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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 also make large contributions. 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_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_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 chemical mechanisms and dynamical schemes 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

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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 O_3 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 O_3 influx of 550±170 Tg/yr from the stratosphere and a surface removal of 1000±200 Tg/yr by dry deposition, with net chemical production making up the balance of 450±300 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 focussed 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 O_3 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 O_3, requires that the principal terms in the O_3 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 O_3, 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 subtle 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 chemical 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, net production 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 O_3 production, making direct comparison of O_3 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

Table 1. Global ozone budgets from published CTM studies[a].

Model	Resolution[b]	Emissions				O₃ Budget						Reference
		NO$_x$	CO	HC[c]	Isop	P	L	P-L	STE	Dep	Burd	
MOGUNTIA	10x10 L10	45	1550	0	0	3609	3183	427	528	953	253	Lelieveld and van Dorland (1995)
ECHAM3.2	T21 L19	40	1400	0	0	3206	3037	170	575	740	236	Roelofs and Lelieveld (1995)
IMAGES	5x5 L25	33	1428	322t	220	4550	4000	550	550	1100	–	Müller and Brasseur (1995)
UIO	8x10 L9	35	1575	150	180	–	–	295	846	1178	370	Berntsen et al. (1996)
GCTM	265 km L11	40	–	0	0	–	–	128	696	825	298	Levy et al. (1997)
ECHAM4	T30 L19	38	1900	0	0	3415	3340	75	459	534	271	Roelofs and Lelieveld (1997)
ECHAM/TM3	3.8x5 L9	38	1089	0	0	2894	3149	–255	740	533	266	Houweling et al. (1998)
ECHAM/TM3	3.8x5 L9	38	1089	108	400	3979	4065	-86	768	681	311	Houweling et al. (1998)
HGISS	4x5 L9	42	1040	99	597	4100	3680	420	400	820	310	Wang et al. (1998)
MOZART	T42 L25	43	1219	251t	220	3018	2511	507	391	898	–	Hauglustaine et al. (1998)
CTMK	4x5 L15	38	–	0	0	3694	3719	–27	1429	1432	–	Wauben et al. (1998)
CTMK	4x5 L15	38	–	0	0	3789	3536	252	1092	1363	–	Wauben et al. (1998)
MATCH	T21 L28	37	1350	0	0	2490	3300	–810	1440	620	–	Crutzen et al. (1999)
MATCH-MPIC	T63 L28	39	1500	0	0	2334	2812	–478	1103	621	–	Lawrence et al. (1999)
HGISS-GCM	4x5 L9	40	1030	100	550	4330	3960	370	390	760	360	Mickley et al. (1999)
STOCHEM	5x5 L9	41	1033	197	446	4323	3888	435	432	862	316	Stevenson et al. (2000)
UCI	8x10 L9	44	1050	92	502	4229	3884	345	473	812	288	Wild and Prather (2000)
TM3	3.8x5 L9	46	1365	160	356	3314	3174	140	565	705	347	Lelieveld and Dentener (2000)
ECHAM4	T30 L19	38	1750	0	0	3663	3699	-36	607	570	271	Roelofs and Lelieveld (2000)
ECHAM4	T30 L19	38	1148	118	400	4375	4302	73	590	668	294	Roelofs and Lelieveld (2000)
GEOS-CHEM	4x5 L20	46	1043	103	397	4900	4300	600	470	1070	315	Bey et al. (2001)
GISS-GCM	4x5 L9	38	1175	0	0	–	–	389	750	1140	262	Shindell et al. (2001)
CHASER	T21 L32	44	1227	145t	400	4895	4498	397	593	990	322	Sudo et al. (2002)
MOZART2	T42 L34	44	1195	218t	410	5258	4749	509	343	857	362	Horowitz et al. (2003)
MATCH-MPIC	T21 L28	43	1261	175	350	4170	4090	80	630	700	306	von Kuhlmann et al. (2003)
MATCH-MPIC	T63 L28	43	1261	175	350	4560	4290	280	540	820	294	von Kuhlmann et al. (2003)
GISS-GCM	4x5 L23	40	988	100	176	–	–	1049	417	1466	349	Shindell et al. (2003)
LMDz-INCA	2.5x3.8 L19	47	1364	0	0	4486	3918	567	523	1090	296	Hauglustaine et al. (2004)
UMD-CTM	4x5 L20	41	1132	54	503	–	–	–	479	1290	340	Park et al. (2004)
IMPACT	4x5 L52	38	1398	52t	502	–	–	161	663	826	–	Rotman et al. (2004)
STOCHEM	5x5 L9	50	1114	179t	507	4975	4421	554	395	949	273	Stevenson et al. (2004)
FRSGC/UCI	T21 L19	42	1248	143	220	4091	3854	237	519	757	283	Wild et al. (2004)
SUNYA-GCCM	T42 L18	43	1167	170	220	–	–	513	606	1127	376	Wong et al. (2004)
All Models	33 studies	41	1270	94	240	3948	3745	245	636	902	307	
(mean±std.dev)		±4	±222	±89	±210	±761	±554	±346	±273	±255	±38	
IPCC-TAR[d]	12 studies	39	1285	75	195	3448	3435	46	765	818	304	Prather and Ehhalt (2001)
		±3	±293	±89	±232	±730	±505	±403	±380	±265	±32	
post-2000	17 studies	43	1186	122	338	4465	4114	396	529	949	314	
		±3	±122	±66	±162	±514	±409	±247	±105	±222	±33	
ACCENT	21 models	51	1078	125t	470	5110	4668	442	552	1003	344	Stevenson et al. (2006)
		±2	±57	–	±66	±606	±727	±309	±168	±200	±39	

