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Modelling the global tropospheric ozone budget: exploring the variability in current models

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Abstract

What are the largest uncertainties in modelling ozone in the troposphere, and how do they affect the calculated ozone budget? Published chemistry-transport model studies of tropospheric ozone differ significantly in their conclusions regarding the importance of the key processes controlling the ozone budget: influx from the stratosphere, chemical processing and surface deposition. This study surveys ozone budgets from previous studies and demonstrates that about two thirds of the increase in ozone production seen between early assessments and more recent model intercomparisons can be accounted for by increased precursor emissions. Model studies using recent estimates of emissions compare better with ozonesonde measurements than studies using older data, and the tropospheric burden of ozone is closer to that derived here from measurement climatologies, 335±10 Tg. However, differences between individual model studies remain large and cannot be explained by surface precursor emissions alone; cross-tropopause transport, wet and dry deposition, humidity, and lightning make large contributions to the differences seen between models. The importance of these processes is examined here using a chemistry-transport model to investigate the sensitivity of the calculated ozone budget to different assumptions about emissions, physical processes, meteorology and model resolution. The budget is particularly sensitive to the magnitude and location of lightning NO\textsubscript{x} emissions, which remain poorly constrained; the 3–8 TgN/yr range in recent model studies may account for a 10% difference in tropospheric ozone burden and a 1.4 year difference in CH\textsubscript{4} lifetime. Differences in humidity and dry deposition account for some of the variability in ozone abundance and loss seen in previous studies, with smaller contributions from wet deposition and stratospheric influx. At coarse model resolutions stratospheric influx is systematically overestimated and dry deposition is underestimated; these differences are 5–8% at the 300–600 km grid-scales investigated here, similar in magnitude to the changes induced by interannual variability in meteorology. However, a large proportion of the variability between models remains unexplained, suggesting that differences in
model chemistry and dynamics have a large impact on the calculated ozone budget, and these should be the target of future model intercomparisons.

1 Introduction

Ozone is an important greenhouse gas, a major component of photochemical smog, and the primary source of hydroxyl radicals which control the oxidizing capacity of the troposphere (e.g., Prather and Ehhalt, 2001). The abundance of O$_3$ in the troposphere is controlled by transport from the O$_3$-rich stratosphere, by chemical production following the oxidation of hydrocarbons and CO in the presence of nitrogen oxides (NO$_x$) and by removal via chemical destruction or dry deposition. The magnitudes of these sources and sinks have not been reliably quantified, and observational constraints on them remain poor. The chemical lifetime of O$_3$ in the troposphere, typically days to weeks, is similar in magnitude to the dynamical timescales for transport and mixing, and thus the factors controlling O$_3$ are not easily separable. The net effects of chemical processing are dependent on the balance between large production and destruction terms which dominate in different regions of the troposphere, and the importance of stratosphere-troposphere exchange (STE) is similarly dependent on the balance between downward transport of O$_3$ from the stratosphere, mostly at mid-latitudes, and a smaller upward flux in tropical regions. The equilibrium between these chemical and dynamical fluxes constitutes a buffering of tropospheric O$_3$, and poor estimates of one or more of these governing processes may be masked by readjustment of the others so that the abundance of O$_3$ in the troposphere is not greatly affected. However, a quantitative understanding of the processes controlling the production, redistribution and fate of O$_3$ in the troposphere is required before a reliable assessment can be made of how O$_3$ may respond to changes in anthropogenic emissions of trace gases or global climate.

Global chemistry-transport models (CTMs) that simulate the chemical and dynamical processes controlling O$_3$ provide a self-consistent estimate of the key budget terms.
Most CTMs can reproduce the seasonality and distribution of tropospheric O₃ measured by ozonesondes in a climatological sense, but assessments of the relative importance of the controlling processes vary widely (Prather and Ehhalt, 2001). Recent model intercomparison studies estimate a net O₃ influx of 550 Tg/yr from the stratosphere and a surface removal of 1000 Tg/yr by dry deposition, with net chemical production making up the balance of 450 Tg/yr (Stevenson et al., 2006). However, there are large differences between individual model studies in the importance of these terms reflecting differences in their treatments of chemical and dynamical processes. These differences highlight significant imperfections in our current understanding of the key factors involved (e.g., in the magnitude and distribution of emissions, chemical processing, and convection) and in their numerical representation at computationally-tractable temporal and spatial scales. CTMs are typically focused on global-scale issues such as attribution of climate impacts due to changing patterns of fossil fuel combustion (Gauss et al., 2003; Dentener et al., 2006a), or assessment of the policy impacts of intercontinental transport of oxidants on air quality (e.g., Holloway et al., 2003). Many of the chemical and dynamical processes controlling O₃ in the troposphere occur at much smaller temporal and spatial scales than can be resolved in these models, and thus important processes are parameterized, introducing additional uncertainty. Nevertheless, improved understanding of the interactions between tropospheric composition and climate, and in particular of how changes in climate may affect the sources and fate of tropospheric O₃, requires that the principal terms in the O₃ budget can be quantified in a reliable and consistent way so that the sensitivity of the budget to changes in transport, convection, chemistry and deposition can be evaluated reliably. Recent model intercomparison exercises have suggested that this may not currently be the case (Prather and Ehhalt, 2001; Stevenson et al., 2006).

The aims of this paper are to explore the differences seen in previous model estimates of the source and fate of tropospheric O₃, and to investigate to what extent these arise from the use of different input conditions or from differences in model formulation. Differences in precursor emissions or meteorological data may mask the more sub-
tles differences that reflect improved scientific understanding or deficiencies in process representation. Identifying the source of these differences is important for reducing the uncertainty in the modelled response of tropospheric O$_3$ to applied changes and for interpreting the results of multi-model “ensemble” studies. The sensitivity of the budget terms to key model processes is explored here in a consistent way with a single model. Section 2 reviews tropospheric O$_3$ budgets from published studies and highlights the origins of some of the differences between them. Section 3 describes the limited observational constraints on the O$_3$ budget. Section 4 then examines the sensitivity of the budget terms to emissions, meteorology, and key physical processes and interprets the variability seen in previous studies in light of these results. The implications of the results for future model intercomparison studies are outlined in Sect. 5.

2 Tropospheric ozone budgets in global models

A comparison of O$_3$ budgets from published global model studies is presented in Table 1. The studies are ordered chronologically by publication date, and statistics from earlier studies summarised in the Intergovernmental Panel on Climate Change (IPCC) Third Assessment Report (TAR) Prather and Ehhalt (2001) are compared with those published since 2000 to show how the calculated O$_3$ budget has evolved. There are large differences in the key terms between individual model studies: STE fluxes vary by a factor of four (340–1440 Tg/yr), deposition fluxes vary by almost a factor of three (530–1470 Tg/yr), and gross chemical production varies by a factor of two (2330–5260 Tg/yr). The tropospheric burden of O$_3$ varies between 240 and 380 Tg. However, these studies vary widely in their precursor emissions and in model formulation and resolution. Many of the pioneering early studies used simplified chemistry schemes omitting oxidation of non-methane hydrocarbons (NMHC), and a number of them had unreasonably high estimates of stratospheric influx; compensation between the key terms in the budget leads several studies to conclude that the troposphere is a net chemical sink of O$_3$. Recent studies have benefited from more detailed chemi-
cal schemes, improved understanding of the emissions of key precursor species, and better quality meteorological data at higher spatial resolution. This has reduced the variability in independent studies published since 2000 compared with those surveyed in the IPCC-TAR, but the 1σ variability remains large: STE 530±100 Tg/yr, chemistry 400±250 Tg/yr, and deposition 950±220 Tg/yr. It is not clear how much of this variability is due to the use of different input data (e.g., emissions or meteorological data) and how much is down to different model treatments of the key processes involved. These studies have typically used their own definitions of the tropopause and of the chemical fluxes constituting O₃ production, making direct comparison of O₃ burdens, lifetimes and tendencies particularly difficult.

