The impact of human activities on the photochemical production and destruction of tropospheric ozone

By W. J. COLLINS*, R. G. DERWENT, C. E. JOHNSON and D. S. STEVENSON

The Met. Office, UK

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SUMMARY

The spatial and temporal distribution of tropospheric ozone is controlled by transport processes, including advection, convection and dispersion and by stratosphere–troposphere exchange, surface deposition to the earth’s surface and by photochemical production and destruction within the troposphere itself. These processes have been represented in some detail in a global three-dimensional Lagrangian chemistry (STOCHEM) model which has been used to construct global ozone budgets and identify the main features in the spatial distribution of daily ozone tendencies. The annually and spatially integrated net chemical production of ozone is about twice as large as the stratosphere–troposphere exchange flux, so that the concentration-dependent surface deposition balancing term is about three times larger than the stratosphere–troposphere exchange term. The total production and loss terms for ozone by tropospheric photochemistry are much greater than the net chemical production, with total chemical production about five times larger than the net term. The ozone turnover time is therefore around 30 days, around one tenth of the turnover time due to stratosphere–troposphere exchange alone. Human activities may influence future tropospheric ozone levels through at least two distinct mechanisms: first, increasing emissions of tropospheric ozone precursor gases: methane, oxides of nitrogen, carbon monoxide and hydrocarbons, leading to increased ozone levels; second, human-induced climate change may lead to increased temperatures and water vapour concentrations, and hence increased ozone destruction and decreased ozone concentrations.

KEYWORDS: Climate change Photochemical destruction Photochemical production Stratosphere–troposphere exchange Surface deposition Tropospheric ozone

1. INTRODUCTION

It is widely accepted that tropospheric ozone (O₃) is one of the most important radiatively active trace gases along with carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O; IPCC 1996). However, assessments of the impact of human activities upon tropospheric ozone are inherently more uncertain than for those other gases because there are no equivalent or comparable ice core records of historical ozone concentrations. Consequently, assessments of the contribution from ozone to climate change have to be made using tropospheric chemistry models, and important questions remain about the adequacy of such models (IPCC 1995).

Global three-dimensional (3-D) chemistry-transport models (CTMs) of tropospheric ozone have increased steadily in complexity since the pioneering study by Levy et al. (1985) which included only stratosphere–troposphere exchange and surface deposition. Descriptions and parametrizations of a number of important processes have been included and improved steadily over the last decade. Tropospheric photochemistry involving the oxides of nitrogen (NOₓ), carbon monoxide (CO) and CH₄ has been added (Crutzen and Zimmerman 1991) and subsequently also biomass burning (Chatfield and Delany 1990), lightning (Price and Rind 1992), mesoscale convection systems (Pickering et al. 1993), deep-cloud convection (Lelieveld and Crutzen 1994) and non-methane hydrocarbon chemistry (Muller and Brasseur 1995; Houweling et al. 1998).

Despite the trends to incorporate more comprehensive chemistry mechanisms, to use state-of-the-art global atmospheric circulation models to drive the transport processes, and to use process-based descriptions of deposition and emissions, there are still large discrepancies between the models (Kanikadou et al. 1999a,b). Furthermore, the models are still poor at simulating some of the features of the observed distribution.

* Corresponding author: The Met. Office, Climate Research Division, London Road, Bracknell, Berkshire RG12 2SZ, UK.
of tropospheric ozone (Wang et al. 1998). Whilst the transport characteristics of the CTMs (Jacob et al. 1997) and their chemistry mechanisms (Olson et al. 1997) have been compared, there is a lack of comparable studies on the detailed chemical production processes which control the model distributions of tropospheric ozone. Here, we present the details of the tropospheric ozone production processes in a 3-D Lagrangian CTM (STOCHEM) model and show how they are influenced by changing emissions from human activities and by predicted human-induced climate change.

2. DESCRIPTION OF THE MODEL

(a) Model description

The model used in this work is The Met. Office tropospheric 3-D chemistry-transport model (STOCHEM). This model takes a Lagrangian approach by dividing the troposphere into 50 000 air parcels, which are advected with a 3-hour time step using archived winds from the Met. Office Unified Model. These winds are 6-hourly instantaneous values, taken either from operational meteorological analyses (~1° x 1° latitude/longitude resolution) or from climate integrations (~3° x 3° resolution).

Each parcel holds the concentrations of 70 chemical species including NOx, O3, OH, HO2, PAN, and hydrocarbons. The hydrocarbons modelled are CH4, ethane (C2H6), ethene (C2H4), propane (C3H8), propene (C3H6), n-butane (C4H10), toluene (CH3C&), o-xylene ((CH3)2C6H4), and isoprene (C5&), along with their oxidation products such as peroxy radicals (RO2), hydroperoxides (ROOH), and carbonyls (e.g. formaldehyde (HCHO), acetaldehyde (CH3CHO), acetone (CH3COCH3), methyl glyoxal (CH3COCHO), and methyl vinyl ketone (CH3COCH=CH2). The chemical species react according to 174 photolytic and thermal reactions, with a 5-minute chemistry time step. The resulting parcel concentrations are mapped to a 5° x 5° x 9 pressure-level grid for output. The vertical coordinate (h) used in STOCHEM and in the global circulation model (GCM) is a hybrid coordinate, terrain-following near the surface and pressure-following above 30 hPa.

The physical processes included are emission, dry and wet deposition, convection, and subgrid-scale mixing between parcels. Emissions can be into the boundary layer or 3-D (from aircraft and lightning) and their rates are given in Table 1. For a more detailed model description see Collins et al. (1997), with subsequent improvements to the model described below.

(b) Meteorological fields and processes

The meteorological fields used are instantaneous values, available every six hours, from the Hadley Centre climate version (Johns et al. 1997) of The Met. Office Unified Model. These data are provided by the GCM at a resolution 3.75° longitude x 2.5° latitude and on 19 unevenly spaced pressure levels between the surface and 4.6 hPa. Note that this grid applies only to fields imported from the GCM. All other input and output data use the grid described in the preceding section.