[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 the entry for Wauben et al. (1998) corrected.

uncertainties by constraining fossil fuel 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
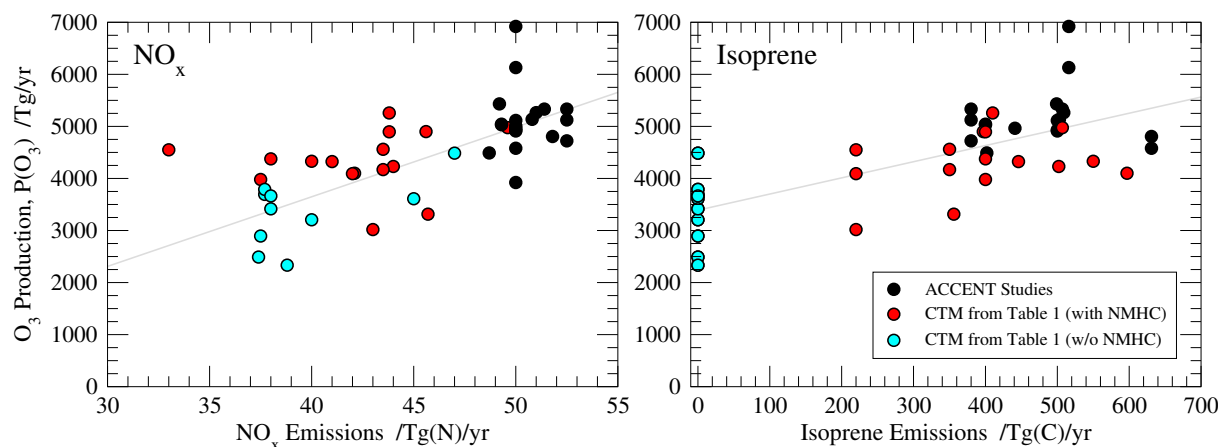
Fig. 1. Relationship between gross O_3 production, $P(O_3)$, and precursor emissions for the model studies described in Table 1 with and without hydrocarbon oxidation and for the ACCENT model intercomparison studies described in Stevenson et al. (2006).

O_3 burden, a 20% increase in deposition, and a drop in the tropospheric lifetime of O_3 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. (2007), and largely reflect improved understanding of NO_x sources and emission factors. The sensitivity of gross O_3 production to surface emissions of NO_x and isoprene (C_5H_8) is shown in Fig. 1 for published studies and for individual models contributing to the ACCENT intercomparison. While the strong dependence on emissions is clear, there is a large scatter in these plots, even for the relatively well-constrained ACCENT studies. The variation in emissions for the ACCENT models reflects differences in natural sources of NO_x and isoprene which are interactive with model vegetation and meteorology in many of the models. The scatter indicates 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_2O–O_3 correlations and an upward flux of N_2O 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_2O–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 and location of 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, satellite 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 O_3 (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-

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.

O_3 Fields	O_3 Tracer Tropopause			Pressure	Thermal Tropopause		Pot. Vorticity
	100 ppb	120 ppb	150 ppb	100/250 hPa	WMO	Cold Point	2.0 PVU
O_3 Climatology							
Li and Shine (1995)	295	318	344	382	383	408	362
Fortuin and Kelder (1998)	295	312	333	345	347	370	332
Logan (1999)	292	307	327	322	325	343	308
CTM O_3 fields							
BASE emissions	260	273	290	266	296	321	285
IIASA emissions	285	300	318	295	327	353	316
ACCENT run	303	316	331	313	338	363	323