A recent model intercomparison coordinated by the European Union project Atmospheric Composition Change: the European Network of Excellence (ACCENT) involved many of the models shown in Table 1 and aimed to reduce these uncertainties by constraining precursor emissions and applying consistent tropopause diagnostics across all participating models (Dentener et al., 2006a; Stevenson et al., 2006). The budget terms calculated in this study were higher than those from previous studies, and the variability in the terms was also larger, despite the more tightly constrained conditions. In particular, there is an increase in gross production between the IPCC-TAR (3450 Tg/yr), studies published since 2000 (4470 Tg/yr) and the ACCENT intercomparison (5110 Tg/yr), which is accompanied by a 10% increase in O₃ burden, a 20% increase in deposition, and a drop in the tropospheric lifetime of O₃ from 24 to 22 days. Higher estimates of precursor emissions make a substantial contribution to the increased production, as noted in regression analyses by Wu et al. (2006). The sensitivity of gross O₃ production to surface emissions of NOₓ and isoprene (C₅H₈) is shown in Fig. 1 for published studies and for individual models contributing to the ACCENT intercomparison. While the strong dependence on surface emissions is clear, there is a large scatter in these plots, even for the relatively well-constrained ACCENT studies, indicating that other factors have an important influence on the budget. A major goal of the present study is to investigate the effects of these processes more closely.
using the tighter constraints imposed by application of a single model framework, and ensuring that comparison of budget terms is fully self-consistent.

3 Constraints from observations

Of the budget terms considered here only influx of O$_3$ from the stratosphere has been adequately estimated from observational data. Murphy and Fahey (1994) used observed mid-latitude N$_2$O–O$_3$ correlations and an upward flux of N$_2$O derived from a budget analysis to derive a net downward flux of O$_3$ of 450 Tg/yr, with a range of 200–870 Tg/yr. Gettelman et al. (1997) used lower stratospheric O$_3$ measurements and calculations of the residual circulation to derive a net downward flux of 510 Tg/yr at 100 hPa (with a range of 450–590 Tg/yr). McLinden et al. (2000) reduced the uncertainty in the analysis of Murphy and Fahey (1994) by considering the tighter N$_2$O–NO$_y$ and NO$_y$–O$_3$ relationships separately, estimating a flux of 475±120 Tg/yr, and further refinements by Olsen et al. (2001) led to the best estimate currently available, 550±140 Tg/yr. Most model studies published since 2000 fall within this range, and the mean influx from the ACCENT model intercomparison was 552 Tg/yr. However, this agreement masks significant differences in the magnitude of gross cross-tropopause fluxes and in treatment of stratospheric O$_3$, and does not constitute an independent comparison as some models apply a flux constraint through use of tuned upper boundary conditions or an artificial stratospheric O$_3$ tracer such as Synoz (McLinden et al., 2000).

In the absence of reliable observation-based estimates of global deposition fluxes or chemical production, the best remaining constraint is on the abundance of O$_3$ itself. Without details of the seasonal, geographical and altitudinal variations in O$_3$ from previous studies only a simple comparison of the mean annual global tropospheric burden is possible here. However, the tropospheric O$_3$ burden and its dependence on the definition of the tropopause has not been evaluated previously. The tropospheric burden is estimated here from three different climatologies built from available ozonesonde, satel-
light and surface measurements, and using a number of different dynamical and thermal definitions of the tropopause, see Table 2. The climatologies were interpolated onto a common 4°×5° grid and integrated from the surface to a tracer tropopause defined by a given abundance of O₃ (100, 120 or 150 ppb), a thermal tropopause based on a lapse rate of 2 K km⁻¹ following the WMO definition, or a dynamical tropopause based on potential vorticity (PV) using the lower of the PV=2.0 surface and the tropical 380 K isentrope. For comparison, a cold-point tropopause based on the tropical temperature minimum is shown (a WMO thermal tropopause was applied in the extra-tropics), and a stepped-isobaric tropopause typical of crude model diagnostics is also used (100 hPa in the tropics and 250 hPa poleward of 30°). Thermal and dynamical tropopauses were calculated using monthly-mean data for year 2000 from the European Centre for Medium-Range Weather Forecasts (ECMWF); burdens calculated with 1997 data differ by less than 2 Tg (<1%). These comparisons provide only crude estimates of the true tropospheric burden, neglecting temporal or spatial variations in tropopause height which may bias it high or low, but they provide a convenient benchmark against which model simulations can be compared.

Use of a tracer tropopause provides the greatest consistency in O₃ burden for the different climatologies, as differences in O₃ distribution are suppressed. This definition is the simplest to employ when comparing model studies, and based on the 150 ppb level recommended by Prather and Ehhalt (2001) suggests a tropospheric burden of 335±10 Tg for the three climatologies used here. Thermal definitions generally give higher burdens, as noted by Bethan et al. (1996), and are more sensitive to O₃ differences in the tropopause region and thus more variable; the WMO lapse-rate definition gives a burden of about 352±30 Tg. Interestingly, the crude pressure tropopause gives very similar burdens to the WMO lapse-rate tropopause for all three climatologies used here, but note that they are quite different for typical model fields (discussed below), highlighting systematic differences in O₃ distribution between modelled and climatological fields. The PV=2.0 dynamical tropopause gives similar burdens to the 150 ppb tracer tropopause for both model and climatological fields, and burdens are consistently
lower than with the WMO lapse-rate definition.

There is considerable uncertainty in these estimates due to the sparse coverage of ozonesonde sites, but the O$_3$ burdens derived here are generally lower than the 370 Tg burden recommended by Prather and Ehhalt (2001). The dynamical tropopause is represented well by the 150 ppb O$_3$ tracer tropopause, and the mean burden of 344 Tg from the ACCENT model intercomparison (reduced to 336 Tg after removing model outliers) (Stevenson et al., 2006) is in good agreement with the 335±10 Tg range estimated here from measurement climatology. The variability in burden for a single O$_3$ distribution based on different definitions of the tropopause is as much as ±15%, suggesting that differences in definition make an important contribution to the differences between model burdens shown in Table 1.

4 CTM sensitivity studies

The dependence of the calculated O$_3$ budget on precursor emissions and on physical and meteorological variables is investigated here with a global CTM. Altering variables independently allows an assessment of their contributions to the model differences seen in Table 1, and use of a single model framework ensures that the comparison of their relative importance is self-consistent. A similar approach has been adopted in a recent study of uncertainties in a regional model (Mallet and Sportisse, 2006). Previous global studies have focussed on the effects of individual variables, e.g., hydrocarbon oxidation (Houweling et al., 1998; Roelofs and Lelieveld, 2000; von Kuhlmann et al., 2004), STE (Wauben et al., 1998), model resolution (von Kuhlmann et al., 2003; Wild and Prather, 2006), lightning NO$_x$ emissions (Labrador et al., 2005), convection (Lawrence et al., 2003; Doherty et al., 2005), and interannual variability in meteorology (Zeng and Pyle, 2005), but have not compared their effects in a comprehensive or systematic way.

The model used here is the Frontier Research System for Global Change (FRSGC) version of the University of California, Irvine (UCI) CTM described in Wild and Prather 2003.
with the configuration used in Wild et al. (2004). Pieced-forecast meteorological data generated by the European Centre for Medium-Range Weather Forecasts Integrated Forecast System (ECMWF-IFS) are used to drive the model. The 70–80 runs performed here use the same initial conditions and spin-up period, but a different variable is altered in each case to quantify its effect on the O₃ budget. The tropopause is diagnosed on-line using the 120 ppb abundance of Linoz, an O₃-like tracer with a linearised O₃ chemistry in the stratosphere, no loss in the free troposphere and a 2-day relaxation to 20 ppb at the surface (McLinden et al., 2000). For consistency with other published studies, O₃ budget terms are diagnosed from monthly-mean model output based on a 150 ppb O₃ tracer tropopause (Prather and Ehhalt, 2001; Stevenson et al., 2006). The difference in O₃ burden between this diagnostic O₃ tropopause and the on-line Linoz tropopause is generally less than 10 Tg, about 3%.

Two sets of emissions scenarios are used in these experiments. The base scenario (“BASE”) for NOₓ, CO and NMHC loosely represents 1990’s understanding, and is taken from version 2 of the EDGAR database for 1990 (Olivier et al., 1996) with isoprene emissions from Guenther et al. (1995) reduced to 220 TgC/yr following Hauglustaine et al. (1998). A second, updated scenario (“IIASA”) uses emission distributions from EDGAR v3.2 for 1995 (Olivier and Berdowski, 2001) scaled to the year 2000 using emission data from the International Institute for Applied Systems Analysis (IIASA) (Dentener et al., 2005), as recommended for the recent ACCENT model intercomparison. The sensitivity studies described here use the BASE emissions unless otherwise indicated, and are run with 1996 meteorology at T21L19 resolution (5.6° resolution with 19 levels).

