Atmos. Chem. Phys. Discuss., 12, 21615–21677, 2012
www.atmos-chem-phys-discuss.net/12/21615/2012/
doi:10.5194/acpd-12-21615-2012
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Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Pre-industrial to end 21st century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP)

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Received: 27 July 2012 – Accepted: 8 August 2012 – Published: 22 August 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Present day tropospheric ozone and its changes between 1850 and 2100 are considered, analysing 15 global models that participated in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP). The multi-model mean compares well against present day observations. The seasonal cycle correlates well, except for some locations in the tropical upper troposphere. Most (75 %) of the models are encompassed with a range of global mean tropospheric ozone column estimates from satellite data, although there is a suggestion of a high bias in the Northern Hemisphere and a low bias in the Southern Hemisphere. Compared to the present day multi-model mean tropospheric ozone burden of 337 Tg, the multi-model mean burden for 1850 time slice is ∼ 30 % lower. Future changes were modelled using emissions and climate projections from four Representative Concentration Pathways (RCPs). Compared to 2000, the relative changes for the tropospheric ozone burden in 2030 (2100) for the different RCPs are: −5 % (−22 %) for RCP2.6, 3 % (−8 %) for RCP4.5, 0 % (−9 %) for RCP6.0, and 5 % (15 %) for RCP8.5. Model agreement on the magnitude of the change is greatest for larger changes. Reductions in precursor emissions are common across the RCPs and drive ozone decreases in all but RCP8.5, where doubled methane and a larger stratospheric influx increase ozone. Models with high ozone abundances for the present day also have high ozone levels for the other time slices, but there are no models consistently predicting large or small changes. Spatial patterns of ozone changes are well correlated across most models, but are notably different for models without time evolving stratospheric ozone concentrations. A unified approach to ozone budget specifications is recommended to help future studies attribute ozone changes and inter-model differences more clearly.

1 Introduction

The Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) is designed to complement the climate model simulations being conducted for the Coupled Model Intercomparison Project (CMIP), Phase 5 (e.g. Taylor et al., 2012), and both will inform the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (AR5). A primary goal of ACCMIP is to use its ensemble of tropospheric chemistry-climate models to investigate the evolution and distribution of short-lived, chemically-active climate forcing agents for a range of scenarios, a topic that is not investigated in such detail as part of CMIP5. Ozone in the troposphere is one such short-lived, chemically-active forcing agent, and, as it is both a pollutant and greenhouse gas, it straddles research communities concerned with air quality and climate. This study is concerned with quantifying the evolution and distribution of tropospheric ozone in the ACCMIP models, detailing the projected ozone changes since the pre-industrial period through to the end of the 21st century, with a focus on where the projected changes from the ensemble are robust.

Ozone is not directly emitted and its abundance in the troposphere is determined from a balance of its budget terms: chemical production and influx from the stratosphere, versus chemical loss and deposition to the surface (e.g. Lelieveld and Dentener, 2000). The magnitudes of these terms are sensitive to the prevailing climate, and the levels and locations of ozone precursor emissions, such as nitrogen oxides (NO and NO_2; referred to as NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs), including methane (e.g. Wild, 2007). A number global model studies have explored how changes in these drivers could affect tropospheric ozone abundances, from the pre-industrial period to future projections (e.g. Johnson et al., 1999; Collins et al., 2003; Prather et al., 2003; Shindell et al., 2003, 2006c; Sudo et al., 2003; Zeng and Pyle, 2003; Mickley et al., 2004; Hauglustaine et al., 2005; Lamarque et al., 2005, 2011; Stevenson et al., 2005; Brasseur et al., 2006; Dentener et al., 2006; West

et al., 2007; Wu et al., 2008; Zeng et al., 2008; Jacobson and Streets, 2009; Young et al., 2009; Kawase et al., 2011).

Estimates of past emissions of anthropogenic ozone precursors are much lower than for the present day (e.g. Lamarque et al., 2010), meaning models project large increases in tropospheric ozone since the pre-industrial era (Hauglustaine and Brasseur, 2001; Lamarque et al., 2005; Shindell et al., 2006a; Cionni et al., 2011). This is in qualitative agreement with observationally based assessments (Volz and Kley, 1988), although matching the estimated low surface ozone concentrations (Marenco et al., 1994; Pavelin et al., 1999) is challenging (Hauglustaine and Brasseur, 2001; Mickley et al., 2001). Future projections of anthropogenic ozone precursor emissions used by earlier model studies were high, resulting in large increases in tropospheric ozone levels (Stevenson et al., 2000; Sudo et al., 2003; Zeng and Pyle, 2003; Shindell et al., 2006c). However, more recent emission projections have included scenarios with reductions in anthropogenic precursor emissions, resulting in decreased tropospheric ozone compared to the present day (Dentener et al., 2005; Stevenson et al., 2006; West et al., 2006, 2007, 2012; Kawase et al., 2011; Lamarque et al., 2011). With regard to natural emissions, lightning NO_x emissions have generally been thought to increase in a warmer climate (e.g. Price and Rind, 1994; Schumann and Huntrieser, 2007), although this result is not universal (Stevenson et al., 2005; Jacobson and Streets, 2009). For biogenic emissions, isoprene is likely the largest contributor (e.g. Guenther et al., 1995). Its emission flux depends on climate (Guenther et al., 2006; Arneth et al., 2010), although whether future climate changes will drive isoprene increases (Sanderson et al., 2003; Lathièire et al., 2005) or decreases (Arneth et al., 2007a; Young et al., 2009) is not clear (see also Pacifico et al., 2009). As the biogenic emissions depend on vegetation type, projecting their past and future emissions also depends on changes in land cover and land use (Sanderson et al., 2003; Wiedinmyer et al., 2006; Arneth et al., 2008; Ashworth et al., 2012). These changes also impact deposition rates (Ganzeveld et al., 2010), all together making for complex biosphere-atmosphere interactions (Arneth et al., 2010).

The impacts of climate change on meteorology and large-scale atmospheric dynamics are also important for tropospheric ozone. For example, several studies report an increase in the stratospheric influx of ozone in response to a warming climate, resulting from a climate change-driven strengthening of the residual circulation (Collins et al., 2003; Sudo et al., 2003; SPARC-CCMVal, 2010), coupled with the impact of higher-than-present levels of stratospheric ozone (Hegglin and Shepherd, 2009; Zeng et al., 2011). On the other hand, increases in specific humidity in a warmer atmosphere can increase the ozone loss rate, speeding up the reaction rate of $O(^1D) + H_2O$ (producing OH) at the expense of collisional quenching, $O(^1D) + M$ (producing ozone again) (Thompson et al., 1989; Johnson et al., 1999). Higher temperatures also reduce the efficacy of peroxy acetyl nitrate (PAN) as a NO_x reservoir, and can mean larger or smaller rate coefficients, depending on the activation energy of the given reaction.