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 O_3 burden for the different climatologies, as differences in O_3 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 O_3 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 O_3 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) which used this tracer tropopause 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 (2000) 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
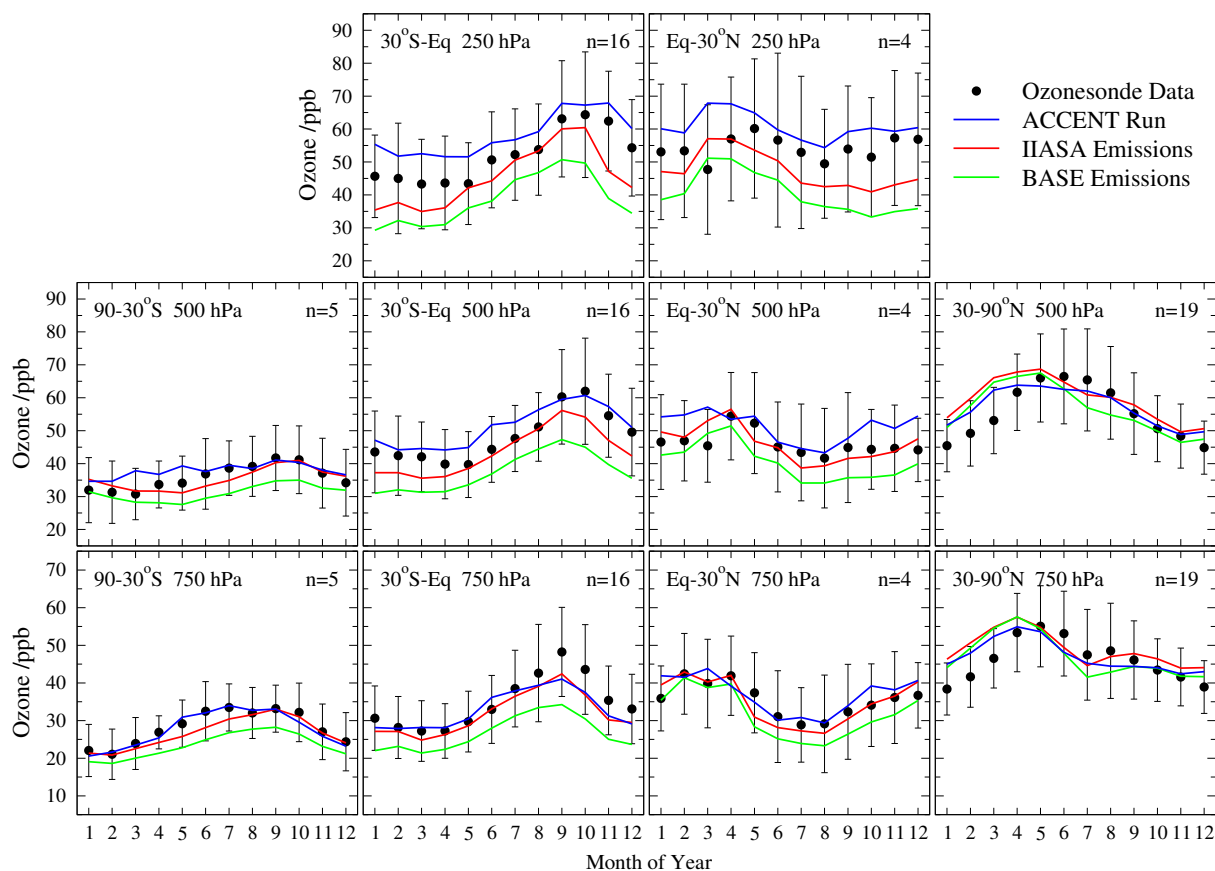
Fig. 2. Comparison of the annual cycle of O_3 in the FRSGC/UCI CTM with ozonesonde measurements at 750, 500 and 250 hPa averaged over four latitude bands. Results for 3 model simulations are shown: the BASE run (green), a run with IIASA emissions (red) and a T42L37 run for year 2000 with IIASA emissions (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".

the model. The model includes an explicit treatment of $HO_x/O_x/NO_x$ chemistry and CH_4 oxidation, and a lumped NMHC chemistry for the representative species butane, propene, xylene and isoprene. The 70–80 runs performed here use the same initial conditions and 8-month spin-up period, but a different variable is altered in each case to quantify its effect on the O_3 budget. The tropopause is diagnosed on-line using the 120 ppb abundance of Linoz, an O_3-like tracer with a linearised O_3 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, O_3 budget terms are diagnosed from monthly-mean model output based on a 150 ppb O_3 tracer tropopause (Prather and Ehhalt, 2001; Stevenson et al., 2006). The difference in O_3 burden between this diagnostic O_3 tropopause and the on-line Linoz tropopause is generally less than 10 Tg, about 3%. The STE flux is inferred as the residual term in the O_3 budget after accounting for the diagnosed net chemical production and deposition and the net change in burden over the year. Gross chemical pro-

duction and destruction of O_3 are diagnosed from the model chemistry scheme; gross destruction is based on the reaction fluxes of $O(^1D)$ with water vapour and of O_3 with HO_x and alkenes, and gross production is taken as the difference between the calculated chemical O_3 tendency and the diagnosed destruction rate to ensure mass consistency.

Two sets of emissions scenarios are used in these experiments. The base scenario ("BASE") for NO_x, 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 industrial emissions 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. Biomass burning emissions from van de Werf et al. (2003) are used with this scenario, together with the full 500 TgC/yr

of isoprene emissions from Guenther et al. (1995). Lightning NO_x emissions of 5 TgN/yr and CH_4 emissions of 550 Tg/yr are used with both these scenarios. The sensitivity studies described here use the BASE emissions unless otherwise indicated, and are run with 1996 meteorology at T21L19 resolution (5.6° × 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 O_3 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 scenarios 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 AC-CENT 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 influenced by the use of marginally higher lightning NO_x emissions in the AC-CENT run (6.5 TgN/yr rather than 5 TgN/yr) and application of the observation-based emissions profiles of Pickering et al. (1998) in place of uniform profiles based on Price and Rind (1992).