Air parcels are advected using a Runge-Kutta fourth-order method with a time-step of 3 hours. Linear interpolation from the wind grid to the parcel position is used in the horizontal and in time, and a cubic interpolation is used in the vertical direction. Random displacements are added to the parcel each time step based on locally prescribed diffusivities. The horizontal diffusivity KH is chosen to be 1300 m2s−1 (5300 m2s−1 in the boundary layer) and the vertical diffusivity Kh is chosen to be in the range 7 x 10−3 to 1 x 10−1 m2s−1.
TABLE 1. EMISSIONS FROM EACH SOURCE CATEGORY FOR EACH MODEL SPECIES USED IN MODEL CALCULATIONS FOR THE PRESENT-DAY ATMOSPHERE

<table>
<thead>
<tr>
<th>Species</th>
<th>Human activities</th>
<th>Biomass burning</th>
<th>Vegetation</th>
<th>Soils</th>
<th>Oceans</th>
<th>Aircraft</th>
<th>Lightning</th>
<th>Others</th>
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<tr>
<td>NOx</td>
<td>21.0</td>
<td>8.0</td>
<td>5.6</td>
<td>0.5</td>
<td>5.0</td>
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<tr>
<td>H2</td>
<td>20.0</td>
<td>20.0</td>
<td>5.0</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CO</td>
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<td>500.0</td>
<td>75.0</td>
<td>50.0</td>
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<td>260.0</td>
<td></td>
<td></td>
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<td>20.0</td>
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<tr>
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<tr>
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<td>12.0</td>
<td>2.0</td>
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<td>C4H10</td>
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<td>2.0</td>
<td>8.0</td>
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</tr>
<tr>
<td>C5H8</td>
<td>506.0</td>
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</tr>
<tr>
<td>C6H10</td>
<td>4.7</td>
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<tr>
<td>C7H8</td>
<td>14.0</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CH3CHO</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CH3COCH3</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Model emissions are in Tg yr\(^{-1}\), except NO\(_x\) and HNO\(_3\), which are in Tg (N) yr\(^{-1}\), and SO\(_2\), which are in Tg (S) yr\(^{-1}\).

1Includes paddies (60 Tg yr\(^{-1}\)), tundra (50 Tg yr\(^{-1}\)), wetlands (65 Tg yr\(^{-1}\)), termites (20 Tg yr\(^{-1}\)), and other animals (85 Tg yr\(^{-1}\)).

2Represents production from terpene oxidation.

The model convection scheme is unchanged from the previous model version. It uses convective diagnostics from the driving GCM in the form of heights of the convective cloud bases and tops, cloud cover, and precipitation rate. These parameters are used to derive probabilities for a Lagrangian parcel to be involved in convective transport. The convective probability is given by the amount of cloud cover for clouds that are not precipitating, or by a mass flux calculated from the precipitation rate for those that are precipitating using a formula taken from Chatfield and Delany (1990). The mass flux is converted to a probability by dividing it by the mass of air beneath the cloud base. Within each grid square, each parcel below the cloud top is randomly designated (according to the above probability) as convected or not. Those that are convected have their chemical species uniformly redistributed among all the convected parcels below the cloud top within a 5° × 5° grid square. The advection, convection and mixing schemes have been validated using \(^{222}\)Rn as a tracer\(^*\) (Stevenson et al. 1998). In reality convection may be more episodic, but the present representation is the best that can be achieved with such large air parcels and grid volumes.

During the advection process the Lagrangian cells are considered to be isolated parcels of air. However, in reality the air is mixed with other parcels by diffusion processes characteristic of the size of a parcel. In this model the mixing ratio, \(c\), of a species in a parcel is brought closer to the average background mixing ratio, \(\bar{c}\), by adding a term \((c - \bar{c})d\), where \(d\) is a parameter representing the degree of exchange, taken to be 10\(^{-3}\) in the troposphere and 10\(^{-6}\) in the stratosphere (the division is taken arbitrarily to be at \(h = 0.4\)). We estimate \(c\) to be the average mixing ratio of all the cells within a grid volume, which are chosen to be 5° × 5° × \(\Delta h = 0.1\), as this gives an average of about one and a half cells per grid volume (more near the equator, less near the poles). The volumes are fixed to the Eulerian grid. The exchange is treated in a more theoretical manner by Walton et al. (1988).

\(^*\) \(^{222}\)Rn is a radioactive gas with a lifetime of 3.8 days emitted more or less uniformly over the continents.
(c) Surface deposition and uptake

In the model, the deposition velocity, \( v \), is a combination of a surface term \( u_d \), and an aerodynamic term \( u_a \), and is given by \( v = 1/[1/(u_a) + 1/(u_d)] \). Values for \( u_d \) are species dependent, and have been taken from Hough (1991); \( u_a \) is species independent and is derived from boundary-layer theory. The scheme is based on calculating a species loss flux in molecules, \( s \), given by \( S \times v \times A \) where \( S \) is the concentration of species \( S \) and \( A \) is the area of the grid square. This loss is spread equally among all the parcels within the boundary layer in a similar way to the treatment of emissions. If no parcels are within the boundary layer, the loss flux is stored for one or more time-steps until an air parcel enters the boundary layer there, and hence this scheme results in a specified loss flux.

(d) Wet deposition

Soluble species are removed by wet deposition depending on the dynamic and convective precipitation rates, using altitude dependent coefficients from Penner et al. (1994). The species deposited are HNO₃, N₂O₅, SO₂, HCHO, H₂O₂, and the organic hydroperoxides (ROOH). The higher organic hydroperoxides are given the same coefficients as methyl hydroperoxide (CH₃OOH).

Convective precipitation is a sub-grid-scale process, removing material efficiently over a narrow column. Our removal rate is modified by the algorithm of Walton et al. (1988) to take account of fractional precipitation area, using a fixed fraction of 0.3. At present, we remove water-soluble species by wet scavenging from every air parcel equally within the square covered by the precipitation data (3.75° x 2.5°) regardless of whether that parcel is subject to convective mixing. This means that the convective wet deposition is not completely coupled to the convective transport scheme.

(e) Stratospheric sources of ozone and nitrogen compounds

The upper boundary of our model is set at \( \sim 100 \) hPa and hence we do not include stratospheric ozone production. To allow for this, 6-hourly vertical wind fields are used to calculate an ozone flux across the h \( \sim 100 \) hPa surface on a 5° x 5° grid using monthly ozone fields from Li and Shine (1995). Using this parametrization, a stratospheric source of ozone is injected into the upper model layer. When integrated over one year with the particular meteorological diagnostics used in this study, the total annual injection amounted to 375 Tg yr⁻¹. No account is taken of any loss of any species due to upward transport into the stratosphere. In the upper troposphere, this stratospheric source dominates during spring in mid latitudes, but other ozone sources dominate during other seasons and in the tropics.

A stratospheric source of nitrogen compounds is also included in STOCHEM. This source is scaled directly to the stratospheric ozone source, on a point-by-point basis and, based on the work of Murphy and Fahey (1994), is set as one thousandth of the ozone flux by mass (as N) and is emitted into the model as HNO₃.