Despite general agreement on how the drivers impact global-scale shifts in tropospheric ozone, magnitudes of the regional changes and the overall ozone budget vary considerably between different models (Stevenson et al., 2006; Wild, 2007; Wu et al., 2007). With the movement to consider more physical processes and create complex Earth system models, uncertainty for future climate and composition projections may well increase (Stainforth et al., 2007). Yet, multi-model evaluation against present day observations and comparisons of the projections between models remains useful, both for benchmarking and for identifying consistent and contradictory results between different parameterisations (e.g. Dentener et al., 2006; Shindell et al., 2006b; Stevenson et al., 2006). In this study we analyse the multi-model ACCMIP ensemble ozone changes, from 1850 through to near- (2030) and further-term (2100) projections, using the latest set of scenarios developed for the CMIP5 simulations. This is the first study to examine the spread of modelled ozone responses using these scenarios, expanding the single-model studies of Kawase et al. (2011), Cionni et al. (2011) and Lamarque et al. (2011), and building on the last major multi-model model comparison for tropospheric ozone changes, coordinated by the European Union project Atmospheric Composition Change: the European Network of Excellence (ACCENT) (Stevenson et al.,

2006). The main focus of this study is on the ensemble mean ozone change, and the robustness of the results across the ACCMIP ensemble. A detailed investigation into the "process-based" drivers of the ozone changes and inter-model differences is not possible due to the limited ozone budget data, and we recommend that this is a priority for future chemistry-climate model comparisons. The analysis complements parallel investigation of the ACCMIP ensemble, related to climate evaluation (Lamarque et al., 2012), OH and methane lifetime (Voulgarakis et al., 2012), and the radiative impact of tropospheric ozone (Bowman et al., 2012; Shindell et al., 2012; Stevenson et al., 2012). This study is also complementary to an investigation of tropospheric and stratospheric ozone in the CMIP5 models (Eyring et al., 2012).

This study is organised as follows: Sect. 2 summarises the salient details of the ACCMIP models and the simulations analysed, followed by a comparison of the model emissions in Sect. 3. Section 4 discusses the present day distribution of tropospheric ozone and the inter-model differences, and presents a reference comparison of the models against a range of ozonesonde and satellite-based measurement data. The modelled ozone changes for the different scenarios are documented in Sect. 5, followed by a brief discussion of all the results in Sect. 6. Finally, Sect. 7 summarises the main conclusions and recommendations for future multi-model investigations of tropospheric ozone.

2 Models, simulations and analysis details

Here we provide brief details of the ACCMIP models and simulations, together with some details on the analysis performed in this study. Lamarque et al. (2012) provide a more complete description of the models and further details for the simulations. Note that the analysis here does not include the ACCMIP model NCAR-CAM5.1 as this did not calculate ozone.

2.1 ACCMIP models

Table 1 summarises the models, scenarios and their time periods analysed in this study (the tropospheric ozone burdens are discussed in later sections of the text). For this study, we used the output from 15 models, although not all of them provided output for every scenario and period, as indicated by "–" in Table 1.

Most of the ACCMIP models are climate models with atmospheric chemistry modules, run in atmosphere-only mode; i.e. the models are driven by sea-surface temperature (SST) and sea-ice concentrations (SICs). GISS-E2-R uniquely was run as a fully coupled ocean-atmosphere climate model, although the closely related GISS-E2-R-TOMAS model was run with SSTs and SICs prescribed. CICERO-OsloCTM2 and MOCAGE are chemical transport models (CTMs), with MOCAGE using offline meteorological fields from an appropriate simulation of a climate model, and CICERO-OsloCTM2 using offline meteorological fields from a single year of a reanalysis dataset. Except for the CTMs, and LMDz-OR-INCA, STOC-HadAM3 and UM-CAM, the calculated ozone concentrations are used in the climate model radiation code, making most of the models chemistry-climate models (CCMs).

The model chemical schemes vary greatly in their complexity (e.g. as measured by the number of species and reactions), particularly in the range of non-methane VOCs (NMVOCs) that they simulate. Complexity ranges from the simplified and parameterized schemes of CMAM (no NMVOCs) and CESM-CAM-superfast (isoprene as the only NMVOC), to the intermediate schemes of HadGEM2 and UM-CAM (include $\leq C_3$-alkanes), to the more complex schemes of the other models, which include the more reactive, chiefly anthropogenic NMVOCs (e.g. higher alkanes, alkenes and aromatic species), as well as lumped monoterpenes. Some representation of stratospheric chemistry is included in many models, with the exception of CICERO-OsloCTM2, HadGEM2, LMDz-OR-INCA, STOC-HadAM3 and UM-CAM. CICERO-OsloCTM2 uses a fixed stratospheric ozone influx of 450 $Tg\,yr^{-1}$ and LMDz-OR-INCA uses a constant (in time) stratospheric ozone climatology (Li and Shine, 1995), whereas the other models without detailed stratospheric chemistry used the time varying stratospheric ozone dataset of Cionni et al. (2011).

2.2 Scenarios and time slices

The ACCMIP simulations broadly correspond with the CMIP5 scenarios (Taylor et al., 2012). Historical (hereafter Hist) simulations cover the preindustrial period to the present day, while a range of Representative Concentration Pathways (RCPs) (van Vuuren et al., 2011) cover 21st century projections. These latter scenarios are named for their nominal radiative forcing level (2100 compared to 1750), such that RCP2.6 corresponds to 2.6 $W\,m^{-2}$, RCP4.5 to 4.5 $W\,m^{-2}$, RCP6.0 to 6.0 $W\,m^{-2}$ and RCP8.5 to 8.5 $W\,m^{-2}$. Ozone precursor emissions from anthropogenic and biomass burning sources were taken from those compiled by Lamarque et al. (2010) for the Hist simulations, whereas emissions for the RCP simulations are described by Lamarque et al. (2012) (see also Lamarque et al., 2011; van Vuuren et al., 2011). Natural emissions, such as CO and VOCs from vegetation and oceans, and NO_x from soils and lighting, were determined by each model group. The emissions used by the individual models are discussed further in Sect. 3.