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 NO_x and isoprene 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 gross 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 more O_3 in the lower troposphere and thus to a decrease in its tropospheric lifetime, 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 budget terms with the OxComp emissions are very similar to those in 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 Ox-Comp 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 (Dentener 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

Table 3. Annual ozone budgets in the FRSGC/UCI CTM: sensitivity to precursor emissions[a].

| Run | Emissions Scenario | Emissions | | | | O_3 Budget | | | | | | Lifetimes | | O_3 Bias | |
		NO_x	Isop	HC	CO	P	L	P-L	STE	Dep	Burd	O_3	CH_4	Mean	RMS
						Sensitivity to Isoprene and NO_x Emissions									
Base	EDGAR v.2	42	220	143	1248	4078	3842	236	519	756	290	23.0	9.07	–5.3	7.8
Base+I	Increased isoprene	42	500	143	1248	4529	4224	305	513	817	303	21.9	9.59	–3.2	6.3
Base+N	Increased NO_x	51	220	143	1248	4512	4227	286	516	803	306	22.2	8.17	–2.8	6.1
Base+NI	NO_x and isoprene	51	500	143	1248	5022	4654	368	510	876	322	21.2	8.56	–0.4	5.1
OxComp	OxComp emis	50	220	161	1550	4454	4166	288	515	802	304	22.3	8.90	–3.1	7.0
IIASA	IIASA 2000 emis	51	500	122	1078	4926	4578	348	510	857	318	21.4	8.37	–1.0	4.6
						Sensitivity to Hydrocarbon Emissions									
Base	EDGAR v.2	42	220	143	1248	4078	3842	236	519	756	290	23.0	9.07	–5.3	7.8
FixCH4	CH_4 at 1760 ppb	42	220	143	1248	4117	3877	241	518	760	292	23.0	9.49	–5.0	7.5
NoIsop	NMHC: no Isoprene	42	0	143	1248	3616	3469	146	525	675	274	24.1	8.75	–7.6	10.0
NoHVOC	NMHC: C_2H_6 only	42	0	14	1248	3233	3183	50	528	584	258	25.0	8.57	–10.0	11.7
NoVOC	NMHC: none	42	0	0	1248	3171	3138	33	529	568	255	25.1	8.52	–10.5	12.1

[a] Emissions/budgets in $Tg\,yr^{-1}$ ($TgN\,yr^{-1}$ for NO_x, $TgC\,yr^{-1}$ for isoprene and NMHC); O_3 lifetime to chemical loss and deposition in days; CH_4 lifetime to removal by tropospheric OH in years; biases in ppb.

isoprene on OH lead to a balance such that the CH_4 lifetime remains little affected by the combined emissions changes between the BASE and IIASA scenarios. However, the gradient of the slope is steep, and small changes in either NO_x or isoprene separately 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., 2007). 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 hydrocarbon emissions. Use of a globally-uniform field of CH_4 instead of a transported CH_4 tracer avoids the long spin-up times associated with CH_4, but is shown to have 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 globally-uniform field. Complete removal of all hydrocarbon 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% displaces O_3 that would have been formed in the troposphere, and is thus 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. Applying an O_3 tracer tropopause, as here, leads to a much smaller increment in the burden as the tropospheric domain
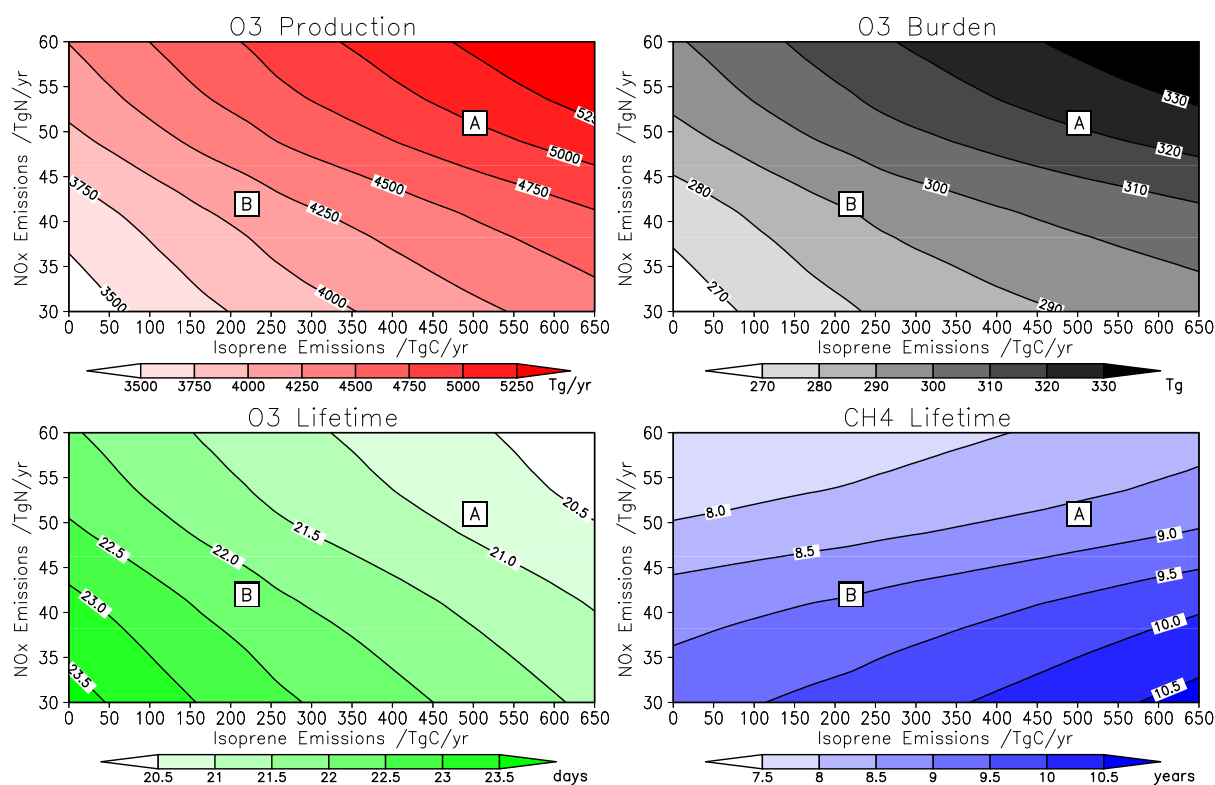
Fig. 3. Isopleth plots showing the variations in O_3 production, O_3 burden and the tropospheric lifetimes of O_3 and CH_4 for different combinations of NO_x and Isoprene emissions using the FRSGC/UCI CTM with 1996 meteorology at T21 resolution. The BASE run ("B") and IIASA run for the ACCENT studies ("A") are indicated.