Model runs are evaluated by comparing with ozonesonde observations from the period 1980–1993 (Logan, 1999), supplemented by additional data from the tropics between 1997 and 2002 (Thompson et al., 2003). Monthly interannual mean O₃ mixing ratios at selected altitudes at each location are averaged over four latitude bands and compared with monthly means from model simulations sampled at the same locations, following the method of Stevenson et al. (2006), see Fig. 2. Three model scenar-
ios are shown to illustrate the range of O_3 responses: the control run (BASE), a run with updated emissions (IIASA), and a run contributed to the ACCENT intercomparison (ACCENT) which used IIASA emissions in different model conditions (year 2000 meteorology with higher horizontal and vertical resolution, T42L37, and minor improvements to model physics described in Wild and Prather, 2006). While the magnitude and seasonality of O_3 are captured reasonably well in these runs, a number of discrepancies clearly remain, most notably in the wintertime at Northern mid-latitudes and in the tropical upper troposphere. The difference between BASE and IIASA runs shows how changes in precursor emissions alone contribute to changes in O_3; comparison with observations suggests that emissions in the BASE scenario are too low, particularly in the tropics. Differences between the IIASA and ACCENT runs reflect changes in meteorology and resolution, although differences in the tropical upper troposphere are dominated by changes in the magnitude and vertical distribution of lightning NO_x emissions in the ACCENT run.

To provide a more quantitative measure of model performance, the mean bias and root mean square (RMS) error are calculated over the ten locations shown in Figure 2 weighted by pressure so that they are representative of the O_3 burden. The annual mean bias over these locations for the BASE, IIASA and ACCENT runs is –5.3, –1.0 and 1.6 ppb, respectively, and the RMS errors are 7.8, 4.6 and 4.3 ppb. Comparison of the annual mean tropospheric O_3 burden with climatologies provides an additional measure of model performance, see Table 2. Using the BASE emissions the O_3 burden is consistently low for all tropopause definitions; the comparison is best for the ACCENT run where there is close agreement with the Fortuin and Kelder (1998) climatology. The largest differences are seen for the simple diagnostic tropopause based on pressure, reflecting differences in the geographical distribution of O_3 in the tropopause region and the lack of longitudinal variation in the climatologies.
4.1 Sensitivity to precursor emissions

The dependence of $O_3$ production on precursor emissions shown in Fig. 1 suggests that increases in $NO_x$ and isoprene emissions between the IPCC-TAR survey and the ACCENT studies make a large contribution to the differences seen in the calculated $O_3$ budget. To examine this, surface emissions of isoprene and $NO_x$ are increased independently by replacing the BASE emissions with the higher values recommended for the ACCENT runs, see Table 3. The increase from 42 to 51 TgN/yr for $NO_x$ and from 220 to 500 TgC/yr for isoprene each contribute an additional 450 Tg of $O_3$ production per year. Scaled to the mean emission increases between the IPCC-TAR survey and the ACCENT studies, these changes account for about 1100 Tg/yr of additional production, 66% of the 1660 Tg/yr increase in mean production between the studies. Production is enhanced more with increased isoprene than with increased $NO_x$, but a greater proportion of this occurs in the boundary layer where surface deposition is greater, and thus the increase in the tropospheric burden is less. Higher $NO_x$ and isoprene emissions both lead to a decrease in the lifetime of tropospheric $O_3$ to loss by chemistry and deposition, but they have opposing effects on the lifetime of $CH_4$, as $NO_x$ is a net source of OH while isoprene is a net sink. The greatly reduced mean bias and RMS error compared with ozonesonde data suggest that the higher $NO_x$ and isoprene emissions recommended for the ACCENT runs are more appropriate for present-day studies than those in the BASE scenario.

These emission scenarios are compared with those used in the OxComp model intercomparison conducted for the IPCC-TAR (Prather and Ehhalt, 2001), and with the IIASA emissions. The OxComp emissions give very similar budget changes to the increased-$NO_x$ run, BASE+N, and the IIASA emissions give budgets similar to the increased-$NO_x$ and isoprene run, BASE+NI. Although the differences in the $O_3$ lifetime between these runs and the equivalent BASE runs are small, the $CH_4$ lifetime changes significantly as emissions of CO and NMHC differ in the OxComp and IIASA scenarios.

To explore the full sensitivity of the $O_3$ budget to emissions of $NO_x$ and isoprene, a
series of 20 runs have been performed using isoprene emissions of 0, 220, 350, 500 and 650 TgC/yr and NO_x emissions of 30, 42, 51 and 60 TgN/yr. Isoprene emissions were scaled linearly on the distribution of Guenther et al. (1995), while NO_x emissions were varied non-linearly, with the 30 TgN/yr scenario representing 1970 conditions and the 60 TgN/yr scenario scaled to IIASA current-legislation emissions for 2030 (Den-tener et al., 2005). The variation in key budget terms is shown in Fig. 3. The gross production and burden of O_3 both increase steadily with increasing precursor emissions, consistent with the changes seen in the published budgets (see Fig. 1 and Table 1) and the O_3 lifetime is reduced as chemical destruction and deposition increase. The contrasting effects of NO_x and isoprene on OH lead to a balance such that the CH_4 lifetime remains little affected, but the gradient of the slope is steep, and small changes in either NO_x or isoprene can affect the lifetime substantially.

Note that the effects seen here are dependent on the complexity of the chemical scheme used in the model. The simplified scheme used here does not include isoprene nitrates, and more detailed studies treating their formation and deposition have found this to be a significant channel for removal of both isoprene intermediates and NO_x (Pöschl et al., 2000; von Kuhlmann et al., 2004). It is not clear how many previous studies have included this pathway, but it has been shown to lead to stabilization of O_3 production with increasing isoprene emissions (Wu et al., 2006). The differing complexity of chemical schemes may be an important source of differences between model studies and merits a more detailed investigation.

Table 3 also shows the sensitivity of the budget terms to the treatment of other hydrocarbons. Use of a globally-uniform field of CH_4 instead of CH_4 emissions and chemical integration avoids the long spin-up times associated with CH_4, but has very little effect on the O_3 budget or lifetime. The CH_4 lifetime is extended by about 5%, reflecting a higher atmospheric burden in the stratosphere when using a uniform field. Removal of all NMHC emissions leads to a reduction in O_3 production of about 900 Tg/yr, half of which is due to isoprene, and a reduction in O_3 burden of about 35 Tg (12%) compared with the BASE scenario. These results are consistent with those of Houweling et al.
(1998) shown in Table 1.

4.2 Sensitivity to physical processes

Meteorological and dynamical processes influence the production, mixing and removal of O$_3$ both directly and indirectly. Humidity, temperature and UV flux govern chemical reaction rates, boundary layer turbulence and convection redistribute O$_3$ and its precursors, influencing O$_3$ production and removal, and deposition processes remove O$_3$ and soluble precursors. Ozone chemistry in the upper troposphere is influenced by the magnitude and distribution of lightning-produced NO$_x$ emissions and by direct influx of O$_3$ from the stratosphere. Perturbation experiments are performed with the FRSGC/UCI CTM to explore the effect of these processes on O$_3$, and the impacts on the key budget terms are shown in Table 4. For compatibility with the emissions studies in Sect. 4.1, the same BASE control run was used.

The stratospheric influx of O$_3$ was increased by applying a consistent scaling of stratospheric Linoz chemistry. This leads to increased chemical removal and deposition in the troposphere, but also to decreased O$_3$ production, as noted by Wauben et al. (1998), due to faster removal of NO$_x$. Of the additional O$_3$ transported from the stratosphere, about 60% is destroyed chemically, 10% is deposited at the surface, and 30% is accounted for by decreased production. Quantifying the impact of STE on the tropospheric burden and lifetime of O$_3$ is complicated by the choice of tropopause, however. Applying a thermal or dynamical tropopause or using the same location as in the control run leads to a large increase in the burden and an increase in lifetime associated with additional O$_3$ at high altitude. However, applying an O$_3$ tracer tropopause leads to a much smaller increment in the burden as the tropospheric domain shrinks, and the O$_3$ lifetime shows a marginal decrease, see Table 4. Use of a tracer tropopause clearly damps the calculated budget response to changes in STE. As removal of O$_3$ by dry deposition changes only slowly along with the burden, the net impact of chemistry, P-L, is very sensitive to the STE flux used.

