

horizontal grid size of 2.8° by 2.8°) which simulates middle and high latitude stratosphere-troposphere exchange more realistically. Second, we may underestimate net chemical production of O₃. This may be partly due to insufficient mixing of chemical species from the polluted boundary layer into the free troposphere, especially important for short-lived NO_x. Also, transport from source areas to remote locations (e.g., the Pacific sites and the poles) seems to be underestimated, possibly connected with flaws in the climate model dynamics. Further, the fact that cloud properties in ECHAM are adequately simulated for the purpose of radiation and precipitation calculations, does not mean that they are comparably suitable for the calculation of the in-cloud and below-cloud scavenging of soluble species, processes that also influence the transport and distribution of NO_x and HNO₃. Further tests are needed in order to evaluate this suitability, using also higher resolutions of the model. Third, the model only considers the basic methane and CO oxidation processes. The influence of higher hydrocarbons may significantly enhance O₃ production locally over polluted regions, while transport of PAN may lead to stronger O₃ formation in remote locations.

Some important model improvements remain to be implemented, to make full use of the possibility to obtain internal consistency within the model by the coupling of chemical and physical processes. These include the new dry deposition scheme presented in an accompanying paper by *Ganzeveld and Lelieveld* [1995], simulation of cloud microphysical and chemical processes, and natural NO and hydrocarbon emissions from a (simplified) biosphere that responds to the model climate. Future developments will also involve descriptions of higher hydrocarbon chemistry and the coupling of natural and anthropogenic sulfur chemistry to the model.

Appendix: Deposition Processes

A1. Dry Deposition

The time rate of change due to dry deposition of the mixing ratio C_i of a tracer i in a surface grid with height h is calculated according to (see *Levy and Moxim* [1989])

$$\frac{\partial C_i}{\partial t} = \frac{v_d}{h} \left\{ \frac{C_i}{1 + v_d/(C_h V_{eff})} \right\}, \quad (\text{A1})$$

where C_h is the drag coefficient for heat, and V_{eff} the wind speed in the surface layer, both calculated by the model.

A2. Wet Deposition

The wet deposition flux of soluble gases W_{surf} (mol per square meter per second) at the surface is given by

$$W_{surf} = \sum_{k=1,19} W(k) = \sum_{k=1,19} W_{pr}(k) + W_{ev}(k) + W_{bc}(k), \quad (\text{A2})$$

where $k = 1, 19$ denotes the ECHAM levels from the top of the model domain to the surface, and $W_{pr}(k)$, $W_{ev}(k)$, and $W_{bc}(k)$ denote the flux divergences integrated between the top and the bottom of each layer k due to in-cloud precipitation formation, evaporation of rain, and below-cloud scavenging, respectively. Consequently, the gas phase mixing ratio of a soluble species in each layer changes according to

$$\frac{\partial C_g(k)}{\partial t} = \frac{\partial C_g(k)}{\partial t} \Big|_{pr} + \frac{\partial C_g(k)}{\partial t} \Big|_{ev} + \frac{\partial C_g(k)}{\partial t} \Big|_{bc} \quad (\text{A3})$$

For calculation of in-cloud scavenging through precipitation formation we distinguish between large-scale and convective clouds. The large-scale cloud scheme calculates for each grid box a cloud cover fraction, f_c , denoting the fractional area actually occupied by clouds. Within the cloud covered area, the change of the mixing ratio in the cloud water of a completely soluble species is given by

$$\frac{\partial C_w(k)}{\partial t} = \beta C_g(k). \quad (\text{A4a})$$

The scavenging coefficient β is evaluated by

$$\beta = 4\pi k_g r_c^2 N_c(k) = 3k_g L_c(k)/r_c, \quad (\text{A4b})$$

where k_g is the mass transfer coefficient calculated with the Frössling equation [e.g., Levine and Schwartz, 1982], r_c is the average cloud drop size (taken to be 10 μm), N_c is the cloud droplet number concentration, and L_c the cloud liquid water content calculated by ECHAM. The transformation of cloud water to precipitation due to coalescence of cloud drops occurs with a precipitation formation rate P_f (kilograms per cubic meter per second). The grid-averaged mixing ratios of dissolved gas present in precipitation water, C_{pr} , and in the gas phase, C_g , change according to

$$\frac{\partial C_{pr}(k)}{\partial t} = -\frac{\partial C_g(k)}{\partial t} = \frac{P_f(k)}{L(k)} f_c C_w(k), \quad (\text{A4c})$$

where $C_w(k)$ follows from the evaluation of (4a). Transformation of cloud to rain water is the rate determining step; uptake of gases (4a) is rate determining only for relatively low liquid water contents of the order of 0.01 g m^{-3} and smaller, which do not produce significant amounts of rain. The wet deposition flux due to precipitation is given by

$$W_{pr}(k) = h(k) \frac{\partial C_{pr}(k)}{\partial t}, \quad (\text{A5})$$

where $h(k)$ is the thickness of layer k . Gases dissolved in cloud water are not transported as such: at the end of each time step they are released and mixed throughout the grid box.