With the exception of GISS-E2-R and LMDz-OR-INCA, each model conducted a set of time slice simulations for each scenario. In this study, we analyse output from the 1850, 1980 and 2000 time slices from the Hist scenario, and the 2030 and 2100 time slices for the RCPs, to provide near-term and longer-term perspectives. Except for the CTMs and GISS-E2-R, each model used climatological SSTs and SICs from coupled ocean-atmosphere CMIP5 simulations of a closely related climate model, typically averaged for the 10 yr about each time slice (e.g. 2026–2035 for the 2030 time slice), although some models had interannually varying boundary conditions. CICERO-OsloCTM2 used the same meteorology for each simulation, whereas MOCAGE was run with meteorological fields from a climate model running the appropriate time slice and scenario, rather than directly using the SSTs and sea-ice to drive an atmosphere model. The number of years that the ACCMIP models simulated for each time slice

mostly varied between 4 and 12 yr for each model, although CICERO-OsloCTM2 only simulated a single year. However, as the boundary conditions were constant for each year of a given time slice (including biomass burning emissions), "interannual" variability is generally small (see Sect. 4).

GISS-E2-R and LMDz-OR-INCA both conducted transient simulations, and the data analysed in this study were averaged for the decade about each time slice (e.g. 1976–1985 for the 1980 time slice), with some minor exceptions as noted in Table 1.

2.3 Analyses: tropopause definition and statistical definitions

Throughout this analysis, the troposphere is defined as air with ozone concentrations less than or equal to 150 ppbv (Prather et al., 2001), which is simple to employ and allows comparison against other model studies (e.g. Stevenson et al., 2006). For a consistent definition of the troposphere for all time slices, the definition is applied using the ozone from the Hist 1850 time slice mean, applied on a per model basis, and varying by month. We used the 1850 time slice to avoid issues with different degrees of stratospheric ozone depletion across the ensemble, particularly in the Southern Hemisphere (SH). While fixing the definition means we compare a consistent region of the atmosphere between different time slices, it does ignore the fact the tropopause height will likely alter with climate change (Santer et al., 2003a,b). Furthermore, values for the tropospheric ozone burdens and columns are obviously sensitive to the tropopause definition (Wild, 2007; Prather et al., 2011), and the differences generally amount to ±5 % compared to using the 2000 time slice mean ozone, although they can exceed 10 % for a few models for the RCPs. We apply a pressure based tropopause definition for the comparison of the modelled tropospheric column ozone against satellite data in Sect. 4.2.

A statistical analysis of whether the projected ozone changes are significant against interannual variability is not possible with the ACCMIP data, mainly because the interannual variability is insufficiently characterised by the time slice runs, as most have constant SSTs and SICs on a year-to-year basis, and all have constant biomass burning emissions. Instead, we assess whether a given multi-model mean ozone change is significantly different from zero by using a paired sample Student's *t* test (e.g. Wilks, 2006). Differences are considered significant if the (absolute) mean difference from all the models is greater than 1.96 times the standard error for the mean difference (i.e. the 5 % level). One weakness of this analysis is that it cannot highlight regions where the models agree that the changes are not significant with respect to interannual variability (see Tebaldi et al., 2011).

For the most part, output from the models was interpolated to the grid used by Cionni et al. (2011), who compiled the ozone dataset recommended for use in the CMIP5 simulations (5° by 5° latitude/longitude and 24 pressure levels). However, the tropospheric burden and columns were calculated on a model's native grid.

3 Emissions: differences and similarities between models

While one goal of ACCMIP was for models to match each other's ozone precursor inputs as closely as possible, differences in model parameterisations and complexity means that some model diversity is unavoidable. In particular, natural emissions were not prescribed as part of the experimental design, and their differing treatment between models broadens the range of ozone precursors. Such differences are examples of why we need model comparisons.

Figure 1 shows the range in ozone precursor emissions in the ACCMIP models, presenting box-whisker plots for each scenario and time slice. The number of models that constitute the spread of the data is different for different simulations – see Table 1. Tabulated emission data for the individual models can be found in Table S1 in the Supplement.

Figure 1a shows that the tropospheric methane burden is generally well constrained in the simulations, with the interquartile range (IQR) being 3–5.5 % of the mean burden. The close agreement is due to all models except LMDz-OR-INCA having used prescribed methane surface concentrations for the Hist simulations, and only GISS-

E2-R and LMDz-OR-INCA not prescribing concentrations for the RCP simulations. The methane burden approximately doubles from 1850 to 2000, but 2100 burdens are 30 %, 10 % and 2.5 % lower than 2000, for the RCP2.6, RCP4.5 and RCP6.0 scenarios, respectively. For RCP8.5, by 2100 the methane burden has more than doubled again compared to 2000.

The general trends in CO (Fig. 1b) and total NO_x (Fig. 1c) emissions are similar, increasing from 1850 to 2000 for the Hist scenario, decreasing thereafter for all the RCPs, except for the 5 % higher NO_x emissions for the 2030 time slice of RCP8.5, compared to Hist 2000. NO_x emissions show a stronger increase over the 20th century, with the mean trebling between 1850 and 2000, whereas CO emissions slightly more than double. Across all RCPs, by 2100 CO and NO_x emissions are lower by 30–45 % compared to 2000.

Both CO and NO_x emissions show a greater degree of variation between the models than the methane burden. For a given time slice, the IQRs vary between approximately 10–30 % of the corresponding mean emission, whereas the full range (maximum minus minimum emission) is between 20–100 % of the mean emission. The spread is due to the varying natural emissions (NO_x from soils and lightning; CO from oceans and vegetation), as well as the less complex chemistry schemes used in some models including extra CO emissions as a surrogate for missing NMVOCs (e.g. CMAM, HadGEM2).

An example of the variation in natural emissions can be seen from Fig. 1d, which shows the spread in the lightning NO_x source (LNO_x) for the models. Parameterisations for LNO_x are generally dependent on cloud top heights and convective mass fluxes (e.g. Price and Rind, 1992; Allen and Pickering, 2002; Tost et al., 2007), which likely show large variability between models, accounting for spread. The IQRs are generally 40–55 % of the mean emission, and the full range is 90–170 % of the mean. The maximum emissions come from the MIROC-CHEM, whose LNO_x was set mistakenly high (by 60 %) in the ACCMIP simulations. The minimum emissions ($< 2\,Tg\,N\,yr^{-1}$) are generally from the low HadGEM2 LNO_x (who mistakenly implemented LNOx at too low a level), although emissions are also low for CMAM for the RCP simulations. Our

knowledge of LNO_x is generally poor, but (excluding HadGEM2 and MIROC-CHEM) LNO_x for the Hist 2000 simulation ranges between 3.8–7.7 $Tg\,N\,yr^{-1}$, within the range of $5 \pm 3\,Tg\,N\,yr^{-1}$ estimated by Schumann and Huntrieser (2007) for a range of LNO_x parameterisations.