Dry deposition affects the O$_3$ budget directly by surface removal of O$_3$ and indirectly...
by removal of precursors such as NO$_x$ and PAN. Increased deposition is balanced largely by decreased chemical loss due to lower O$_3$, with a small increase in production caused by lower OH and hence an increased lifetime for NO$_x$. The decreased chemical loss is responsible for lower OH formation and hence for the increased CH$_4$ lifetime. The net impact of chemistry is very sensitive to dry deposition as the net STE flux changes only marginally in response to changes in the tropospheric burden. Note the non-linear response of the dry deposition rate to the applied increases in deposition velocity as the surface O$_3$ abundance falls. In contrast, wet deposition does not affect O$_3$ directly but leads to the removal of soluble species such as HNO$_3$ and H$_2$O$_2$ which influence the availability of NO$_x$ and OH. Increasing removal of these species by 50% causes both production and loss of O$_3$ to fall by about 2.5%, and the tropospheric burden drops proportionately. The small drop in net chemical production is balanced by reduced dry deposition, and the lifetime of O$_3$ is little affected. However, the decrease in OH leads to a significant increase in the lifetime of CH$_4$, and the OH response is 60–90% larger than for equivalent changes in the dry deposition rate. A non-linear response is also evident here, as a 50% reduction in wet deposition rates has twice the effect on the O$_3$ burden and removal as a 50% increase.

The effects on oxidant chemistry of small, globally uniform changes in temperature and humidity representing the uncertainty in meteorological fields are also examined. Increases in temperature affect chemical reaction kinetics and lead to significantly increased O$_3$ production and loss rates, but net production and other key budget terms are largely unaffected, and the tropospheric burden drops by less than 1% for a temperature rise of 5°C. However, the faster chemistry leads to a higher abundance of OH, and the CH$_4$ lifetime is reduced by almost 10% for a 5°C rise. This sensitivity of CH$_4$ oxidation to temperature provides a small negative feedback on climate warming, as noted by Fiore et al. (2006), and highlights temperature as a significant source of uncertainty in model-derived CH$_4$ lifetimes, as noted by Stevenson et al. (2000). Increased humidity leads to more efficient O$_3$ loss and greater OH production. Additional OH boosts O$_3$ production, but this only makes up about 45% of the additional O$_3$ loss,
and net production falls. Surface deposition falls by about 6% with a 20% increase in humidity, balancing the increased chemical loss, and the O₃ burden is reduced by 5%. The global O₃ burden is much more sensitive to changes in humidity than in temperature, and the CH₄ lifetime is also strongly affected. Note that the uncertainty in the tropospheric water vapour burden in current climate models is about 10% (Stevenson et al., 2006), and this would introduce a 3% (9 Tg) variability in the O₃ burden, a 3% (0.8 day) variability in O₃ lifetime and a 3% (0.3 year) variability in CH₄ lifetime based on these sensitivity studies.

Deep convection mixes O₃-rich air from the upper troposphere down towards the surface where the O₃ lifetime is shorter and lifts freshly-emitted O₃ precursors into the upper troposphere where O₃ production may be greater. Previous studies with and without convection have disagreed on the relative importance of these pathways, with Lawrence et al. (2003) finding a 12% increase in O₃ burden when including convection due to the dominant effect of increased production, and Doherty et al. (2005) finding a 14% decrease in burden as greater descent and destruction outweighed increased production. In the present study smaller changes in convection have been applied, and these were allowed to affect convective washout as well as lifting processes. Stronger convection leads to increased O₃ production in the upper troposphere but to decreased production in the lower troposphere, where the washout of soluble precursors is greater. There is an increase in the inferred influx from the stratosphere, indicating that convection penetrates above the tracer tropopause used here. Greater tropospheric overturning leads to higher surface O₃ and greater deposition, and the tropospheric burden decreases. Comparison with the wet deposition sensitivity runs presented above suggests that this is partly due to increased washout, and that the effect of lifting alone is small. These results lie midway between those presented by Lawrence et al. (2003) and Doherty et al. (2005), and highlight the large uncertainty in modelled O₃ responses to convection. It is not clear if this uncertainty reflects differences in convection schemes, lightning emissions or chemical complexity, as discussed in Doherty et al. (2005), but the uncertainty is sufficiently large that this topic
would be a valuable target for future model intercomparison studies.

The magnitude and distribution of lightning-produced NO\(_x\) emissions are highly uncertain (e.g., Price et al., 1997) but are important for O\(_3\) due to the longer lifetime of NO\(_x\) in the upper troposphere and its greater efficiency for O\(_3\) production. Increased emissions cause a large increase in production and in tropospheric burden, as seen in previous studies (Labrador et al., 2005); about 10% of the additional O\(_3\) produced is removed by deposition, and the rest is destroyed by chemistry, contributing to a higher abundance of OH and to a reduced CH\(_4\) lifetime. The sensitivity of the O\(_3\) burden and the CH\(_4\) lifetime are notably larger than for the other processes considered here. The range of lightning emissions used in the ACCENT model studies, 3–8 TgN/yr, would account for a 10% difference in O\(_3\) burden, a 0.7 day difference in O\(_3\) lifetime and a 1.4 year difference in CH\(_4\) lifetime between models. Note also that the study here uses uniform vertical emission profiles for inter-cloud and cloud-to-ground lightning strokes based on Price and Rind (1992). Inclusion of more realistic profiles based on observations (Pickering et al., 1998) (run Alt5) leads to a 25% greater increase in O\(_3\) production and a 50% greater increase in burden for the same 5 TgN/yr emissions, as a greater proportion of the NO\(_x\) emissions occur at high altitudes where the lifetimes of O\(_3\) and NO\(_x\) are longer.

Finally, a number of additional sensitivities related to model methodology have been examined, see Table 4. The dry deposition scheme of Isaksen et al. (1985) used in some studies (e.g., Berntsen et al., 1996; Wild and Prather, 2000; Zeng and Pyle, 2005) is a simpler alternative to the resistances-in-series scheme of Wesely (1989) used here. Application of this scheme with 1-m deposition velocities from Hough (1991) leads to 30% greater O\(_3\) deposition, an additional 260 Tg/yr. Faster removal of NO\(_x\) suppresses production, but chemical destruction falls by a greater margin to compensate for the increased deposition. The tropospheric O\(_3\) burden is almost 10% less than in the BASE run, and underestimation of the ozonesonde measurements suggest that the deposition rate with this scheme is too high. However, the lack of good observational constraints on deposition prevents this from being determined uniquely.
The deposition rate is also reduced by application of a non-local boundary layer mixing scheme (Holtslag and Boville, 1993) in place of the simple hourly bulk-mixing used in the BASE run. Less efficient vertical mixing leads to stronger near-surface gradients and reduced deposition of O₃, but a smaller proportion of NOₓ escapes into the free troposphere, so chemical production is suppressed. The net effect of these changes on the global burden is small, less than 1%.

A major source of uncertainty not considered here is in the calculation of photolysis rates. A number of different methods are currently used, ranging in complexity from tabulated rates based on climatological conditions to fully-interactive schemes accounting for absorption and scattering of aerosol and cloud particles calculated online. A simple test removing all cloud cover in the interactive Fast-J scheme used here (Wild et al., 2000) indicates that the global budget of O₃ is relatively insensitive to cloud cover. However, global O₃ production at the surface is 15% higher without cloud cover, balanced by lower production in the upper troposphere, and regional and seasonal differences can be much larger. Tie et al. (2003) found larger global effects (as much as 8%) suggesting that the impacts may depend on details of the cloud scheme used. Inclusion of monthly-mean aerosol fields for the scattering code similarly lead to regional differences in O₃ production, but the global impacts appear to be small.