(f) Chemistry

The main additions to the chemistry since Collins et al. (1997) have been propane and acetone chemistry, organic hydroperoxide formation, dimethyl sulphide oxidation, and aqueous phase SO₂ oxidation. The last two have only small effects on ozone levels (mostly due to the aqueous H₂O₂ + SO₂ reaction) and will not be discussed further. Of the new species that have been added, those of most importance to this study are HO₂NO₂, C₃H₈, C₃H₇O₂, CH₃COCH₃, CH₃COCH₃O₂, C₂H₅OOH, C₃H₇OOH,
C₄H₉OOH, OHC₃H₈OOH, and MVKOOH. Altogether, 7 additional photochemical and 27 thermal reactions have been added to the model chemistry.

STOCHEM contains a description of the heterogeneous reactions of HNO₃ and N₂O₅ on aerosols. It does not, however, include any treatment of the heterogeneous reactions occurring on cirrus clouds which may deplete NOₓ concentrations near the tropopause (Bormann et al. 1996), nor of the reactions leading to springtime ozone destruction at the polar sunrise (Barrie et al. 1988).

(g) Parallelization

The STOCHEM model was initially developed to run on a single processor DEC Alpha workstation. To utilize the advantages of running a code on a massively parallel CRAY T3E computer, each processor needs to compute a fraction of the calculations and hold a fraction of the data. Consequently the model has been split by geographical region. For optimum efficiency each processor has been assigned a similar number of Lagrangian parcels rather than Eulerian grid points. This means that the geographic regions need to be of equal area. We achieved this by splitting the model domain into a small number of latitude bands, which are divided longitudinally into varying numbers of columns so that each region covers approximately the same surface area. Parcels are allowed to move freely between all the regions. If parcels move out of the geographical region for a particular processor after advection, they are swapped to their new processor, passing over all the information on parcel position and species concentrations.

The geographical division of parcels gives roughly, but not exactly, equal numbers of cells on each processor. Since most of the computational load is in the chemistry integration, it is essential to balance the load between processors as evenly as possible for this routine. This is done by swapping extra parcels on processors responsible for more than the average number of parcels onto those responsible for less than the average. After the chemical integration the parcels have to be swapped back to their original processors (geographically allocated). The other routines need the parcels to be grouped geographically and are not so computationally expensive.

3. TROPOSPHERIC OZONE BUDGETS

The distribution of ozone in the global troposphere has been characterized through surface observation, ozone-sondes and 3-D (altitude, latitude and longitude) modelling. Ozone concentrations, expressed as volume mixing ratios in p.p.b. (1 p.p.b. represents 1 part by volume in 10¹⁹ parts of air), are highest in high latitudes in the upper troposphere of both hemispheres where monthly mean concentrations may exceed 100 p.p.b. Lowest concentrations are found close to the surface in the tropics where monthly mean concentrations approach 10 p.p.b. Elevated concentrations are found over the industrialized continents of the northern hemisphere during summertime. These broad features of the tropospheric ozone distribution are well reproduced by both observations and models (Kanikadou et al. 1999a), STOCHEM included. As an example, Fig. 1 illustrates some of these features in the STOCHEM model results for July. Detailed comparisons of STOCHEM with the observed seasonal variations at sixteen baseline stations and vertical profiles with ozone-sonde data at eight sites show good agreement (Collins et al. 1997). STOCHEM appears to perform well within the range of up to 10 other 3-D chemistry-transport models in a global-model intercomparison exercise for both ozone (Kanikadou et al. 1999a) and CO (Kanikadou et al. 1999b).
Figure 1. Surface ozone concentrations and cross-sections through the tropospheric ozone distribution in parts per billion along 37°N and 22°E, during July.

(a) Ozone production and destruction processes

The global ozone distribution arises from the complex interplay between a set of highly variable ozone production and destruction processes. The fluxes through each of these production and destruction processes have been integrated from pole-to-pole and throughout one complete annual cycle, to quantify their relative magnitudes throughout the lower atmosphere from the surface up to a pressure level of 100 hPa. These production and destruction terms can then be used to construct an annual global ozone budget, and the budget terms are each tabulated in Table 2. In summary, the lower atmosphere contains an inventory of about 300 Tg of ozone, supported by an ozone production term that approaches 4400 Tg yr⁻¹. From the balancing ozone destruction term and the inventory, a turnover time of 29 days can be estimated. Strictly, these budget quantities and lifetimes include atmospheric regions which in some locations and during some times of the year may be above the local tropopause. However, in this study no correction has been made for these locations and occasions in the calculation of tropospheric ozone budgets and lifetimes.

On the basis of the ozone production and destruction terms, ozone is seen as one of the most reactive trace gases present in the lower atmosphere. The corresponding turnover time due to stratosphere–troposphere exchange alone would be almost one year, over an order of magnitude longer in time-scale, reconciling the historic view of ozone being apparently unreactive in the lower atmosphere. In the paragraphs below, each of the ozone production and destruction terms are investigated in some detail, and features
of their seasonal and geographical distributions and the extent of human influence on them, are described.

These production and destruction terms are obtained from the STOCHEM model diagnostics for each month, and are expressed as the number of ozone molecules produced or destroyed in each month. These fluxes have either been scaled by the local atmospheric number density and the units changed to p.p.b. per day, or annually and globally integrated and expressed on a mass basis. These former ozone fluxes are termed ‘daily ozone tendencies’ in the remainder of this study, whilst the latter are termed ‘ozone budget quantities’. Ozone tendencies may be positive representing local ozone production, or negative representing local ozone destruction. Each process in the ozone budget has, therefore, been characterized either as an annual global total flux such as those presented in Table 2, or as a spatial distribution of daily local ozone tendencies. We have also distinguished between those processes that act at the model boundaries, ‘external’ processes or fluxes, and those which act within the model domain, the ‘internal’ processes or fluxes.