Possible changes in lightning activity with climate change (e.g. Williams, 2009 and refs. therein) have been recognised as potentially important for LNO_x and the subsequent impact on tropospheric composition (e.g. Price and Rind, 1994; Hauglustaine et al., 2005; Fiore et al., 2006; Schumann and Huntrieser, 2007; Zeng et al., 2008), even if only the spatial distribution changes (Stevenson et al., 2005). An increase in LNO_x from 2000 to 2100 (RCP8.5; strongest warming) is generally robust across the ACCMIP models, and ranges in magnitude from 10–75 %. CMAM is an outlier in this case, with 45 % lower emissions for RCP8.5 2100 compared to Hist 2000. CMAM is also the only model using an LNO_x parameterisation based on the study of Allen and Pickering (2002). Jacobson and Streets (2009) also modelled lower LNO_x in a warmer climate, using a different parameterisation based on cloud ice. Clearly further study is required into the implications of the use of different parameterisations for LNO_x, and the different sensitivities across models.

Finally, Fig. 1e shows the VOC emissions used in the ACCMIP models. As with LNO_x, the emissions cover a wide range and there is no clear trend in the mean across the simulations. Many of the reasons for the differences are familiar from the above discussion, particularly the fact that some models include more VOC species than others. Another reason for the spread in VOC emissions comes from treatment of VOCs of biogenic origin, particularly isoprene, which likely dominates the total NMVOC emissions (e.g. Guenther et al., 1995). EMAC, GEOSCCM, GISS-E2-R and STOC-HadAM3 simulations were the only ones to include climate-sensitive isoprene emissions, and these are the only models with a positive change in VOC emissions between Hist 2000 and RCP8.5 2100, arising from the positive temperature dependence of isoprene emission algorithms (e.g. Guenther et al., 2006; Arneth et al., 2007b). Arneth et al. (2011) noted that the isoprene emission computed from a given algorithm is highly sensitive to the

input meteorological data and vegetation boundary conditions, giving further cause for variation in VOC emissions between models. For the rest of the ACCMIP ensemble, if they included isoprene chemistry, constant present day isoprene emissions were used for all simulations, and their individual VOC emission trends broadly resemble those of CO and NO_x.

4 Present day ozone distribution and model-observation comparison

This section presents the distribution of tropospheric ozone (surface, column and zonal mean) as simulated by the ACCMIP models for the Hist 2000 simulation. The ozone concentrations and columns from this simulation are then compared against observational datasets, from both satellites and ozonesondes. We do not over-interpret these comparisons since they exclude observational error, and they differ in the periods covered. The emphasis is largely on the distribution and measurement-model comparison for the multi-model mean, describing the spread of model results with statistical metrics. The distributions of ozone for all the individual models can be found in the Supplement (Figs. S1–S3).

4.1 Zonal mean, tropospheric column and surface ozone from Hist 2000

Figure 2 shows the ensemble mean, annual mean distribution of ozone, presenting the zonal mean, tropospheric column and surface ozone concentrations, as well as their inter-model variability. The general patterns of the ozone distribution in Fig. 2a, d, g are consistent with those reported from satellite (Fishman et al., 1990; Ziemke et al., 2011) and ozonesonde (Logan, 1999; Thompson et al., 2003) measurements, as well as the multi-model data shown by Stevenson et al. (2006). The increase in ozone concentration with height is clear, in accordance with the increase in ozone lifetime. Convective lifting of low-ozone air masses coupled with lofting of ozone precursors (Lawrence et al., 2003; Doherty et al., 2005) results in the characteristic tropical zonal mean pro-

file in Fig. 2a. The hemispheric asymmetry in mid-tropospheric ozone concentrations reflects the larger input of stratospheric ozone in the NH, due to the stronger Brewer-Dobson circulation there (Rosenlof, 1995), as well as the larger emissions of ozone precursors (Lamarque et al., 2010). While both the tropospheric column (Fig. 2d) and surface concentrations (Fig. 2g) also show higher ozone levels over source regions, these plots also indicate enhanced concentrations downwind of the source regions, due to transport of ozone, ozone precursors including "reservoir" species, such as PAN (Moxim et al., 1996; Fiore et al., 2009). Figure 2d also shows the "wave-1" pattern in the tropical tropospheric ozone column (Thompson et al., 2003; Ziemke et al., 2011), with a minimum in ozone over the Pacific Ocean and maximum over the Atlantic. Surface ozone concentrations are also very low over the equatorial Pacific Ocean.

There is generally good agreement between the models for the zonal mean profile of ozone. Figure 2c shows that the standard deviation is less than 20 % of the mean throughout much of the troposphere, with exception of some lower troposphere regions and the upper troposphere. The spatial patterns of the spread in surface ozone concentrations in Fig. 2h and i suggest that much of the lower troposphere variability is over regions with large anthropogenic, pyrogenic or biogenic emissions, where both the absolute and relative uncertainty is largest. In anthropogenic and biomass burning source regions, much of the model diversity could reflect the spread in VOC composition (low vs. high reactivity species), which means different ozone production efficiencies (e.g. Russell et al., 1995), as well as using different injection heights for biomass burning emissions. For tropical Africa and especially South America, large variations are apparent over isoprene source regions (surface and column), which reflects differences in the total emission (some models have no isoprene), as well as potentially differences in isoprene chemistry (Archibald et al., 2010).

Large model variation is also found for the high latitude SH, chiefly for the tropospheric column. Tropospheric ozone levels in the SH are generally low, but there is relatively large diversity in the overhead stratospheric ozone column (standard deviation for the total ozone column is 10–15 % of the mean; not shown). This results in a spread

in the stratospheric input as well as potentially some impacts through changes in photolysis rates, for those models with photolysis schemes that use the model-calculated ozone column (e.g. Fuglestvedt et al., 1994; see also Voulgarakis et al., 2012). There is less (relative) variation in the tropospheric column in the Northern Hemisphere (NH), coupled with less spread between models for the total ozone column (not shown). But larger uncertainty for the surface at high latitudes could be related to differences in precursor transport and chemistry from lower latitudes (Shindell et al., 2008). As was also found by Stevenson et al. (2006), there are large relative uncertainties in tropospheric column ozone over the equatorial Pacific Ocean, but the concentrations here are very low.