4.3 Sensitivity to meteorology and resolution

Differences in meteorological data may affect the O₃ budget through self-consistent variations in the physical processes considered in Sect. 4.2. Meteorological data from the ECMWF-IFS model for 1997 and 2000 are compared with the fields for 1996 used in this study, and the impact on the O₃ budget is shown in Table 5 and in Fig. 4. The CTM is run at T21L19 with each meteorology, and is additionally run at T21L37 and T42L37 to test the effects of doubled vertical and horizontal resolution. Precursor emissions are taken from IIASA for closer comparison with the ACCENT studies, and the same emissions are used for each year. Total lightning NOₓ emissions are constrained to 5 Tg/yr, although the location of the emissions differs from year to year following the...
occurrence of deep convection events. Differences in O$_3$ burden and lifetime between the different years are small, but differences in STE, deposition and chemistry reach 7–8%. The lifetime of CH$_4$ is 5% longer in 1997 than in 2000, suggesting that OH levels are significantly lower and reflecting shifts in humidity and convection during the 1997–1998 El Niño period (Chandra et al., 1998; Sudo et al., 2001). The chemical production of O$_3$ is lower in 1997, and influx from the stratosphere is greater. These results are in good qualitative agreement with those of Zeng and Pyle (2005) who examined the evolution of the O$_3$ budget between 1990 and 2001 with a global climate model. The magnitude of this interannual variability indicates that model intercomparisons focussed on differences due to chemical or dynamical schemes should recommend use of the same meteorological fields.

Model O$_3$ budgets are sensitive to the horizontal and vertical resolution used, both through their effects on transport and mixing processes and through their impacts on O$_3$ chemistry from the spatial averaging of emissions (e.g., Chatfield and Delany, 1990). At the highest resolution used here, T42L37, there is a significant reduction in STE (8%, 40 Tg/yr) compared with T21L19 due to better resolution of the tropopause and there is an increase in surface deposition (5%, 40 Tg/yr). Increased net chemical production (25%, 80 Tg/yr) balances the budget, but there is a 2–4% drop in the O$_3$ burden. The magnitude of these effects is highly consistent for 1997 and 2000 meteorology, and confirms the results of previous studies (von Kuhlmann et al., 2003; Wild and Prather, 2006). The changes due to resolution seen here are similar in magnitude to those with different meteorological fields, but are systematic in nature. Increased vertical resolution has relatively little effect on gross chemical production or surface deposition, but accounts for at least half of the decrease in STE and for about one third of the increase in net production. Increased horizontal resolution dominates the changes in deposition and gross chemical production due to better localisation of boundary layer O$_3$, its production and convection, and better resolution of the tropopause region leads to an additional reduction in STE. Although the mean tropospheric lifetime of O$_3$ is only marginally affected by increased resolution, the chemical lifetime of CH$_4$ is substantially
increased, by as much as 5% for the 2000 case, reflecting lower OH and O₃ production at higher resolution.

4.4 Examining inter-model variability

To what extent do the sensitivities examined here account for the variability in published model budgets seen in Table 1? The results of these sensitivity studies and of earlier published studies are shown in Fig. 5. The variability is examined in two different parameter spaces which summarize the fate of O₃ and the abundance of OH, following Stevenson et al. (2006). Results from published model studies and from individual models from the ACCENT model intercomparison are shown in Figs. 5a and b, and results from the sensitivity studies over part of these parameter spaces are shown in Figs. 5c and d. The sensitivities examined here do not reflect the same level of uncertainty in the different variables, but are intended to be loosely comparable so that the relative importance of different processes is evident.

Differences in the abundance and fate of O₃ are revealed by the relationship between the tropospheric burden and the lifetime of O₃ to chemical removal and deposition and are shown in Fig. 5a. Inclusion of hydrocarbon chemistry and increased surface emissions lead to higher burdens and shorter lifetimes, but cannot account for the large spread in lifetime and burden seen in the ACCENT studies where emissions varied little. Figure 5c suggests that differences in humidity and in surface deposition may make important contributions to this variation, as they affect the O₃ burden and lifetime without changing gross tropospheric removal significantly. A 10% variation in humidity and a 200 Tg/yr variation in dry deposition, as seen in the ACCENT studies (Stevenson et al., 2006), could each account for 9 Tg in O₃ burden and 1 day in O₃ lifetime. Variations in temperature and convection have a similar but smaller effect. Wet deposition and STE lead to changes in the gross removal of O₃, but the scatter in this dimension is strongly influenced by emissions. Lightning NOₓ emissions varied between 3 and 8 Tg/yr for the ACCENT models and may account for 30 Tg in O₃ burden and 500 Tg/yr in O₃ removal. Isoprene emissions varied between 220 and 630 TgC/yr,
and may thus account for 20 Tg in O\textsubscript{3} burden and 650 Tg/yr in O\textsubscript{3} removal. However, the sensitivity studies performed here only account for a proportion of the variability seen in the ACCENT runs, and it is likely that differences in chemical mechanisms and model dynamics also make large contributions to this variability.

The relationship between the chemical loss of O\textsubscript{3}, governing the source of OH, and the lifetime of CH\textsubscript{4}, controlled by OH, is shown in Fig. 5b. The variability in this relationship is more restricted, and most points lie close to a single line, as processes that increase O\textsubscript{3} production and loss are associated with a higher level of OH and hence with a shorter CH\textsubscript{4} lifetime. Surface emissions of isoprene have a significantly different effect, however, as greater OH formation from higher O\textsubscript{3} production and loss is outweighed by the direct removal of OH that initiates hydrocarbon oxidation, and thus CH\textsubscript{4} lifetime increases with higher isoprene emissions as other studies have noted (von Kuhlmann et al., 2004). Model studies omitting higher hydrocarbons underestimate both O\textsubscript{3} loss and CH\textsubscript{4} lifetime. The mean chemical lifetime of CH\textsubscript{4} from the ACCENT studies is 9.8 years, close to the 9.6 years recommended by Prather and Ehhalt (2001), but the variability is large, 6.9–15.2 years. The variation in lightning emissions may account for almost 1.5 years in the CH\textsubscript{4} lifetime, but differences in temperature, humidity, wet and dry deposition, and STE also contribute significantly to this variability. The abundance of OH is very sensitive to the chemistry and photolysis schemes used, factors which are not quantified in this study. However, determination of the climate impacts of CH\textsubscript{4} and other tracer gases depends on a reliable quantification of chemical removal by OH, and the large variability seen in the ACCENT studies suggests that further work is needed to reduce the uncertainty in current models.

To estimate the contribution of the processes examined here to the variability in the budget terms from the ACCENT intercomparison, the terms are standardized by applying correction factors based on the sensitivities derived with the FRSGC/UCI CTM, see Table 6. A sensitivity factor for the change in each of these budget terms with respect to STE, dry deposition, lightning and surface emissions is derived from Table 4, and a correction factor is then applied for each model by scaling the fractional devia-
tion from the ensemble mean by the respective sensitivity factor. The mean production and loss terms decrease marginally, but the variability is significantly reduced, by more than 100 Tg/yr for production and 200 Tg/yr for loss, and the difference between the outlying models is reduced by almost 40%. The largest contributions to this reduced variability in production come from standardizing the isoprene emissions and lightning NO\textsubscript{x}, while for loss the greatest impact is from standardizing deposition. The 1σ variability in the CH\textsubscript{4} lifetime is reduced by about 25%, from 1.7 to 1.3 years, and lightning NO\textsubscript{x} emissions make the largest contribution to this. Although this standardization is approximate, it demonstrates that the biases imposed by the treatment of these processes are systematic, and that the differences between models would be reduced in more tightly constrained studies.

5 Conclusions

This study has examined how the tropospheric O\textsubscript{3} budget calculated in global CTMs has evolved over the past decade and has explored the sensitivity of the key budget terms to variability in precursor emissions, physical processes and meteorology. Large differences apparent in early CTM studies reflect overestimation of stratosphere-troposphere exchange and omission of hydrocarbon chemistry. The increases in O\textsubscript{3} production and tropospheric burden in more recent studies are principally due to use of higher surface emissions of NO\textsubscript{x} and isoprene. Increases in these emissions alone lead to an increase in O\textsubscript{3} production of 1100 Tg/yr in the FRSGC/UCI CTM, accounting for about 66% of the increase in production seen between the IPCC-TAR and ACCENT studies. Recent analysis by Wu et al. (2006) has shown similar results. Comparison with ozonesonde measurements suggests that precursor emissions used in earlier studies were too low, and that O\textsubscript{3} distributions are reproduced better with recent IIASA emissions data.

The burden of O\textsubscript{3} in the troposphere in CTMs has increased from around 300 Tg to around 340 Tg following the increase in precursor emissions, but is strongly influ-
enced by the tropopause definition used. Comparison of three O\textsubscript{3} climatologies with seven different tropopause definitions suggests that as much as ±15% of the variability in the burden may be due to the choice of tropopause. Recent model assessments have recommended use of an O\textsubscript{3} tracer tropopause of 150 ppb (Prather and Ehhalt, 2001), and this gives a tropospheric burden of 335±10 Tg based on the measurement climatologies used here. The mean burden from the ACCENT model intercomparison is 344 Tg, close to this value, but the 1σ variability remains large, 39 Tg, even with consistent use of the 150 ppb O\textsubscript{3} tracer tropopause, highlighting substantial differences in O\textsubscript{3} distribution between the models.