(b) Stratosphere–troposphere exchange

Historically, this has been considered the most important source of ozone throughout the troposphere and, in particular, for the upper troposphere. Early estimates equated stratosphere–troposphere exchange with the surface ozone dry deposition or destruction flux on the assumption that internal tropospheric ozone production was of negligible importance. On this basis, stratosphere–troposphere exchange was found to be about 1000 Tg yr⁻¹ on an annual basis. These early studies recognized that this flux had important hemispheric, latitudinal and seasonal differences, and varied in intensity from year-to-year. Over the intervening years, understanding of the meteorological processes

<table>
<thead>
<tr>
<th>Term</th>
<th>Integrated flux, Tg yr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone production terms</td>
<td></td>
</tr>
<tr>
<td>Stratosphere–troposphere exchange</td>
<td>375</td>
</tr>
<tr>
<td>HO₂ + NO</td>
<td>2805</td>
</tr>
<tr>
<td>methyl peroxy + NO</td>
<td>820</td>
</tr>
<tr>
<td>acetyl peroxy + NO</td>
<td>163</td>
</tr>
<tr>
<td>isoprene peroxy + NO</td>
<td>97</td>
</tr>
<tr>
<td>ethylene peroxy + NO</td>
<td>62</td>
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<tr>
<td>other RO₂ + NO</td>
<td>78</td>
</tr>
<tr>
<td>Total</td>
<td>4400</td>
</tr>
<tr>
<td>Ozone destruction terms</td>
<td></td>
</tr>
<tr>
<td>surface deposition</td>
<td>1125</td>
</tr>
<tr>
<td>O₃ + hv + H₂O</td>
<td>1800</td>
</tr>
<tr>
<td>HO₂ + O₃</td>
<td>970</td>
</tr>
<tr>
<td>OH + O₃</td>
<td>355</td>
</tr>
<tr>
<td>other chemical losses</td>
<td>155</td>
</tr>
<tr>
<td>Total</td>
<td>4405</td>
</tr>
</tbody>
</table>

Ozone inventory, 350 Tg; ozone turnover time, 29.2 days. All the table entries have been integrated globally and annually from the surface to 100 hPa and hence may include some portions of the atmosphere considered under other definitions to be in the lower stratosphere. The turnover time was estimated by dividing the global inventory by the total destruction term.
which underpin stratosphere–troposphere exchange have developed progressively, and some of the published estimates of this ozone production term are reviewed in Table 3.

In STOCHEM stratosphere–troposphere exchange is parametrized using the 3-D wind field at the upper boundary of the model at 100 hPa and an observed ozone climatology at 70 and 100 hPa (Li and Shine 1995). The annually integrated stratosphere–troposphere exchange flux was accordingly found to be 375 Tg yr⁻¹, within the range of previously published estimates, see Table 3, though towards the lower end of the published range. The stratosphere–troposphere exchange flux quoted for STOCHEM describes the flux of ozone that permanently resides in the troposphere. Some of the other figures in Table 3 are considerably higher, because they have not been corrected for any return flux of ozone from the troposphere back into the stratosphere.

On this basis, in STOCHEM stratosphere–troposphere exchange accounts for about 10% of the total tropospheric ozone source term, see Table 2. Clearly, this source term is not of crucial importance to the troposphere as a whole. However, because this flux acts as a source at the upper boundary of the model, it is necessarily the most important ozone source of all in the upper troposphere and therefore must be represented quantitatively in any 3-D model study.

(c) Surface deposition and uptake

The removal of ozone at the earth’s surface by destruction on soils and uptake by plants has historically been one of the better-understood processes controlling the life cycle of tropospheric ozone. Early studies identified that land surfaces acted as efficient ozone sinks and that water surfaces did not (Aldaz 1969; Galbally 1971) and gave globally integrated ozone removal fluxes of about 1000 ± 500 Tg yr⁻¹ (Aldaz 1969; Fishman and Crutzen 1978; Galbally and Roy 1980). It is now recognized that the surface deposition flux is somewhat larger than that of stratosphere–troposphere exchange, pointing to the troposphere being a slight net sink for ozone, with a net balancing tropospheric source due to tropospheric photochemistry.

Ozone surface deposition is parametrized through a combination of observed deposition velocities and model surface-layer ozone concentrations. The globally integrated ozone surface deposition flux in Table 1 of 1125 Tg yr⁻¹ is well within the range of the early deposition budgets of 1000 ± 500 Tg yr⁻¹ described above. Furthermore, the
TABLE 4. THE GLOBALLY AND ANNUALLY INTEGRATED OZONE PRODUCTION AND DESTRUCTION TERMS USED TO CALCULATE TROPOSPHERIC OZONE BUDGETS FOR PRESENT-DAY CONDITIONS IN A NUMBER OF GLOBAL 3-D CTMs

<table>
<thead>
<tr>
<th>CTM</th>
<th>Stratosphere–troposphere exchange Tg yr(^{-1})</th>
<th>Internal chemical production Tg yr(^{-1})</th>
<th>Internal chemical destruction Tg yr(^{-1})</th>
<th>Net chemical production/destruction Tg yr(^{-1})</th>
<th>Surface destruction Tg yr(^{-1})</th>
<th>Global inventory Tg</th>
<th>Turnover time days</th>
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<tr>
<td>MATCH</td>
<td>a 1440</td>
<td>2490</td>
<td>3300</td>
<td>-810</td>
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<td>ECHAM/TM3</td>
<td>c 768</td>
<td>3979</td>
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Mean ± 1σ range: 349–930 Tg yr\(^{-1}\)

Notes:
- a. Crutzen et al. (1999); b. Lawrence et al. (1999); c. Houweling et al. (1998), with NMHC chemistry; d. Houweling et al. (1998), with methane only chemistry; e. Wang et al. (1998); f. Lelieveld and Crutzen (1994), with deep cloud convection; g. Lelieveld and Crutzen (1994), without deep cloud convection; h. The and Beck (1995); i. Levy et al. (1997); j. Bernsten et al. (1996); k. Bernsten and Isaksen (1997); l. Roelofs and Lelieveld (1995); m. Roelofs and Lelieveld (1997); n. Muller and Brasseur (1995); o. Hauglustaine et al. (1998); p. Table 2; q. Turnover times are estimated by dividing the global inventories by the sum of the 'internal' and 'external' destruction terms.

STOCHEM budget flux compares favourably with the range of 533 to 1178 Tg yr\(^{-1}\) found for a number of chemistry-transport models, see Table 4, though close to the uppermost values.

The surface deposition budget flux appears to be about three times larger than the stratosphere–troposphere exchange flux at 375 Tg yr\(^{-1}\), pointing to an imbalance between these two external fluxes. There must be an internal photochemical ozone production of about 750 Tg yr\(^{-1}\) to balance the difference between these external ozone fluxes. This internal net ozone production involves the fast photochemistry of the troposphere and is the subject of the next sections.

**(d) Photochemical ozone production**

Photochemical ozone production occurs through the peroxo radical-driven (HO\(_2\) and RO\(_2\)) conversion of nitric oxide (NO) to nitrogen dioxide (NO\(_2\)), followed by the sunlight-driven photolysis of the NO\(_2\) to form ozone. HO\(_2\) radicals are produced by the attack of hydroxyl radicals on both CO and organic compounds, whilst RO\(_2\) radicals are produced by the attack of OH radicals only on organic compounds. In these reactions, organic peroxy radicals (RO\(_2\)) are converted to oxy radicals (RO) whose main fate is to react to produce a carbonyl intermediate and a HO\(_2\) radical. Since carbonyl compounds also react with OH radicals to produce peroxy radicals, ozone production can, in principle, occur at many different steps in the sunlight-driven atmospheric degradation
of the emitted organic compounds, involving several different peroxy RO\textsubscript{2} radicals and ultimately HO\textsubscript{2} radicals.