Figure 3a shows the annual mean tropospheric ozone burden for all the models, as well as the ACCMIP mean. Values for the tropospheric burden for all models and scenarios can also be found in Table 1. The mean burden is 337 ± 23 Tg, very close to the 336 ± 27 Tg reported for a subset of the ACCENT models (Stevenson et al., 2006), and the 335 ± 10 Tg estimated from measurement climatologies by Wild (2007), although the latter estimate is from pre-2000 ozone data. Figure 3a also indicates the uncertainty in the ozone burden, as represented by the standard deviation of the range of burdens computed for individual years of the time slice. As might be expected from successive years of the same boundary conditions (for most models), the uncertainty is small, and the standard deviations are less than 2 % of the burden.

There is a significant correlation ($r = 0.67$) between the modelled ozone burden and the total VOC emissions; the models are arranged in order of increasing VOC emissions in Fig. 3a. In the absence of ozone budget data and information on the VOC make-up of the models, it is difficult to rationalise this correlation satisfactorily. However, Wild (2007) demonstrated increased VOC emissions lead to an increased ozone burden. There is not a similar correlation between the ozone burden and total NO_x emissions.

Figure 3b indicates the distribution of the mean ozone burden throughout the troposphere, using the regions defined by Lawrence et al. (2001) (that they used to describe

the distribution of OH) to give a mass-weighted view of the zonal ozone distribution. The hemispheric asymmetry in ozone is apparent from Fig. 3b, which shows that 57.5 % of the ozone mass is in the NH. The NH extratropics has 60 % more ozone than the SH extratropics overall, but the NH tropics has only slightly more ozone (~ 3 %) than the SH tropics overall. The greatest burdens are found in the extratropical upper troposphere, reflecting the importance of stratosphere-to-troposphere transport of ozone. The next largest ozone burdens are found in the comparatively more polluted NH lower troposphere, as well as the tropical upper troposphere. This latter region is impacted by convective transport of ozone precursors and lightning emissions (Jacob et al., 1996). The standard deviation in the fractional distribution of ozone is also in Fig. 3b, showing that the model uncertainty in distribution of ozone mass is largest in the NH extratropics and in the upper troposphere in general, consistent with the results in Fig. 2.

4.2 Comparison to ozonesondes and satellite data

Figure 4 compares the ACCMIP mean, median and individually modelled ozone concentrations from the Hist 2000 simulation against ozonesonde data, in the same manner as Stevenson et al. (2006). Ozonesonde measurements are taken from datasets described by Logan (1999) (representative of 1980–1993) and Thompson et al. (2003) (representative of 1997–2011), and consist of 48 stations, split 5, 15, 10 and 18 between the SH extratropics, SH tropics, NH tropics and NH extratropics, respectively. The models were sampled at the ozonesonde locations. In addition, Fig. 4 shows satellite-derived ozone concentrations retrieved from the Tropospheric Emission Spectrometer (TES), which is a Fourier transform spectrometer on board the NASA Aura spacecraft in 2004 (Beer, 2006). TES ozone from a 2005–2010 climatology was interpolated to the same grid as the ACCMIP models and sampled at the ozonesonde locations. Figure 4 also shows the ACCENT model mean (Stevenson et al., 2006), to place the ACCMIP results in context of recent multi-model comparisons. The correlation and mean normalised bias error (MNBE) are shown for multi-model mean from the ACCMIP and ACCENT ensembles, relative to the ozonesonde observations.

Both the ACCMIP multi-model mean and median are within the standard deviation of the observations for all locations and altitudes. Compared to the mean observations, the largest relative errors are found for the NH extratropics, where the mean model overestimates the concentrations, and SH tropics, where the mean model underestimates the concentrations. The individual model biases in these locations are significantly correlated with total VOC emissions ($r = 0.57$; i.e. more VOC emissions give a more positive, or less negative, bias), although several other chemical and transport factors likely play a role. However, the mean model captures the annual cycle in ozone concentrations extremely well in most locations (as measured by the correlation coefficient), suggesting that, broadly speaking, the seasonality in circulation patterns, stratosphere-to-troposphere exchange and natural emissions (chiefly biomass burning in the tropics, and isoprene in the NH extratropics) is captured well. The statistics for the NH tropical mid and upper troposphere suggest that the seasonality is less well modelled, although we note that, (1) the observed-model correlation is significant ($r > 0.58$), (2) there is considerable observed interannual variability in ozone the upper troposphere, and (3) the bias and correlation are improved compared to the ACCENT mean. Compared to ACCENT, the correlation is improved with the ACCMIP mean model for most locations, and the bias for some locations, both most prominently in the NH.

Except for the NH tropics at 250 hPa, the TES data are positively biased compared to the ozonesondes, broadly consistent with the 2–10 ppbv high bias that Nasser et al. (2008) noted for TES (see also Zhang et al., 2010). However, taking the interannual variability into account, and the fact that we have neither applied the TES operators in this analysis (Worden et al., 2007), nor considered measurement uncertainty, the TES and ozonesonde data are not notably different. This positive bias means that, compared to the ozonesonde data, the ACCMIP mean model bias against TES is improved for the NH extratropics, about the same for the NH tropics (opposite in sign), but worsened for the SH; changes in correlation compared to the ACCMIP-ozonesonde comparison are marginal. As mentioned above both the ozonesondes and TES see a

sharp increase in ozone between March and April at EQ-30N, not captured in the ACCMIP mean. TES (and several ACCMIP models) do not show the same low values in the winter months as the ozonesonde data. For TES, this is likely due to lower thermal contrast which will make the satellite retrievals relax to an a priori value (Bowman et al., 2006). Bowman et al. (2012) pursue comparisons of the ACCMIP models against TES further.

Figure 5 makes a similar comparison to ozonesonde data, this time using the compilation of Tilmes et al. (2011). This dataset mostly consists of the same station data described by Logan (1999) and Thompson et al. (2003), but covering 1995–2009, and aggregated into 12 regions that exhibit similar ozone concentration characteristics (see the top panel of Fig. 5 and Tilmes et al., 2011). The figure presents the mean, median and spread of the MNBE for the individual ACCMIP models (cf. Fig. 1), showing that the full range of performance encompasses positive and negative biases for each region and altitude.