Sensitivity studies have been performed to examine how differences in key model processes might account for the difference in O\textsubscript{3} budget terms seen in the relatively well-constrained ACCENT model intercomparison. The magnitude and vertical distribution of lightning NO\textsubscript{x} emissions is shown to be a major source of uncertainty, and the 3–8 TgN/yr range in ACCENT study may account for a 10% difference in tropospheric ozone burden and a 1.4 year difference in CH\textsubscript{4} lifetime. Processes affecting the O\textsubscript{3} distribution, such as dry deposition, STE, and convection, and those affecting chemical production and loss, such as temperature, humidity, photolysis and wet removal of precursors, also have an important role and may account for much of the year-to-year variability in the budgets of O\textsubscript{3} and CH\textsubscript{4}. The uncertainty in these processes is not well characterised, but dry deposition, STE and surface and lightning emissions account for about 25% of the model variability in the ACCENT intercomparison. The large spread in CH\textsubscript{4} lifetime suggests that the climate response of changes in O\textsubscript{3} precursors in current models may differ substantially. Tighter constraints on lightning NO\textsubscript{x} emissions and meteorological fields would allow future model intercomparisons to focus more closely on the impacts of different chemistry schemes and different parameterizations of convection and mixing which are difficult to discern from recent studies.

Further development of CTMs with greater chemical detail, better treatment of scavenging and aerosol processes and finer resolution of small-scale processes is expected to lead to refinement of the O\textsubscript{3} budget terms explored here. As improved parameteri-
zations of the key processes become available, widely-differing models should start to converge on the same budget terms, with differences driven only by interannual variability in meteorology and emissions. Tightly-constrained model intercomparisons will continue to be valuable in identifying those areas where significant differences exist between models, and should ultimately allow a more rigorous quantification of uncertainty in the key budget terms. Important targets for future intercomparisons should be the distribution and speciation of NO\textsubscript{y} and the treatment of oxygenated VOCs, both of which have been implicated in the ACCENT studies as major sources of uncertainty (Dentener et al., 2006b; Shindell et al., 2006). Observational constraints on the key terms in the O\textsubscript{3} budget remain very poor, and improved estimates based on satellite or in-situ measurements would be valuable.

Acknowledgements. The author is grateful for discussions with D. Jacob (Harvard) and D. Stevenson (University of Edinburgh) which initiated this work, and would like to thank all those who contributed to the ACCENT model intercomparison. The study was supported by the Frontier Research Center for Global Change of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan, and by the NERC QUEST project in the UK.

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Table 1. Global ozone budgets from published CTM studies.\(^{a}\)

<table>
<thead>
<tr>
<th>Model</th>
<th>Resolution</th>
<th>Emissions</th>
<th>O(_3) Budget</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG0UNIA</td>
<td>10x10 L10</td>
<td>45 1550 0 0 3809 3183 427 528 953 253</td>
<td>Lelieveld and van Dorland (1995)</td>
<td></td>
</tr>
<tr>
<td>ECHAM3.2</td>
<td>T21 L19</td>
<td>40 1400 0 0 3206 3037 170 575 740 236</td>
<td>Roelofs and Lelieveld (1995)</td>
<td></td>
</tr>
<tr>
<td>IMAGES</td>
<td>5x5 L25</td>
<td>33 1428 322 220 4550 4000 550 550 1100</td>
<td>Muller and Brasseur (1995)</td>
<td></td>
</tr>
<tr>
<td>UISO</td>
<td>8x10 L9</td>
<td>35 1575 150 180 - - 295 846 1178 370</td>
<td>Bernsten et al. (1996)</td>
<td></td>
</tr>
<tr>
<td>GCTM</td>
<td>265 km L11</td>
<td>40 - 0 0 128 686 825 298</td>
<td>Levy et al. (1997)</td>
<td></td>
</tr>
<tr>
<td>ECHAM4</td>
<td>T30 L19</td>
<td>38 1900 0 0 3415 3340 75 459 534 271</td>
<td>Roelofs and Lelieveld (1997)</td>
<td></td>
</tr>
<tr>
<td>ECHAM/EM3</td>
<td>3.8x8 L9</td>
<td>38 1089 0 0 2894 3149 -255 740 533 266</td>
<td>Houweling et al. (1996)</td>
<td></td>
</tr>
<tr>
<td>ECHAM/EM3</td>
<td>3.8x8 L9</td>
<td>38 1089 108 400 3979 4065 -86 768 681 311</td>
<td>Houweling et al. (1996)</td>
<td></td>
</tr>
<tr>
<td>HGISP</td>
<td>4x5 L9</td>
<td>42 1040 99 597 4100 3680 420 400 820 310</td>
<td>Wang et al. (1998)</td>
<td></td>
</tr>
<tr>
<td>MOZART</td>
<td>T42 L25</td>
<td>43 1219 251 191 3018 2511 507 391 898</td>
<td>Hauglustaine et al. (1998)</td>
<td></td>
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<tr>
<td>CTMK</td>
<td>4x5 L15</td>
<td>38 - 0 0 3694 3719 -27 1429 1432</td>
<td>Wauben et al. (1998)</td>
<td></td>
</tr>
<tr>
<td>CTMK</td>
<td>4x5 L15</td>
<td>38 - 0 0 3789 3536 252 1092 1363</td>
<td>Wauben et al. (1998)</td>
<td></td>
</tr>
<tr>
<td>MATCH</td>
<td>T21 L28</td>
<td>37 1350 0 0 2490 3300 -810 1440 620</td>
<td>Cretz et al. (1999)</td>
<td></td>
</tr>
<tr>
<td>MATCH-MPC</td>
<td>T63 L28</td>
<td>39 1500 0 0 2334 2812 -478 1103 621</td>
<td>Lawrence et al. (1999)</td>
<td></td>
</tr>
<tr>
<td>HGISP2</td>
<td>4x5 L9</td>
<td>40 1030 100 550 4330 3960 370 390 760 360</td>
<td>Mickley et al. (1999)</td>
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<tr>
<td>STOCHEM</td>
<td>5x5 L9</td>
<td>41 1033 19 44 4323 3888 435 432 862 316</td>
<td>Stevenson et al. (2000)</td>
<td></td>
</tr>
<tr>
<td>UCI</td>
<td>8x10 L9</td>
<td>44 1050 92 502 4229 3884 345 473 812 288</td>
<td>Wild and Prather (2000)</td>
<td></td>
</tr>
<tr>
<td>TM3</td>
<td>3.8x5 L9</td>
<td>46 1365 160 356 3314 3174 140 565 705 347</td>
<td>Lelieveld and Dentener (2000)</td>
<td></td>
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<tr>
<td>ECHAM4</td>
<td>T30 L19</td>
<td>38 1750 0 0 3663 3699 -36 607 570 271</td>
<td>Roelofs and Lelieveld (2000)</td>
<td></td>
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<tr>
<td>ECHAM4</td>
<td>T30 L19</td>
<td>38 1148 118 400 4375 4302 73 590 668 294</td>
<td>Roelofs and Lelieveld (2000)</td>
<td></td>
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<tr>
<td>GEOS-CHEM</td>
<td>4x5 L20</td>
<td>46 1043 103 397 4900 4300 600 470 1070 315</td>
<td>Bey et al. (2001)</td>
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<tr>
<td>GISS-GCM</td>
<td>4x5 L9</td>
<td>38 1175 0 0 - - 389 750 1140 262</td>
<td>Shindell et al. (2001)</td>
<td></td>
</tr>
<tr>
<td>CHASER</td>
<td>T2 L32</td>
<td>42 2277 145 400 4895 4498 397 593 990 322</td>
<td>Sudo et al. (2002)</td>
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<tr>
<td>MOZART2</td>
<td>T42 L34</td>
<td>44 1195 218 410 5258 4794 509 343 857 362</td>
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<tr>
<td>MATCH-MPC</td>
<td>T21 L28</td>
<td>43 1261 175 350 4170 4090 80 630 700 306</td>
<td>von Kuhlmann et al. (2003)</td>
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<tr>
<td>GISS-GCM</td>
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<td>43 988 100 176 - - 1049 417 1466 349</td>
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<tr>
<td>LMD2-UKCA</td>
<td>25x3.8 L9</td>
<td>47 1364 0 0 4486 3918 554 523 1090 296</td>
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<td>UMD-CTM</td>
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<td>41 1132 54 503 - - 479 1290 340</td>
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<td>IMPACT</td>
<td>4x5 L23</td>
<td>38 1398 52 502 - - 161 663 826</td>
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<td>STOCHEM</td>
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<td></td>
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<tr>
<td>SUNYA-GCM</td>
<td>T42 L18</td>
<td>43 1167 170 220 - - 513 606 1127 376</td>
<td>Wong et al. (2004)</td>
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</table>

\(^{a}\) Emissions and budgets are in Tg yr\(^{-1}\) (TgN yr\(^{-1}\) for NO\(_x\) and TgC yr\(^{-1}\) for hydrocarbons); dashes indicate budget data unavailable.