As Table 2 shows, reactions of the HO\textsubscript{2} radical with NO account for the bulk, about 70\%, of the tropospheric photochemical ozone production, with organic peroxy radical reactions accounting for the remaining 30\%. The reaction of methyl peroxy radicals with NO provides the largest contribution of all of the organic peroxy radicals, about two-thirds. Non-methane hydrocarbon chemistry drives ozone production from all the RO\textsubscript{2} + NO reactions which involve the isoprene peroxy, acetyl peroxy, ethylene peroxy and the other RO\textsubscript{2} radical terms in Table 2. Non-methane hydrocarbons must therefore contribute at least 10\% of the tropospheric photochemical ozone production globally, and a significantly greater percentage close to the surface over the polluted northern hemisphere continents. Non-methane hydrocarbon-driven ozone production appears to be controlled by the natural biogenic emissions of isoprene and the emissions of ethylene, propylene and of alkanes from human activities.

\textit{(e) Photochemical ozone destruction}

In Table 2, surface deposition appears to be occurring at a rate which is globally three times larger than that of stratosphere–troposphere exchange, showing that the troposphere has an internal net ozone source. Internal photochemical ozone production, through conversion of NO to NO\textsubscript{2} appears to produce ozone at a rate which is about five times faster than the net rates of dry deposition and stratosphere–troposphere exchange. There must therefore be a balancing ‘internal’ ozone destruction term that finally closes the tropospheric ozone budget.

The balancing internal ozone destruction term involves the sunlight-driven photolytic destruction of ozone, producing oxygen atoms (O\textsuperscript{3}P and O\textsuperscript{1}D). Ozone destruction only occurs through the reaction of O\textsuperscript{1}D atoms with water vapour, which accounts for less than 0.1\% of O\textsuperscript{3}P and O\textsuperscript{1}D atoms produced by ozone absorption in the visible and ultraviolet regions of the solar spectrum. The annually integrated ozone photolytic destruction flux amounts to about 1800 Tg yr\textsuperscript{-1}, see Table 2. The free-radical products of the ozone photolysis can react further, leading to significant additional photochemical ozone destruction fluxes of 975 and 355 Tg yr\textsuperscript{-1} through the reactions of OH and HO\textsubscript{2} with ozone, see Table 2.

\textit{(f) Distribution of tropospheric ozone production and destruction with altitude}

The distribution with altitude of the annually and horizontally averaged ozone production flux in Tg yr\textsuperscript{-1} is plotted against altitude in Fig. 2(a). The ozone production flux is relatively high in the lowest two model levels, falling off sharply to a fairly constant value of 150 to 300 Tg yr\textsuperscript{-1} throughout the remainder of the model. The balance between the main internal production terms: HO\textsubscript{2} + NO, CH\textsubscript{3}O\textsubscript{2} + NO and RO\textsubscript{2} + NO remains remarkably consistent between the model levels.

The annually, latitudinally and longitudinally averaged ozone-destruction flux is plotted against altitude in Fig. 2(a). The ozone-destruction flux is about 800 Tg yr\textsuperscript{-1} in each of the two lowest model levels, and falls off steadily with altitude across the entire model domain, reaching a value of less than 50 Tg yr\textsuperscript{-1} in the uppermost model level. The balance between the main internal destruction terms: O\textsubscript{3} + h\nu + H\textsubscript{2}O, HO\textsubscript{2} + O\textsubscript{3} and OH + O\textsubscript{3}, changes across the model domain. These relative changes and the fall-off in the total destruction rate are driven mainly by the steep altitude variation in the solar ultraviolet photolysis term O\textsubscript{3} + h\nu + H\textsubscript{2}O term, which is due in turn to the steep vertical gradient in the distribution of water vapour in the lower atmosphere.
(g) *Net tropospheric ozone production and destruction*

Because the altitude profiles of the tropospheric ozone and production terms each have such different shapes, the altitude profile of the net ozone production–destruction, see Fig. 2(b), also shows a complex dependence on altitude. In the lowest model level the balance between internal ozone production and destruction favours ozone production. Between 900 and 500 hPa the balance shifts completely over to ozone destruction. Throughout the remainder of the model domain above 500 hPa, the balance favours ozone production. Integrating over the entire vertical column, the internal production–destruction adds up to a net internal production of 745 Tg yr$^{-1}$, which balances the net external destruction from stratosphere–troposphere exchange and dry deposition.

The global budget analysis emphasises four principal tropospheric ozone regimes:

(i) ozone production close to the surface over the industrialized northern hemisphere continents;
(ii) ozone production close to the surface from biomass burning in the tropics;
(iii) a lower and mid-tropospheric ozone destruction regime; and
(iv) an upper tropospheric ozone production regime.

These regimes are studied in further detail in the paragraphs below to identify their spatial and temporal patterns, and the chemical and meteorological processes that underpin them.

4. **TROPOSPHERIC OZONE PRODUCTION AND DESTRUCTION REGIMES**

The monthly averaged ozone distributions in the lowermost model level in each of the seasons are plotted in Fig. 3. These plots reveal areas with elevated ozone concentrations relative to the global mean, which are located over the industrialized regions of the northern hemisphere continents in North America, Europe and Asia, particularly during July. These elevated ozone concentrations reflect regional ozone formation from industrial ozone precursor emissions. Furthermore, the plots for both January and July reveal the presence of elevated ozone concentrations in the tropics, reflecting ozone formation from biomass-burning precursor emissions. The plots also show the presence of a large area with depleted ozone concentrations relative to the
global mean, particularly over the southern hemisphere oceans. Attention is directed firstly to the ozone production regions and then to the ozone destruction regions in the paragraphs which follow.

(a) Ozone production in the lower troposphere

The areas with ozone concentrations which are significantly larger than the global mean, coincide with those regions where the daily ozone tendencies are positive, see Fig. 4(a); that is to say, where internal chemical ozone production, \( P \), exceeds the sum of both internal ozone destruction, \( L \), and external surface deposition, \( D \), each term measured in p.p.b. per day. In January, the daily ozone tendencies over the industrialized continents are negative due to the wintertime depletion reactions of \( \text{NO}_x \) with ozone. Significant positive ozone tendencies, reaching up to 30 p.p.b. per day, are confined to the biomass-burning regions in the latitude band 0–20° N.