The information in Fig. 5 is consistent with that in Fig. 4, but with more longitudinal information. For instance, we see that the negative bias in the SH tropical ozone is driven by the less favourable comparison of the model mean with the sites in the Atlantic/Africa region (dark green), and the sign of the bias is consistent across more than 75 % of the models. A positive bias is apparent in all the NH extratropical regions in the low and mid-troposphere, and again is shared by the majority of the models. Figure 5 also shows low biases for the high latitude regions in the upper troposphere/lower stratosphere (UT/LS; a region not shown in Fig. 4). A comparison of the ACCMIP mean total ozone column against satellite measurements from the merged Total Ozone Mapping Spectrometer/solar backscatter ultraviolet (TOMS/SBUV) data (Stolarski and Frith, 2006) suggests that the models overestimate the total ozone column by around 5 % at high latitudes (not shown), although the total column bias is not necessarily related to UT/LS biases. Validation of stratospheric ozone in these models is beyond the scope of this study, but this would help resolve whether ozonesonde-model comparisons at higher altitudes are consistent with the satellite data. (A comparison of the multi-model

mean ozone column against TOMS data can be found in the Supplement, along with a comparison of late twentieth century trends.)

Tropospheric ozone columns are available from a combination of the Ozone Monitoring Instrument (OMI) and Microwave Limb Sounder (MLS) data. Figure 6 compares the ACCMIP mean tropospheric column ozone against the OMI-MLS climatology derived by Ziemke et al. (2011), covering October 2004 to December 2010. Tables 2 and 3 summarise the comparisons between the OMI/MLS data and individual models, showing the global (60° S–60° N) column biases and spatial correlations, and biases by latitude bands, respectively. For each model, the column was defined using the tropopause pressures provided by Ziemke et al. (2011) (from the National Centers for Environmental Prediction, NCEP), meaning that Fig. 6a is subtly different from Fig. 2d.

From Table 2, the global, multi-model mean tropospheric ozone column is 30.8 DU, compared to 31.1 DU for OMI/MLS, although the latter has a root-mean square interannual variability of ∼3 DU (Ziemke et al., 2011), which overlaps an additional observationally-based estimate from the TES instrument of 29.8–32.8 DU (H. Worden, personal communication, 2012). The range from these two instruments encompasses the columns calculated by 75 % of the models. The spatial correlation between OMI/MLS and the models is generally very high (cf. Fig. 6a, b).

Many of the differences between the multi-model mean and OMI/MLS are broadly consistent with the comparison against ozonesonde data (Fig. 6c; Table 3), and biases in the mean column for a given latitude band are well correlated with those for the ozonesondes ($r \geq 0.75$ for any pressure level). Compared to OMI/MLS, the multi-model mean overestimates the column across the NH mid-latitudes, and underestimates the column over tropical oceans and for all regions poleward of approximately 30° S, although the underestimate is stronger than suggested by the ozonesonde data. The negative bias over the equatorial Pacific in Fig. 6c is not consistent with the ozonesonde comparison in Fig. 5, which suggests a neutral or positive bias for the mean model. However, this region is poorly represented by ozonesonde measurements. Correlations between the biases for the NH and SH tropical columns are strong ($r = 0.88$),

suggesting that similar processes are operating in the regions, even if the sign of the bias is different between them (i.e. a model with a stronger positive NH tropical bias likely has a SH tropical bias that is either positive, or less negative than the ensemble mean).

Overall, compared to the ensemble of observations, the models may have a systematic high bias in the NH, and a systematic low bias in the SH, although they typically fall within the interannual variability of the observations.

5 Tropospheric ozone from 1850 to 2100

In this section we consider the changes in tropospheric ozone projected by the ACCMIP models for the past (1850 and 1980), as well as for the near (2030) and more distant (2100) future, using the range of RCPs. We begin by discussing global-scale changes, followed by regional changes, before considering the drivers of the change.

5.1 Global-scale changes: tropospheric ozone burden

Figure 7a shows the annual average tropospheric ozone burden for the ACCMIP models for all the simulations and time slices considered. Figure 7b shows the difference in the tropospheric ozone burden compared to the Hist 2000 simulation. Data for individual models burdens and their differences can be found in Tables 1 and 4, respectively.

The evolution of the mean tropospheric burden in Fig. 7a shows a 25 % increase between 1850 and 1980, and a 29 % increase between 1850 and 2000 (very close to the results of Lamarque et al., 2005); the burden increases by 4 % between 1980 and 2000. Future projections vary with the scenario. Compared to the 2000 burden of 337 Tg, the relative changes in 2030 (2100) for the different RCPs are: −5 % (−22 %) for RCP2.6, 3 % (−8 %) for RCP4.5, 0 % (−9 %) for RCP6.0, and 5 % (15 %) for RCP8.5. RCP8.5 is the only scenario to show an ozone increase for both time slices (23 Tg and 60 Tg), whereas RCP4.5 shows an increase in 2030 (6 Tg), before decreasing in 2100

(−25 Tg). The ozone burden for the 2030 time slice of RCP6.0 is unchanged compared to 2000, although it is still higher than 1980.

Figure 7 also shows a large range in the modelled ozone burdens and their differences, with overlapping IQRs between many of the time slices. There is a good, but not perfect, correlation between the modelled ozone burden for Hist 2000 and that of another time slice (i.e. models generally simulate consistently high or low burdens). However, there is no relationship between the modelled ozone burden and a given burden change, nor between the changes in ozone burden for any two periods; i.e. there are not any models that consistently simulate large (or small) ozone changes, at least at the global scale.

The significance of the burden change with respect to Hist 2000 can also be assessed, using the inter-model spread of the differences (Sect. 2.3). This analysis suggests that all the changes in the ozone burden are significantly different from zero at the 5 % level, except for between Hist 2000 and RCP6.0 2030, which is anticipated from Fig. 7b, as this is the only time slice where the models do not agree on the sign of the change. We again note that "significance" here does not mean that the change is significant with respect to interannual variability, merely a measure of whether the models agree on a change. As shown by Table 4, agreement between models on the magnitude of the burden change is generally better for the larger changes, namely Hist 1850, RCP2.6 2100 and RCP8.5 2100, where, as a percentage of the mean change, the standard deviation is 17 %, 31 % and 37 %, respectively. The standard deviations in the differences for the other scenarios vary between 40–85 %, although it is very large for RCP6.0 2030.

5.2 Regional-scale changes: burdens, columns and concentrations

Figure 8 shows the mean model regional ozone burden changes relative to Hist 2000 for the Hist 1850 and the four RCP 2100 simulations, dividing up the troposphere in the same manner as Fig. 3b. The figure also indicates the fraction that each region contributes to the overall ozone change, i.e. highlighting asymmetries in the change.