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. Dry deposition velocities were altered for all species simultaneously in this sensitivity study. Increased O_3 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. Decreased chemical loss of O_3 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_2O_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 of temperature and humidity on oxidant chemistry are examined by applying small, globally uniform changes representative of the uncertainty in meteorological fields to the chemistry only. 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

Table 4. Annual ozone budgets in the FRSGC/UCI CTM: sensitivity to physical processes[a].

Run	Brief Description	O$_3$ Budget						Lifetimes		O$_3$ Bias	
		P	L	P-L	STE	Dep	Burd	O$_3$	CH$_4$	Mean	RMS
Effects of Stratosphere-Troposphere Exchange											
STE1	50% decreased O$_3$ STE	4183	3700	484	253	737	281	23.1	9.20	–7.2	8.9
STE2	20% decreased O$_3$ STE	4126	3776	351	395	746	286	23.1	9.13	–6.2	8.2
Base	Control Run	4078	3842	236	519	756	290	23.0	9.07	–5.3	7.8
STE3	20% increased O$_3$ STE	4047	3893	154	606	761	293	22.9	9.02	–4.6	7.4
STE4	50% increased O$_3$ STE	3975	4013	-38	812	776	299	22.8	8.90	–3.0	7.1
Effects of Dry Deposition											
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	–5.9	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
Base	Control Run	4078	3842	236	519	756	290	23.0	9.07	–5.3	7.8
Wet3	20% increased wet dep	4028	3797	231	520	752	287	23.1	9.22	–5.6	8.1
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	3940	3706	233	519	753	292	23.9	9.86	–4.8	7.4
Tem2	2°C lower temperature	4019	3785	235	519	754	291	23.4	9.38	–5.1	7.7
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	783	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 NO$_x$											
Lit1	No lightning NO$_x$	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 (5 TgN/yr)	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 NO$_x$	4236	4003	232	517	750	304	23.3	8.72	–3.5	6.6

[a] Budgets in Tg yr^{-1}; lifetimes in days for O$_3$ and years for CH$_4$; biases in ppb.

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 O_3 burden is reduced by 5%. The global O_3 burden is much more sensitive to changes in humidity than in temperature, and the CH_4 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 O_3 burden, a 3% (0.8 day) variability in O_3 lifetime and a 3% (0.3 year) variability in CH_4 lifetime based on these sensitivity studies.