In the corresponding July plot, see Fig. 4(b), daily ozone tendencies over the industrialized continents lie in the range +5 to −10 p.p.b. per day during July over central Europe, +10 to −20 p.p.b. per day over much of eastern North America, and reach a peak of just under +30 p.p.b. per day over the south-eastern USA. Similar peak daily ozone tendencies are found over the biomass-burning regions of South America and Africa.

The daily ozone tendencies over the industrialized continents and the biomass-burning regions have their own distinct seasonal variations, see Fig. 5(a) and (b). The shapes of these curves appear to be influenced by the relative magnitudes of the precursor emissions, and by latitude which influences the length of time over which daily ozone tendencies are positive. These two main factors generate a ranking with North America > Europe > Asia, in terms of daily ozone tendencies integrated over the year, see Fig. 5(a).

Daily ozone tendencies over the tropics are heavily influenced by biomass burning, see Fig. 5(b). Biomass burning generates large positive daily tendencies over Brazil during the months of August through October, with Africa and south-east Asia next in magnitude. An additional peak in daily ozone tendency during January through March is located over Africa, when it is the largest photochemical ozone source found anywhere within the model domain at that time, see Fig. 5(b).

(b) Ozone destruction in the lower troposphere

A comparison of Figs. 3 and 4 shows that the regions of depressed ozone concentrations relative to their global mean coincide with regions of negative daily ozone tendencies. Daily ozone tendencies are negative, between −1 and −5 p.p.b. per day, over most of the ocean areas. Areas of greatest ozone destruction, with daily ozone tendencies as low as −5 to −10 p.p.b. per day, are found in the regions where regionally polluted continental air flows out over the oceans. These continental outflow regions are found downwind of North America over the Atlantic Ocean and downwind of Asia over the Pacific Ocean.

Whilst elevated ozone precursor emissions are clearly responsible for the elevated surface ozone and daily ozone tendencies over the continental land regions, it is not at all obvious what are the main driving factors which influence the spatial pattern in ozone destruction. In Fig. 6, the daily ozone tendencies during July are plotted against the monthly mean \( \text{NO}_x \) concentrations for a selection of locations in eastern North America, including the continental outflow region over the North Atlantic Ocean. There appears to be a uniform relationship between daily ozone tendency and \( \text{NO}_x \) concentration that spans the entire range from intense ozone production through to ozone destruction.
Figure 4. Daily ozone tendencies in parts per billion (p.p.b.) per day for the surface model layer including dry deposition, where $P$ is the chemical production, $L$ the chemical destruction and $D$ the surface deposition, for:
(a) July; and (b) January.
Figure 5. Variations in the monthly mean ozone tendencies in parts per billion (p.p.b.) per day through the year for: (a) the industrialized continental regions; and (b) the tropical biomass-burning regions. \( P \) is the chemical production, \( L \) the chemical destruction and \( D \) the surface deposition.

Intense ozone production requires the presence of adequate supplies of HO\(_2\) and RO\(_2\) radicals, together with NO\(_x\). As the ozone production progresses, NO\(_x\) levels begin to fall through their rapid oxidation to nitric acid. Because of the exceedingly short lifetime of NO\(_x\) and of the relative reactivities of NO\(_2\) and organic compounds, NO\(_x\) concentrations fall off more quickly away from the major source regions of the ozone precursors, compared with concentrations of HO\(_2\) and RO\(_2\). At some limiting NO\(_x\) concentration when there is not enough NO\(_x\) to complete the HO\(_2\) to OH recycling, net ozone production turns over to net ozone destruction. Figure 6 reveals that this limiting NO\(_x\) concentration is about 60–70 p.p.t \( (1 \text{ p.p.t. is one part in } 10^{12} \text{ mixing value by} \)
Figure 6. Scatter plot of daily ozone tendencies during July in parts per billion (p.p.b.) per day against local NOx concentrations in parts per $10^{12}$ (p.p.t.) for: (a) the North American continental outflow region at the surface; and (b) the 20–30°S region at 750 hPa.
volume) in North American regionally polluted air masses flowing out over the North Atlantic Ocean. In the outflow regions daily ozone tendencies decrease to about −1 to −4 p.p.b. per day.

(c) **Ozone destruction in the middle troposphere**

In Figs. 7(a) and (b) the daily ozone tendencies in p.p.b. per day are plotted for a slice through the troposphere from the surface to 100 hPa for the latitude ranges 35°–45°N and 20°–30°S, respectively. Both plots show the intense production regions of surface ozone over the continents, together with the associated surface ozone destruction regions in their outflow. Throughout the lower and middle troposphere up to about 400 hPa, daily ozone tendencies appear to be negative with typical values in the range −1 to −3 p.p.b. per day. The factors that control ozone destruction in this broad region of the global troposphere are the subject of the paragraphs below.

One of the main factors controlling the mid-tropospheric ozone regime is the availability of NOx, just as in the continental outflow regions. Three areas of ozone production are apparent in the upper troposphere in both Figs. 7(a) and (b), caused by convective uplifting of NOx, carriers of organic nitrogen compounds, and transfer of ozone into the upper troposphere from the surface, over the continents. This convection process, together with the surface and stratospheric NOx sources, produces a ‘C’-shaped distribution in the observed altitude profiles of NO, NO2, and NO3 (Thakur et al. 1999). The model is able to reproduce many, but not all, of the salient features of the observations of NOx and HNO3 in the remote free troposphere. The negative ozone tendencies in Figs. 7(a) and (b) are associated with the minima in these ‘C’-shaped distributions of NOx in the mid-troposphere.

Figure 6(b) shows how the daily ozone tendencies are related to local NOx concentrations at 750 hPa over the latitude band 20°–30°S during July. Daily ozone tendencies become increasingly positive with increasing NOx concentrations above 20–40 p.p.t. Low NOx concentrations are associated with negative daily ozone tendencies. At the lowest NOx concentrations, however, daily ozone tendencies level out at about −1 p.p.b. day−1, a level which is significantly different from the limiting negative daily ozone tendency found near the surface of −5 p.p.b. day−1. The reduction in apparent efficiency of the ozone destruction processes between the surface and the mid troposphere is accounted for by the decreasing water-vapour concentration found with increasing altitude in the troposphere, which decreases markedly the efficiency of the photolytic destruction route (O3 + hv + H2O).

A complex interplay of factors and processes, therefore, controls the spatial and seasonal variations of daily ozone tendencies in the mid troposphere, and act to make this region a significant ozone destruction regime. These factors and processes include:

- outflow of regional ozone precursor emissions into the mid troposphere involving CO and organic compounds rather than NOx because of the short lifetime of the latter;
- convective uplift of surface NOx, organic compounds and ozone from the surface into the upper troposphere;
- the decrease with altitude of water-vapour concentrations and hence the decreasing efficiency of ozone photolytic destruction.