From Fig. 7, we see that the overall ozone burden change is negative for all of these simulations, except RCP8.5 2100. Based on the spread of model results, all of the regional burden changes are significantly different from zero.

For Hist 1850 and RCP2.6 2100 the burden change is negative for all regions, with the largest contribution to the change coming from the lower ozone precursor emissions in the NH extratropics compared to Hist 2000. Unlike for the other RCPs, stratospheric ozone recovery (e.g. Eyring et al., 2010) does not force an increase in tropospheric ozone for the SH upper troposphere, despite a 30 % increase in the total column ozone (not shown). However, an increase in stratospheric influx is likely masking what would otherwise be stronger negative changes due to the precursor decreases. The SH extratropics makes a small contribution to the overall change for both the Hist 1850 and RCP2.6 2100 case.

The overall decrease for RCP4.5 2100 is about half of that between RCP2.6 2100 and Hist 2000, but is still largely dominated by the decrease in precursor emissions in the NH extratropics, with some contribution from the NH tropical lower troposphere. This overall decrease is countered by a relatively large increase in the SH upper troposphere, likely related to ozone recovery. The magnitude and patterns of absolute ozone changes are similar for RCP6.0, although the tropical upper troposphere makes more of a contribution to the overall change than in RCP4.5, in both absolute and relative terms. For RCP8.5, ozone increases everywhere, although the largest contribution is from the 500 to 250 hPa pressure band.

Figures 9, 10 and 11 present information on the annual mean spatial patterns of ozone concentration changes, relative to Hist 2000, for all the time slices, showing the absolute changes in zonal mean ozone, the tropospheric ozone column and surface ozone, respectively. White areas indicate where the multi-model mean change in ozone is not significantly different from zero, based on the spread of the model results. Corresponding ozone differences for the individual models can be found in the Supplement (Figs. S4–S6).

Concentrations for Hist 1850 are less than Hist 2000 everywhere except the stratosphere (Fig. 9a), showing the impact of increased precursors (Fig. 1) and CFC-induced ozone depletion respectively. Relative decreases exceed 40 % for the column (Fig. 10a) and surface for NH mid-latitudes (Fig. 11a). For the latter, absolute decreases are > 25 ppbv for the Mediterranean, much of Asia, and the Western USA due to less precursor emissions. Differences between Hist 1980 and Hist 2000 are also significant in many parts of the atmosphere. These are distributed in a qualitatively similar manner to the Hist 1850 differences, but with smaller decreases due to the smaller change in precursor emissions, although the lower surface concentrations over South and East Asia highlight the recent emission growth in that region (e.g. Zhang et al., 2009). A notable non-significant change is seen for surface ozone concentrations over the Eastern US, where ∼ 50 % of the models simulate higher ozone for 1980 compared to 2000. This is in qualitative agreement with the recent analysis of ozone trends by Parrish et al. (2012), although transient simulations, better constrained to observed interannual changes in meteorology and emissions would be needed to investigate this further.

For RCP2.6, the distribution of tropospheric ozone changes is very similar to the Hist 1850 difference, with peak reductions of 30–40 % by 2100 (Figs. 9c, 10c and 11c) reflecting the partial reversal of the anthropogenic ozone precursor changes compared to 1850 and 2000. Similar patterns are evident again for RCP4.5 and RCP6.0 in 2100 (Fig. 9f, h), although (non-significant) increases in SH ozone penetrate deeper into the troposphere compared to RCP2.6 (see below). RCP4.5 also shows significant increases throughout the tropical and SH troposphere for the 2030 time slice (Fig. 9e), reflecting a redistribution in precursor emissions: tropical NO_x emissions are higher for this scenario in 2030 than all others, except RCP8.5. Despite non-significant changes in the ozone burden for RCP6.0 2030 (Fig. 7), there are significant decreases in ozone in the tropical regions (Fig. 9f). RCP8.5 has significant increases throughout the troposphere, except for surface concentrations and the column over the equatorial Pacific

in 2100, where the dominant effect may be increased specific humidity in the warmer climate increasing the ozone loss rate (e.g. Johnson et al., 1999; Zeng and Pyle, 2003).

The zonal mean ozone changes by 2100 for the different RCPs are qualitatively similar to those presented by Kawase et al. (2011), except that the ACCMIP multi-model mean does not show upper tropospheric ozone increases in the NH mid-latitudes for RCP4.5 and 6.0. Sensitivity experiments by Kawase et al. (2011) demonstrated the importance of an enhanced Brewer-Dobson circulation (BDC) and recovery of stratospheric ozone levels in increasing future upper tropospheric ozone levels for RCP4.5, 6.0 and 8.5 in 2100. Stratospheric chemistry-climate models are robust in projecting recovery of the ozone layer due to a reduction in halogen levels (Eyring et al., 2010), as well as an intensification of the BDC with increased greenhouse gas concentrations (Butchart et al., 2006). The change in zonal mean ozone in Fig. 9 is characteristic of these processes, and, in particular, the reduction in tropical lower stratospheric ozone and enhancement of high latitude ozone is indicative of stronger BDC (Randel et al., 2002). This tropical/high-latitude seesaw pattern of the changes intensifies with the increased climate change from RCP2.6 to 8.5, further illustrating the coupling of the BDC to greenhouse gas levels in these models (see also Lamarque et al., 2011). The mid-latitude peaks in the tropospheric ozone column changes (Fig. 10j) are also indicative of increases in the stratospheric ozone influx (Olsen et al., 2004). For RCP8.5, the simulations of Kawase et al. (2011) also showed that the very large increase in methane levels was driving increases throughout most of the troposphere (see also Brasseur et al., 2006; Fiore et al., 2008).

With the exception of the upper troposphere and lower stratosphere, the ozone differences in regions with non-significant changes are small, and it may be that the models agree that these changes in these regions are not significant in the context of interannual variability (Tebaldi et al., 2011). For the regions of significant change, the standard deviation of the differences can exceed 100 % of the multi-model mean difference, though generally for surface and column values close to emission regions. (By construction, the colour-filled regions of Figs. 9–11 indicate where most models agree

on the sign of change, but they do not show where there are large ranges modelled for positive or negative changes). However, as noted for changes in the total tropospheric burden, there is no apparent correlation with a model's present day ozone level in one region and the change in ozone that is modelled for the same region.