\(^{b}\) Resolution in degrees (latitude by longitude) and number of model levels; spectral truncations of T21, T30, T42 and T63 are used to label Gaussian grids with approximate resolutions of 5.6°, 3.8°, 2.8° and 1.9° respectively.

\(^{c}\) Non-methane hydrocarbons excluding isoprene and terpenes; \(t\) label indicates terpenes also emitted (an additional 100–170 TgC yr\(^{-1}\)).

\(^{d}\) Selected studies published before 2000 shown in Table 4.12 of the IPCC Third Assessment Report, with Wauben et al. (1998) corrected.

2025
**Table 2.** Estimated annual mean tropospheric O$_3$ burdens (in Tg) based on O$_3$ climatologies and FRSGC/UCI CTM fields with different definitions of the tropopause.

<table>
<thead>
<tr>
<th>O$_3$ Fields</th>
<th>O$_3$ Tracer Tropopause</th>
<th>Pressure 100/250 hPa</th>
<th>Thermal Tropopause</th>
<th>Pot. Vorticity</th>
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<tr>
<td>Li and Shine (1995)</td>
<td>295</td>
<td>318</td>
<td>344</td>
<td>382</td>
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<td>Fortuin and Kelder (1998)</td>
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<td>Logan (1999)</td>
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<td>307</td>
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<td>322</td>
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<td>CTM O$_3$ fields</td>
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<td></td>
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<td>BASE emissions</td>
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<td>266</td>
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<td>IIASA emissions</td>
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<td>300</td>
<td>318</td>
<td>295</td>
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<tr>
<td>ACCENT run</td>
<td>303</td>
<td>316</td>
<td>331</td>
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2026
### Table 3. Annual ozone budgets in the FRSGC/UCI CTM: sensitivity to precursor emissions$^a$.  

<table>
<thead>
<tr>
<th>Run</th>
<th>Emissions Scenario</th>
<th>NO$_x$</th>
<th>Isop</th>
<th>CO</th>
<th>P</th>
<th>L</th>
<th>P-L</th>
<th>STE</th>
<th>Dep</th>
<th>Burd</th>
<th>O$_3$</th>
<th>CH$_4$</th>
<th>Mean</th>
<th>RMS</th>
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<tbody>
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<td>Base</td>
<td>EDGAR v.2</td>
<td>42</td>
<td>220</td>
<td>1248</td>
<td>4078</td>
<td>3842</td>
<td>236</td>
<td>519</td>
<td>756</td>
<td>290</td>
<td>23.0</td>
<td>9.07</td>
<td>-5.3</td>
<td>7.8</td>
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<tr>
<td>Base+I</td>
<td>Increased isoprene</td>
<td>42</td>
<td>500</td>
<td>1248</td>
<td>4529</td>
<td>4224</td>
<td>305</td>
<td>513</td>
<td>817</td>
<td>303</td>
<td>21.9</td>
<td>9.59</td>
<td>-3.2</td>
<td>6.3</td>
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<tr>
<td>Base+N</td>
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<td>51</td>
<td>220</td>
<td>1248</td>
<td>4512</td>
<td>4227</td>
<td>286</td>
<td>516</td>
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<td>306</td>
<td>22.2</td>
<td>8.17</td>
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<tr>
<td>Base+NI</td>
<td>NO$_x$ and isoprene</td>
<td>51</td>
<td>500</td>
<td>1248</td>
<td>5022</td>
<td>4654</td>
<td>368</td>
<td>510</td>
<td>876</td>
<td>322</td>
<td>21.2</td>
<td>8.56</td>
<td>-0.4</td>
<td>5.1</td>
</tr>
<tr>
<td>OxComp</td>
<td>OxComp emis</td>
<td>50</td>
<td>220</td>
<td>1550</td>
<td>4454</td>
<td>4166</td>
<td>288</td>
<td>515</td>
<td>802</td>
<td>304</td>
<td>22.3</td>
<td>8.90</td>
<td>-3.1</td>
<td>7.0</td>
</tr>
<tr>
<td>IIASA</td>
<td>IIASA 2000 emis</td>
<td>51</td>
<td>500</td>
<td>1078</td>
<td>4926</td>
<td>4578</td>
<td>348</td>
<td>510</td>
<td>857</td>
<td>318</td>
<td>21.4</td>
<td>8.37</td>
<td>-1.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

$^a$ Emissions/budgets in Tg yr$^{-1}$ (TgN yr$^{-1}$ for NO$_x$, TgC yr$^{-1}$ for isoprene); lifetimes in days for O$_3$ and years for CH$_4$; biases in ppb.
Table 4. Annual ozone budgets in the FRSGC/UCI CTM: sensitivity to physical processes.

<table>
<thead>
<tr>
<th>Run</th>
<th>Brief Description</th>
<th>P</th>
<th>L</th>
<th>P-L</th>
<th>STE</th>
<th>Dep</th>
<th>Burd</th>
<th>O₃</th>
<th>CH₄</th>
<th>Mean</th>
<th>RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>STE1</td>
<td>50% decreased O₃ STE</td>
<td>4183</td>
<td>3700</td>
<td>484</td>
<td>253</td>
<td>737</td>
<td>281</td>
<td>23.1</td>
<td>9.20</td>
<td>-7.2</td>
<td>8.9</td>
</tr>
<tr>
<td>STE2</td>
<td>20% decreased O₃ STE</td>
<td>4126</td>
<td>3776</td>
<td>351</td>
<td>395</td>
<td>746</td>
<td>286</td>
<td>23.1</td>
<td>9.13</td>
<td>-6.2</td>
<td>8.2</td>
</tr>
<tr>
<td>Base</td>
<td>Control Run</td>
<td>4078</td>
<td>3842</td>
<td>236</td>
<td>519</td>
<td>756</td>
<td>290</td>
<td>23.0</td>
<td>9.07</td>
<td>-5.3</td>
<td>7.8</td>
</tr>
<tr>
<td>STE3</td>
<td>20% increased O₃ STE</td>
<td>4047</td>
<td>3903</td>
<td>154</td>
<td>606</td>
<td>761</td>
<td>293</td>
<td>22.9</td>
<td>9.02</td>
<td>-4.6</td>
<td>7.4</td>
</tr>
<tr>
<td>STE4</td>
<td>50% increased O₃ STE</td>
<td>3975</td>
<td>4013</td>
<td>-38</td>
<td>812</td>
<td>776</td>
<td>299</td>
<td>22.8</td>
<td>8.90</td>
<td>-3.0</td>
<td>7.1</td>
</tr>
</tbody>
</table>