(d) **Upper tropospheric ozone formation**

The altitude distributions of the daily ozone tendencies in Figs. 7(a) and (b), show that, overall, chemical processes in the upper troposphere act as a net source of ozone.
Figure 7. Daily ozone tendencies ($\eta$) in parts per billion (p.p.b.) per day for vertical cross-sections through the model domain during July for: (a) $45^\circ$–$55^\circ$N, and (b) $20^\circ$–$30^\circ$S.
This internal ozone source acts in addition to the other important ozone source in the upper troposphere, which is stratosphere–troposphere exchange.

Four important NO\textsubscript{x} sources, identified in previous modelling studies, have been represented in some detail in STOCHEM and contribute to upper tropospheric NO\textsubscript{x} levels. These are:

- transport of HNO\textsubscript{3} from the lower stratosphere by stratosphere–troposphere exchange, followed by photochemical conversion to NO\textsubscript{x};
- export of peroxyacetyl nitrate and other organic nitrogen compounds carriers from the upper troposphere;
- deep convective uplift of NO\textsubscript{x}, organic nitrogen compounds from surface sources;
- \textit{in situ} sources such as lightning and aircraft.

These NO\textsubscript{x} sources act in concert to produce ‘C’-shaped NO\textsubscript{x} concentration profiles with altitude, with maxima in the upper troposphere.

Figure 8 shows the relationship between daily ozone tendency and NO\textsubscript{x} levels in the upper troposphere for the highest model level, 150 hPa, over the North American continent. Also shown is the modelled relationship between daily ozone tendency and NO\textsubscript{x} concentration that has been fitted through the aircraft observations of Wennberg \textit{et al.} (1998) in the upper troposphere above the North American continent. This good agreement between the STOCHEM model and the observed ozone tendencies and their respective dependences on NO\textsubscript{x} concentrations is most heartening.

A further comment about Fig. 8 concerns the limiting daily ozone tendencies at low NO\textsubscript{x} concentrations. The observations of Wennberg \textit{et al.} (1998) and the STOCHEM model results both show that daily ozone tendencies do not go significantly negative.
even at the lowest NO\textsubscript{x} concentrations. The reason appears to be the very low water-vapour concentrations in the uppermost troposphere, which reduce losses through ozone photolysis to negligible importance. The only destruction routes operating in the upper troposphere appear to be OH + O\textsubscript{3} and HO\textsubscript{2} + O\textsubscript{3}, and NO\textsubscript{x} concentrations of less than 10 p.p.t. would be required to produce the situation where the two routes dominated over ozone production through HO\textsubscript{2} + NO. Such conditions appear not to be found in the upper troposphere over the major continental regions because of the ubiquitous influence of lightning as a NO\textsubscript{x} source.

5. IMPACT OF EMISSIONS FROM HUMAN ACTIVITIES ON FUTURE TROPOSPHERIC OZONE PRODUCTION AND DESTRUCTION

Human activities, through increasing emissions of the tropospheric ozone precursor gases: CH\textsubscript{4}, CO, NO\textsubscript{x} and hydrocarbons NMHC, are considered likely to cause an increase in future tropospheric ozone concentrations (IPCC 1996). In this section, the role of increased emissions in driving up future ozone concentrations is identified through the analysis of the future global ozone budgets.

In Fig. 9, the results of a series of six STOCHEM model experiments have been summarized in terms of the global ozone budgets. One of the model experiments is nominally a base case for the 1990 model atmosphere, and the remaining five experiments address the future atmosphere in the year 2100. All six experiments used identical meteorological data from the Hadley Centre climate model (HADCM3) appropriate to the year 1990 (Johns \textit{et al.} 1997). The emissions of CH\textsubscript{4}, CO, NO\textsubscript{x} and NMHC for 1990 and 2100 base cases were taken from the IPCC SRES A2 scenario (Stevenson \textit{et al.} 1999). The four additional variants of the 2100 scenario involved setting the emissions of each named species 'low' at their 1990 values, whilst the remaining emissions were kept at their 2100 values. In order to maintain consistency across all the six model experiments in Fig. 9, the basic emissions and meteorological databases employed for the present day atmosphere were slightly different from those used elsewhere in this study. The base-case ozone budgets were therefore not identically consistent with those presented in the sections above.

Looking first at the 1990 and 2100 base cases: ozone inventories appear to have increased from 316 to 469 Tg due to the influence of increasing emissions of tropospheric ozone precursor gases and hence increased photochemical ozone production. The increase in global ozone inventories amounts to a factor of 1.48 between the two cases. Global ozone production (and loss) has increased from 4320 to 8483 Tg yr\textsuperscript{-1}, an increase of a factor of 1.96. Net chemical production in the troposphere has accordingly increased from 434 Tg yr\textsuperscript{-1} to 1113 Tg yr\textsuperscript{-1}, an increase by a factor of 2.56. In summary, therefore, to drive up the global inventory by a factor of 1.48, net chemical production has had to increase by the substantially larger factor of 2.56, because of the increased ozone destruction that has occurred simultaneously with the increased ozone production. Because of the increased ozone destruction, the ozone turnover time has decreased by a factor of 0.79, dampening the impact of the increased ozone production.

Looking, then, at the five scenario cases for 2100, turnover times remain relatively constant and changes in global inventory accurately reflect changes in the net chemical production in the troposphere, driven by increased photochemical ozone production through the HO\textsubscript{2} + NO and RO\textsubscript{2} + NO reactions. The four sensitivity cases were chosen to provide an indication of whether the increased emissions of CH\textsubscript{4}, CO, NO\textsubscript{x} or of hydrocarbons were individually, more or less, responsible for the overall increase in ozone between 1990 and 2100. In each of the four variants one of the emissions increases
was set to zero in turn. The largest difference in net chemical production between any of the four sensitivity cases and the base case was found for the 'low NOx' case, followed by the 'low CH4', 'low CO' and 'low NMHC' cases in decreasing order of importance. Accordingly therefore, the increase in ozone between the present-day and year 2100 appears to be driven more by the increase in NOx emissions, with those in CH4, CO and hydrocarbons following in order of decreasing importance. The significant differences found in the regional patterns of the ozone production and destruction terms in the future scenarios are beyond the scope of this present study.

6. IMPACT OF HUMAN-INDUCED CLIMATE CHANGE ON FUTURE TROPOSPHERIC OZONE PRODUCTION AND DESTRUCTION

Whilst it is now recognized that increased emissions of tropospheric ozone precursor gases from human activities may cause an increase in future tropospheric ozone concentrations (IPCC 1996), it has only recently become apparent that human-induced climate change may itself influence future ozone concentrations (Johnson et al. 1999). In this section, the influence of human-induced climate change on tropospheric ozone is identified through the analysis of global ozone budgets.