Deep convection mixes O_3-rich air from the upper troposphere down towards the surface where the O_3 lifetime is shorter and lifts freshly-emitted O_3 precursors into the upper troposphere where O_3 production may be greater. Previous studies with and without convective transport have disagreed on the relative importance of these pathways, with Lawrence et al. (2003) finding a 12% increase in O_3 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, unlike in the previous studies. Stronger convection leads to increased O_3 production in the upper troposphere but to decreased production in the lower troposphere, where precursors are removed by greater convective lifting and washout. There is an increase in the inferred influx from the stratosphere, reflecting both convective steepening of the O_3 gradient near the tropopause and direct convective penetration above the monthly-mean tracer tropopause used here. Greater tropospheric overturning leads to higher surface O_3 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 O_3 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. This sensitivity is examined here by varying the magnitude of lightning emissions from 0 to 7.5 TgN/yr in steps of 2.5 TgN/yr. 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 vertically-uniform emission profiles for inter-cloud and cloud-to-ground lightning strokes based on Price and Rind (1992). Use 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 increase, 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 O_3, but a smaller proportion of NO_x 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 on-line. 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 O_3 is relatively insensitive to cloud cover. However, global O_3 production at the surface is 15% higher without cloud cover,
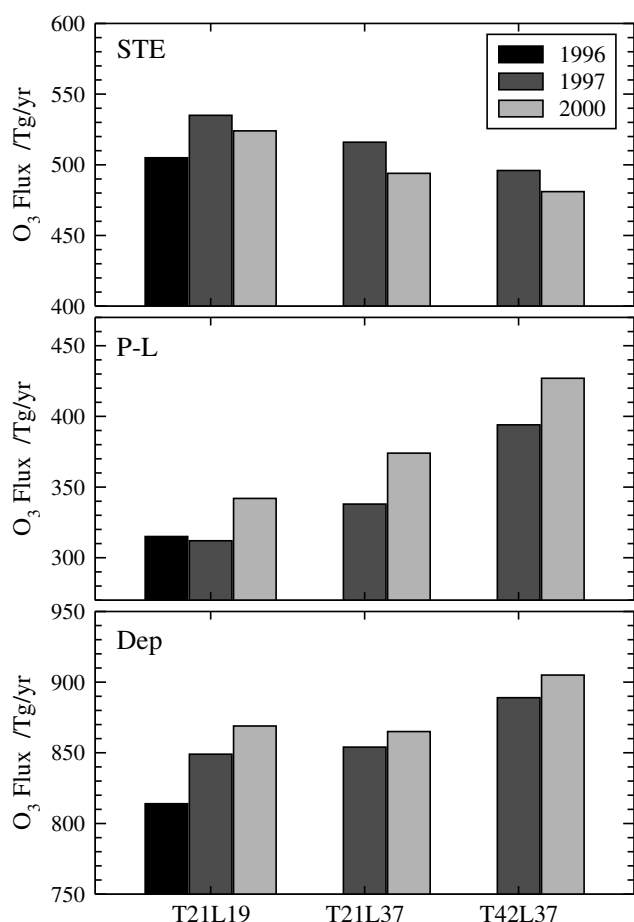
Fig. 4. Effects of meteorology and model resolution on the annual flux of O_3 through stratosphere-troposphere exchange (STE), net chemistry (P-L) and surface deposition (Dep).

cal and horizontal resolution. The lower resolution fields are derived from the parent T42L37 data so that advective and convective mass fluxes are the same across the different resolutions. Precursor emissions are taken from IIASA for closer comparison with the ACCENT studies, and the same emissions are used for each year. For this sensitivity study only, total lightning NO_x emissions are constrained to 6.5 TgN/yr and are distributed vertically following the profiles of Pickering et al. (1998); the geographical distribution 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). It is worth noting that some studies have found greater STE at higher horizontal resolution (Kentarchos et al., 2001; van Noije et al., 2004), although this may be strongly influenced by excessive vertical motions in the lower stratosphere associated with the assimilation methods used during generation of meteorological reanalyses (Douglass et al., 1996; van Noije et al., 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

balanced by lower production in the upper troposphere, and regional and seasonal differences can be much larger. The global O_3 burden change of 2.5% is comparable to the 3–5% changes found by Liu et al. (2006), but is clearly smaller than the 8–12% changes found by Tie et al. (2003), 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 O_3 production, but the global impacts appear to be small.

4.3 Sensitivity to meteorology and resolution

Differences in meteorological data may affect the O_3 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 O_3 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 verti-

Table 5. Annual ozone budgets in the FRSGC/UCI CTM: sensitivity to meteorology and resolution[a].

| Run | Description | Meteorological Data | | | O$_3$ Budget | | | | | | Lifetimes | | O$_3$ Bias | |
		Resolution	Year	P	L	P-L	STE	Dep	Burd	O$_3$	CH$_4$	Mean	RMS
Met96	IFS 1996 data	T21 L19	1996	5247	4932	315	505	814	342	21.7	8.38	2.1	5.0
Met97	IFS 1997 data	T21 L19	1997	4975	4663	312	535	849	336	22.2	8.79	0.9	5.9
Met97L	– 37 levels	T21 L37	1997	5103	4766	338	516	854	340	22.1	8.54	2.3	6.0
Met97R	– T42 resolution	T42 L37	1997	4982	4588	394	496	889	331	22.0	8.89	1.5	5.3
Met00	IFS 2000 data	T21 L19	2000	5314	4972	342	524	869	345	21.5	8.02	2.4	5.6
Met00L	– 37 levels	T21 L37	2000	5310	4935	374	494	865	341	21.5	8.10	2.1	5.3
Met00R	– T42 resolution	T42 L37	2000	5160	4734	427	481	905	331	21.4	8.45	1.7	4.3

[a] Budgets in Tg yr^{-1}; lifetimes in days for O$_3$ and years for CH$_4$; biases in ppb.