**Effects of Stratosphere-Troposphere Exchange**

**Dry1** 50% decreased dry dep 4051 4108 -57 517 460 302 24.1 8.78 -3.2 7.1

**Dry2** 20% decreased dry dep 4066 3936 130 518 649 295 23.5 8.97 -4.5 7.5

**Base** Control Run 4078 3842 236 519 756 290 23.0 9.07 -5.3 7.8

**Dry3** 20% increased dry dep 4091 3761 329 520 850 285 22.6 9.16 -6.9 8.2

**Dry4** 50% increased dry dep 4109 3656 453 521 975 280 22.0 9.28 -6.7 8.8

**Effects of Wet Deposition**

**Wet1** 50% decreased wet dep 4302 4046 255 517 772 300 22.7 8.52 -3.7 6.8

**Wet2** 20% decreased wet dep 4146 3905 242 518 760 293 22.9 8.89 -4.8 7.5

**Wet3** Control Run 4078 3842 236 519 756 290 23.0 9.07 -5.3 7.8

**Wet4** 50% increased wet dep 3972 3745 227 521 749 285 23.1 9.40 -6.0 8.4

**Effects of Temperature on Chemistry**

**Tem1** 5°C lower temperature 4141 3905 235 519 754 291 23.4 9.38 -5.1 7.7

**Tem2** 2°C lower temperature 4078 3842 236 519 756 290 23.0 9.07 -5.3 7.8

**Base** Control Run 4078 3842 236 519 756 290 23.0 9.07 -5.3 7.8

**Tem3** 2°C higher temperature 4141 3905 237 519 757 289 22.6 8.76 -5.4 7.9

**Tem4** 5°C higher temperature 4245 4005 239 519 760 288 22.1 8.32 -5.5 8.1

**Effects of Humidity on Chemistry**

**Hum1** 20% decreased humidity 4030 3730 300 516 815 309 24.8 9.69 -2.3 6.0

**Hum2** 10% decreased humidity 4055 3789 266 518 785 299 23.8 9.35 -3.9 6.8

**Base** Control Run 4078 3842 236 519 756 290 23.0 9.07 -5.3 7.8

**Hum3** 10% increased humidity 4100 3891 209 520 731 282 22.3 8.82 -6.5 8.8

**Hum4** 20% increased humidity 4121 3936 185 521 709 275 21.6 8.61 -7.6 9.8

**Effects of Convection**

**Cnv1** 50% reduced convection 4118 3861 257 488 746 295 23.3 9.03 -4.9 7.5

**Cnv2** 20% reduced convection 4092 3850 242 508 751 291 23.1 9.05 -5.2 7.7

**Base** Control Run 4078 3842 236 519 756 290 23.0 9.07 -5.3 7.8

**Cnv3** 20% greater convection 4067 3837 230 529 760 289 22.9 9.08 -5.3 8.0

**Cnv4** 50% greater convection 4055 3830 224 542 767 287 22.8 9.09 -5.4 8.2

**Effects of Lightning NOₓ**

**Lit1** No lightning NOₓ 3460 3284 176 524 701 260 23.8 11.03 -9.7 11.9

**Lit2** 50% decreased lightning 3802 3593 209 521 731 277 23.4 9.84 -7.2 9.5

**Base** Control Run 4078 3842 236 519 756 290 23.0 9.07 -5.3 7.8

**Lit3** 50% increased lightning 4316 4058 258 517 776 301 22.7 8.50 -3.6 6.6

**Effects of Alternate Treatments**

**Alt1** Simple dry deposition 3914 3419 495 522 1019 268 22.0 9.67 -8.6 10.3

**Alt2** non-local PBL mixing 3971 3799 172 519 691 288 23.4 9.20 -5.6 8.1

**Alt3** Clear-sky photolysis 4060 3813 248 521 770 283 22.6 9.07 -6.1 8.7

**Alt4** Aerosol in photolysis 4064 3830 233 519 753 290 23.1 9.13 -5.1 7.7

**Alt5** C-profile lightning NOₓ 4236 4003 232 517 750 304 23.3 8.72 -3.5 6.6

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*a Budgets in Tg yr⁻¹; lifetimes in days for O₃ and years for CH₄; biases in ppb.*

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2028
Table 5. Annual ozone budgets in the FRSGC/UCI CTM: sensitivity to meteorology and resolution$^a$.

<table>
<thead>
<tr>
<th>Run</th>
<th>Description</th>
<th>Resolution</th>
<th>Year</th>
<th>P</th>
<th>L</th>
<th>P-L</th>
<th>STE</th>
<th>Dep</th>
<th>Burd</th>
<th>O$_3$</th>
<th>CH$_4$</th>
<th>Mean</th>
<th>RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Met96</td>
<td>IFS 1996 data</td>
<td>T21 L19</td>
<td>1996</td>
<td>5247</td>
<td>4932</td>
<td>315</td>
<td>505</td>
<td>814</td>
<td>342</td>
<td>21.7</td>
<td>8.38</td>
<td>2.1</td>
<td>5.0</td>
</tr>
<tr>
<td>Met97</td>
<td>IFS 1997 data</td>
<td>T21 L19</td>
<td>1997</td>
<td>4975</td>
<td>4663</td>
<td>312</td>
<td>535</td>
<td>849</td>
<td>336</td>
<td>22.2</td>
<td>8.79</td>
<td>0.9</td>
<td>5.9</td>
</tr>
<tr>
<td>Met97L</td>
<td>37 levels</td>
<td>T21 L37</td>
<td>1997</td>
<td>5103</td>
<td>4766</td>
<td>338</td>
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<td>340</td>
<td>22.1</td>
<td>8.54</td>
<td>2.3</td>
<td>6.0</td>
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<td>Met97R</td>
<td>T42 resolution</td>
<td>T42 L37</td>
<td>1997</td>
<td>4982</td>
<td>4588</td>
<td>394</td>
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<td>331</td>
<td>22.0</td>
<td>8.89</td>
<td>1.5</td>
<td>5.3</td>
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<td>Met00</td>
<td>IFS 2000 data</td>
<td>T21 L19</td>
<td>2000</td>
<td>5314</td>
<td>4972</td>
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<td>524</td>
<td>869</td>
<td>345</td>
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<td>2.4</td>
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<td>T21 L37</td>
<td>2000</td>
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<td>4734</td>
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<td>481</td>
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<td>331</td>
<td>21.4</td>
<td>8.45</td>
<td>1.7</td>
<td>4.3</td>
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</tbody>
</table>

$^a$ Budgets in Tg yr$^{-1}$; lifetimes in days for O$_3$ and years for CH$_4$; biases in ppb.
Table 6. Budget terms from the ACCENT model intercomparison corrected for differing emissions, deposition and STE fluxes.

<table>
<thead>
<tr>
<th></th>
<th>O\textsubscript{3} Prod (Tg/yr)</th>
<th>O\textsubscript{3} Loss (Tg/yr)</th>
<th>CH\textsubscript{4} Lifetime (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACCENT study</td>
<td>5110±606</td>
<td>4668±727</td>
<td>9.79±1.74</td>
</tr>
<tr>
<td>Standardized values</td>
<td>5079±494</td>
<td>4639±513</td>
<td>9.71±1.33</td>
</tr>
</tbody>
</table>
Fig. 1. Relationship between gross O$_3$ production, P(O$_3$), and precursor emissions for the model studies described in Table 1 with and without hydrocarbon oxidation and for the ACCENT model intercomparison studies described in Stevenson et al. (2006).
**Fig. 2.** Comparison of the annual cycle of $O_3$ in the FRSGC/UCI CTM with ozonesonde measurements at 750, 500 and 250 hPa averaged over four latitude bands. Results for 3 model simulations are shown: the BASE run (green), a run with IIASA emissions (red) and a T42L37 run for year 2000 with IIASA emissions (blue). Monthly mean mixing ratios at each site are averaged over each band and are compared with model fields sampled in the same way; error bars show the average interannual standard deviation at each station. Ozonesonde data are from Logan (1999) and Thompson et al. (2003); the number of stations in each band is given by “n”.
Fig. 3. Isopleth plots showing the variations in O$_3$ production, O$_3$ burden and the tropospheric lifetimes of O$_3$ and CH$_4$ for different combinations of NO$_x$ and Isoprene emissions using the FRSGC/UCI CTM with 1996 meteorology at T21 resolution. The BASE run (“B”) and IIASA run for the ACCENT studies (“A”) are indicated.
Fig. 4. Effects of meteorology and model resolution on the annual flux of O$_3$ through stratosphere-troposphere exchange (STE), net chemistry (P-L) and surface deposition (Dep).
Fig. 5. The relationship between the tropospheric burden of O₃ and its lifetime to chemical removal and deposition (left panels, a and c) and between the chemical removal of O₃ and the chemical lifetime of CH₄ (right panels, b and d). The upper panels (a and b) show results from published studies summarized in Table 1 and the lower panels (c and d) show the results of sensitivity studies listed in Table 3. Tropospheric O₃ removal rates are shown as diagonal lines in the left panels (labelled in Tg/yr). For ease of comparison the domain of the sensitivity studies shown in the lower panels c and d is highlighted in the upper panels with a box.