In Fig. 10 the results of two STOCHEM model experiments are presented for conditions appropriate to the years 1990 and 2075. Both model experiments used identical present-day emissions for the main tropospheric ozone precursor gases. The model experiments, however, used two different years of meteorological data from the same Hadley Centre climate model (HADAM2b), one appropriate to the present day and the other with doubled CO2 concentrations (Senior 1999). These meteorological datasets differed significantly in detail, due to the impact of human-induced climate change on temperatures, humidities, cloud amounts and the atmospheric circulation patterns. In order to maintain consistency across the two model experiments in Fig. 10, the
emissions and meteorological databases for the present-day atmosphere were slightly different from those used elsewhere in this study, leading to slight differences in the ozone budgets. Lightning NOx emissions were held constant at 5 Tg N yr\(^{-1}\).

Looking first at the global ozone inventories in Fig. 10, the ozone inventory appears to have declined from its present-day value of 364 Tg to 327 Tg, following a doubling in CO\(_2\). This decline represents a 10% decrease relative to the present-day atmosphere. The global ozone production (or loss) has increased from 4678 to 4900 Tg yr\(^{-1}\), an increase of 5%. In contrast, net chemical production has decreased by 26% from 507 Tg yr\(^{-1}\) to 375 Tg yr\(^{-1}\), driven largely by increased ozone destruction through O\(_3\) + hv + H\(_2\)O. In summary then, to drive down the global ozone inventory by 10%, net chemical production has had to decrease by 26%, because of the increase in photochemical ozone production. As a result the mean ozone turnover time shortens from 28 to 23 days, exacerbating the impact of the enhanced ozone destruction.

The main influence of human-induced climate change on tropospheric ozone appears to involve increased temperatures, hence increased water-vapour concentrations and hence increased photochemical destruction through the O\(^1\)D + H\(_2\)O reaction. The resulting increased production of hydroxyl radicals leads to a small increase in photochemical ozone production, which partially offsets the increased ozone destruction which drives it. However, it must be remembered that many of the differences in the ozone budget terms between 1990 and 2050 in Fig. 10 are much smaller than the differences in the 1990 budget terms across the range of models in Table 4.

7. DISCUSSION AND CONCLUSIONS

In this study, ozone budgets and ozone daily tendencies have been used to quantify the main processes that control tropospheric ozone production and destruction, and to describe their spatial and temporal variations. We have then shown how emissions
from human activities can stimulate further tropospheric ozone production and lead to increased future global ozone inventories. Furthermore, human-induced climate change, through increased global temperatures and water-vapour concentrations, can lead to increased tropospheric ozone destruction and decreased global ozone inventories.

Whether any of these statements concerning future tropospheric ozone concentrations will be borne out in the global atmosphere will depend on the validity of the STOCHEM model, the adequacy and completeness of the model formulation and the validity of the assumptions and approximations which have been made in the descriptions of the model processes. Comparison of model results with observations provides the crucial test of model performance and STOCHEM performs well within the range of current models. However, it is recognized that there are not enough observations of tropospheric ozone and its related reactive H O X, N O X and organic species, to constrain model performance adequately.

We have therefore evaluated STOCHEM model performance in a much less rigorous manner by reference to other 3-D chemistry-transport models and their published ozone budgets. This comparison is contained in Table 4 and provides details of the globally and annually integrated ozone production and destruction terms used to calculate ozone budgets in a range of 3-D CTMs for present-day conditions. Many of the models share common features and use common descriptions and parametrizations of the important processes. However, each model exhibits its own point of departure and focuses in detail on different aspects of the tropospheric ozone life cycle. STOCHEM can be distinguished from the other CTMs in Table 4 because of its uniquely Lagrangian approach, and because of its extensive representation of tropospheric chemistry. An indication of the spread of the different model results is provided using the range from the mean value to plus and minus the standard-deviation (σ).

The ozone budget terms from STOCHEM can, therefore, be compared with the corresponding ranges from the global 3-D CTMs, see Table 4. For the stratosphere–troposphere exchange source of ozone the STOCHEM value, although within the range of other studies, is well towards the bottom end of the range. The internal chemical production budget term from STOCHEM is within the range of the other studies, but well towards the top end. This would point to an apparent overestimation of photochemical ozone formation in STOCHEM, either because of its more detailed chemistry or because of its more complete representation of hydrocarbon degradation. Necessarily, internal chemical destruction of ozone must be towards the upper end of the model range to balance internal chemical production, and this is indeed seen to be the case. The STOCHEM estimate of surface deposition falls at the upper end of the model range.

Of all of the budget terms in Table 4, the most important for diagnosing model performance is the net chemical production–destruction term. The range of available model studies shows a surprising range with some global 3-D CTMs indicating a large net sink in the troposphere for ozone. However, such CTMs are in the minority with the majority of 3-D CTM studies demonstrating that the troposphere contains a net internal source of ozone, that is to say, surface deposition is greater than stratosphere–troposphere exchange. STOCHEM generates a net internal source term which is above the upper end of the model range, reflecting its detailed representation of the degradation of a wide range of individual hydrocarbon species. Indeed, many of the CTMs in Table 4 include no organic compounds other than CH₄ to drive their tropospheric ozone production.

Overall, the global 3-D CTMs produce ozone inventories that span the range 260 to 350 Tg, that is with a 1σ range of about ± 15% of a mean value of 306 Tg. This
is our best estimate of the remaining uncertainty in current state-of-the-art CTMs. The STOCHEM model generates an ozone inventory at the upper bound of the model range. Ozone turnover times are constrained to roughly the same precision by the available model studies, 26 ± 3 days. STOCHEM model turnover times are well within the range of the available model studies.

In summary, by comparison with other global CTM model studies, we have been able to characterize STOCHEM model performance and to provide some confidence in the ozone budgets and daily ozone tendencies that it generates. On this basis, we can have some confidence in the model results that confirm that human activities may exert a significant influence on future tropospheric ozone concentrations. Firstly, increasing emissions of tropospheric ozone precursor gases, such as CH₄, NOₓ, CO and hydrocarbons from human activities may well lead to increased ozone production and increased ozone concentrations. Secondly, human-induced climate change may increase temperatures and water-vapour concentrations, leading to increased ozone destruction and lower ozone concentrations. Whether any of these changes in tropospheric ozone will actually occur in the future atmosphere will depend on the adequacy and completeness of the treatment of tropospheric ozone in current global 3-D CTMs.

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