For convective clouds, in-cloud scavenging due to precipitation formation is evaluated using the mass fluxes calculated in the convective cloud scheme. The mass fluxes for chemical tracers are computed analogously to those for water vapour. ECHAM accounts for grid box averaged mass fluxes associated with updrafts, downdrafts, entrainment, and detrainment. For in-cloud scavenging it is assumed that the gases that are transported in updrafts dissolve in the liquid (cloud and rain) water present. HNO_3 is assumed to dissolve completely; H_2O_2 is distributed over the gas and liquid phases using a partitioning factor (presented later in this section). Only the fraction of gases dissolved in rain water contributes to the wet deposition flux. When rain evaporates in downdrafts, dissolved gases are released to the atmosphere.

Evaporation of large-scale precipitation takes place in grid cells that are not or partly covered with clouds. The change of the gas flux due to precipitation evaporation is

$$W_{ev}(k) = -f_{ev} \sum_{j=1, k-1} W_{(j)}, \quad (\text{A6})$$

where f_{ev} is the fraction of the rain water flux that evaporates during a time step in layer k . The gas phase concentration changes according to

$$\left. \frac{\partial C_g(k)}{\partial t} \right|_{ev} = -\frac{W_{ev}(k)}{h(k)}. \quad (\text{A7})$$

If precipitation does not evaporate completely, the released gas is subject to scavenging by the remaining precipitation flux.

The time rate of change in layer k of the concentration of a completely soluble species in precipitation, C_{pr} , due to below-cloud scavenging is given by

$$\left. \frac{\partial C_{pr}(k)}{\partial t} \right|_{bc} = \beta C_g(k) \quad (\text{A8a})$$

with

$$\beta = 3k_g L_p(k)/r_p. \quad (\text{A8b})$$

The effective rain drop radius r_p and the effective liquid water content L_p are calculated according to the empirical relationship by Mason [1971]:

$$r_p(\text{mm}) = 0.3659 \left(\frac{I_{k-1}}{f_{pr}} \right)^{0.21} \quad (\text{A9a})$$

$$L_p(\text{mg m}^{-3}) = 72 \left(\frac{I_{k-1}}{f_{pr}} \right)^{0.88}, \quad (\text{A9b})$$

where I_{k-1} (millimeter per hour) is the intensity of the rain entering level k , averaged over the grid cell, and f_{pr} is the fraction of the grid cell where the precipitation occurs. For precipitation from large-scale clouds, f_{pr} has the value of the cloud cover fraction in the grid cell where the rain is formed; when there are two or more levels containing clouds that produce rain, a maximum overlap is assumed. In the convective mass flux scheme the cloud cover is not calculated explicitly. For below cloud scavenging we have assumed a value of 5%, which is also adopted in the GCM radiation scheme as convective cloud cover. The change in the wet deposition flux and the corresponding decrease of the gas phase concentration in layer k are then computed by

$$W_{bc}(k) = h(k) f_{pr} \left. \frac{\partial C_{pr}(k)}{\partial t} \right|_{bc} \quad (\text{A10a})$$

and

$$\left. \frac{\partial C_g(k)}{\partial t} \right| = -f_{pr} \left. \frac{\partial C_{pr}(k)}{\partial t} \right|_{bc}. \quad (\text{A10b})$$

Note that the gas phase concentration decrease as expressed in (4a) and (8a) is valid only for completely soluble species as HNO_3 . For the partly soluble H_2O_2 , the integrated concentration decrease is scaled with a gas-liquid partitioning factor:

$$\frac{C_{w,eq}}{C_{g,eq} + C_{w,eq}} = \frac{1}{1 + 10^3 H/L}, \quad (\text{A11})$$

where $C_{w,eq}$ and $C_{g,eq}$ are the equilibrium liquid and gas phase mixing ratios, H is the Henry's law coefficient (the dimensionless Henry's law coefficient), and L is the liquid water content (liter per cubic-meter of air).

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