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 O$_3$ 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 O$_3$ 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 O$_3$ are revealed by the relationship between the tropospheric burden and the lifetime of O$_3$ 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 burden (274–407 Tg), lifetime (17–28 years) and removal rate (4500–7600 Tg/yr) 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 O$_3$ 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 O$_3$ burden and 1 day in O$_3$ lifetime. Variations in tempera-

ture and convection have a similar but smaller effect. Wet deposition and STE lead to changes in the gross removal of O$_3$, but the scatter in this dimension is strongly influenced by emissions. Lightning NO$_x$ emissions varied between 3 and 8 Tg/yr for the ACCENT models and may account for 30 Tg in O$_3$ burden and 500 Tg/yr in O$_3$ removal. Isoprene emissions varied between 220 and 630 TgC/yr, and may thus account for 20 Tg in O$_3$ burden and 650 Tg/yr in O$_3$ removal. Differences in meteorological data reflecting inter-annual variability between the three years studied here introduce less variability, about 5 Tg in O$_3$ burden and 0.5 days in O$_3$ lifetime, although increased resolution may lead to a 5–15 Tg reduction in burden. However, the sensitivity studies performed here clearly do not account for the full variability in O$_3$ budgets seen in the ACCENT runs, and it is likely that differences in chemical mechanisms, in model dynamics, and in the reanalysis methods used to generate the meteorological data also make large contributions to this variability.

The relationship between the chemical loss of O$_3$, governing the source of OH, and the lifetime of CH$_4$, 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$_3$ production and loss are associated with a higher level of OH and hence with a shorter CH$_4$ lifetime. Surface emissions of isoprene have a significantly different effect, however, as greater OH formation from higher O$_3$ production and loss is outweighed by the direct removal of OH that initiates hydrocarbon oxidation, and thus CH$_4$ lifetime increases with higher isoprene emissions as other studies have noted (von Kuhlmann et al., 2004). Ozone loss and CH$_4$ lifetime are systematically lower in model studies omitting higher hydrocarbons. The mean chemical lifetime of CH$_4$ 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. This variability implies a large uncertainty in CH$_4$ emissions, as the global CH$_4$ burden is relatively well constrained. The variation in lightning
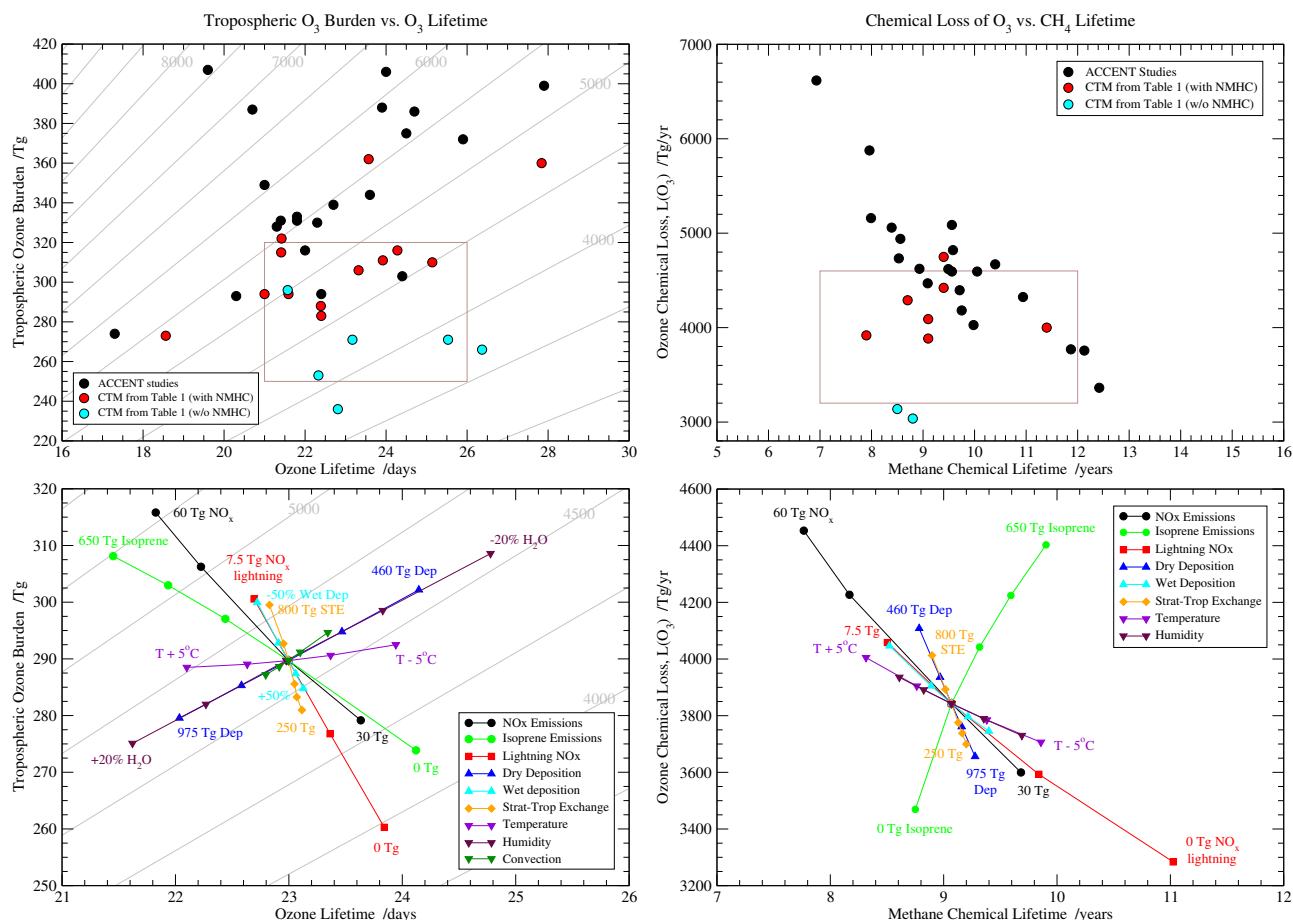
Fig. 5. The relationship between the tropospheric burden of O_3 and its lifetime to chemical removal and deposition (left panels, **a** and **c**) and between the chemical removal of O_3 and the chemical lifetime of CH_4 (right panels, **b** and **d**). The upper panels (a and b) show results from published studies summarized in Table 1 and the lower panels (c and d) show the results of sensitivity studies listed in Table 3. Tropospheric O_3 removal rates versus chemistry and deposition 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.

NO_x emissions may account for almost 1.5 years in the CH_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, and the effects of these have not been examined in this study. However, determination of the climate impacts of CH_4 and other trace 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 O_3 budget terms for each model are standardized by applying corrections 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

Table 6. Budget terms from the ACCENT model intercomparison corrected for different surface and lightning emissions, dry deposition and STE fluxes.

	O_3 Prod (Tg/yr)	O_3 Loss (Tg/yr)	CH_4 Lifetime (years)
ACCENT study	5110±606	4668±727	9.79±1.74
Standardization: All	5110±506	4668±518	9.71±1.33
Standardization of Separate Processes			
NO_x emissions only	5110±596	4668±721	9.78±1.72
Isoprene emissions only	5110±539	4668±667	9.78±1.73
Lightning NO_x only	5110±563	4668±656	9.72±1.42
Dry Deposition only	5110±608	4668±664	9.78±1.69
STE only	5110±621	4668±682	9.78±1.72

with respect to STE, dry deposition, lightning and surface emissions is derived from Table 4, and a correction is then applied for each model by scaling the sensitivity factor by the deviation from the ACCENT ensemble mean. As an example, the sensitivity factor for O_3 production from lightning NO_x emissions is 150 Tg/TgN based on run Alt5 in Table 4, and the ensemble mean lightning emission is 5.7 TgN/yr, so the correction for gross O_3 production for a model with 5.0 TgN/yr lightning NO_x is +105 Tg/yr. Note that this simple approach assumes a linear response and therefore the ensemble mean production and loss terms remain unaltered. However, this standardization leads to a reduction in the 1σ variability of 100 Tg/yr for production and 200 Tg/yr for loss when applied to all budget terms considered here, and the difference between the outlying models is reduced by more than 35%. The largest contributions to this reduced variability in production come from standardizing the isoprene emissions and lightning NO_x, while for chemical loss there is also a large impact from standardizing deposition. There is a small decrease in the mean CH_4 lifetime as corrections are applied to CH_4 loss rates, but the 1σ variability in the CH_4 lifetime is reduced by about 25%, from 1.7 to 1.3 years, and the difference between the outlying models is also reduced by 25%. Lightning NO_x emissions make the largest contribution to this reduced variability. 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_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_3 production and tropospheric burden in more recent studies are principally due to use of higher surface emissions of NO_x and isoprene. The higher NO_x emissions largely reflect a better understanding of sources and emission factors, while higher isoprene emissions suggest greater confidence in the large emission estimates within the modelling community. Increases in these emissions alone lead to an increase in O_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. (2007) has shown similar results. Comparison with ozonesonde measurements suggests that precursor emissions used in earlier studies were too low, and that O_3 distributions are reproduced better with recent IIASA emissions data.

The burden of O_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 influenced by the tropopause definition used. Comparison of three O_3 climatologies with seven different tropopause definitions suggests that as much as $\pm 15\%$ of the variability in the burden may be due to the choice of tropopause. Recent model assessments have recommended use of an O_3 tracer tropopause of 150 ppb (Prather and Ehhalt, 2001), and this provides a robust definition consistent with that of a dynamical tropopause based on PV, giving a tropospheric burden of 335 ± 10 Tg with the monthly-mean 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_3 tracer tropopause, highlighting substantial differences in O_3 distribution between the models. Further exploration of the sensitivity of the mean burden and the cross-tropopause flux to the choice of upper boundary for O_3 and to the reanalysis method used in generating the meteorology would be valuable.

Sensitivity studies have been performed to examine how differences in key model processes might account for the difference in O_3 budget terms seen in the relatively well-constrained ACCENT model intercomparison. The magnitude and vertical distribution of lightning NO_x emissions is shown to be a major source of uncertainty, and the 3–8 TgN/yr range in the ACCENT study may account for a 10% difference in tropospheric ozone burden (about 30 Tg) and a 1.4 year difference in CH_4 lifetime. This accounts for about 10% of the variability in the ACCENT O_3 budgets and almost 20% of the variability in the CH_4 lifetime. Processes affecting the O_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_3 and CH_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_4 lifetime suggests that the climate response of changes in O_3 precursors in current models may differ substantially. Tighter constraints on lightning NO_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_3 budget terms explored here. As improved parameterizations 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_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_3 budget remain very poor, and improved estimates based on satellite or in-situ measurements would be valuable.

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