Model agreement on the distribution of the differences is very good, with most models being highly spatially correlated with the multi-model mean difference (see Supplement). Notable exceptions are LMDz-OR-INCA and CICERO-OsloCTM2, which have fixed stratospheric ozone levels or influx. This testifies to the potential importance of stratospheric circulation and ozone changes for tropospheric ozone, as most of those models that include some representation of stratospheric ozone evolution have changes that are generally well correlated with each other. However, for RCP8.5 2100 MOCAGE and STOC-HadAM3 are not well correlated with the other models, despite having some representation of stratospheric ozone change. MOCAGE strongly concentrates tropospheric ozone increases at high latitudes rather than the mid latitudes and tropics in Figs. 9j and 10j. This could relate to systematic differences in the locations of stratosphere-to-troposphere ozone transport, the distribution of stratospheric ozone, or a combination of the two. While STOC-HadAM3 makes use of the time-evolving stratospheric ozone dataset of Cionni et al. (2011), it uses it to help constrain ozone concentrations at the model top, rather than simply to overwrite ozone above the tropopause. This may account for the outlying stratospheric ozone trends seen for this model in the Supplement. A STOC-HadAM3 simulation where only the climate is changed to RCP8.5 2100 conditions concentrates tropospheric ozone column increases over continental regions, perhaps implying a stronger role for LNO_x increases instead of more stratospheric ozone influx (see Supplement of Stevenson et al., 2012).

5.3 NO_x, methane and the implied role of climate change as drivers of the total ozone changes

The relationship of modelled tropospheric ozone burdens with methane and NO_x is well established (Stevenson et al., 2006; Wild, 2007, 2012; Fiore et al., 2008) and

Fig. 12 presents how the ACCMIP multi-model mean ozone burden changes for each simulation, together with (a) changes in the mean NO_x emission and (b) changes in the mean tropospheric methane burden.

Figure 12a shows that the evolution of tropospheric ozone from the pre-industrial period to present day tracks the change in NO_x emissions in a near linear fashion, similar to the relationship presented by Stevenson et al. (2006). The decrease in NO_x emissions for RCP2.6, 4.5 and 6.0 sees the ozone burden decrease again, although at a slightly reduced rate than for the Hist simulations partially due to the redistribution of precursor emissions equatorward, where the ozone production efficiency is greater (Gupta et al., 1998; Wild and Palmer, 2008). This is particularly the case for RCP4.5 2030, which – as noted above – has an increase in tropical NO_x emissions compared to Hist 2000, despite an overall decrease.

RCP8.5 is the clear outlier for the simple NO_x-ozone relationship, with a 60 Tg increase in the tropospheric ozone burden coupled with a 12 $Tg\,N\,yr^{-1}$ reduction in NO_x emissions. Based on the results of the other simulations, and only considering NO_x changes, we might expect a 40–50 Tg decrease in the tropospheric ozone burden. However, as already noted, a defining feature of RCP8.5 is the large increase in methane concentrations through the 21st century, and the relationship between ozone changes and methane changes for the simulations is shown in Fig. 12b. Taking in data across all the simulations shows that the relationship is not linear, and it clearly at least partially depends on the levels of other ozone precursors, as well as their distribution (e.g. see Wild, 2007). For instance, the change between Hist 2000 and RCP8.5 2030 qualitatively sits on the same line as the ozone-methane relationship for the Hist simulations, likely due to the methane increase in RCP8.5 2030 being accompanied by an increase in NO_x emissions. Between 2030 and 2100, the reduction in NO_x (and other) emissions for RCP8.5 contributes to the fact that a given methane increase does not produce as much of an ozone increase.

The impacts of climate change further complicate this correlation. Using the parameterised relationship between ozone abundance and the levels of its precursor emis-

sions (but excluding climate) developed by Wild et al. (2012), we would expect an ozone burden increase of approximately 30 Tg between Hist 2000 and RCP8.5 in 2100. However, at 60 Tg the ACCMIP multi-model mean increase in ozone is double that expected, and consistent with equal roles for methane increases and the net impacts of climate change, i.e. through promoting increased influx of stratospheric ozone, changing LNO_x, and impacting reaction rates, through temperature and humidity changes. This is broadly similar to the result from the RCP8.5 sensitivity simulations of Kawase et al. (2011), which showed a 5.5 DU increase in the global mean tropospheric column when all drivers changed, and a 2.0 DU increase when only (non-methane) greenhouse gases changed – i.e. assuming linearity, climate change accounted for 36 % of the total tropospheric ozone change.

6 Discussion

Considering the full ACCMIP ensemble, the results for ozone change are least ambiguous for Hist 1980, RCP2.6 2100 and RCP8.5 2100, both in terms of magnitude and distribution. These represent the extremes of the spectrum of historical and RCP scenarios, with the former two having the lowest concentrations of all ozone precursors, and RCP8.5 having relatively low NO_x, CO and NMVOC emissions, but very high methane coupled with a strong warming (see Lamarque et al., 2012). With the generally low concentrations of the more "complex" VOC precursors, "basic" tropospheric chemistry (i.e. involving methane, CO, NO_x, HO_x and ozone) becomes more important. The reactions describing this chemistry are generally very similarly represented in most models (e.g. Emmerson and Evans, 2009), and, with the reduced importance of the chemistry of more complex VOCs, this could potentially be driving a lot of the similarity between the models. We cannot test this idea further, due to lack of ozone budget data, but useful information could come from a systematic investigation of the response of ozone to idealised precursor changes in the different models, such as through the sensitivity studies of Wild (2007).

While there is good agreement between the models for the ozone changes between Hist 1850 and Hist 2000, we note that none of the ACCMIP models can reproduce the low surface ozone concentrations suggested by late-19th century measurements using the Schönbein method (Pavelin et al., 1999; Hauglustaine and Brasseur, 2001). Compared to the data presented by Hauglustaine and Brasseur (2001), biases for the multi-model mean are 40–350 % (not shown). This result has not changed greatly over the last two decades (e.g. Pavelin et al., 1999). Indeed, one of the only model studies to simulate ozone in line with these Schönbein data invoked large perturbations in the emissions of VOC and NO_x, compared to those imposed in this study (Mickley et al., 2001).

As well as uncertainty in ozone precursor emissions, there is scope for uncertainty in the representation of the oxidation chemistry during the cleaner pre-industrial period, where, in particular, levels of NO_x are expected to have been much lower than today. Since isoprene emissions may not have changed dramatically since the pre-industrial period (e.g. Arneth et al., 2010), modifications to the low-NO_x chemistry of isoprene may be important. Novel isoprene chemistry has recently been included in simulations of pre-industrial ozone by Archibald et al. (2011). However, the changes they imposed to rectify problems with simulating surface OH in the tropics led to an increase in surface ozone everywhere. Biogenic hydrocarbon emissions play a dual role in ozone production acting as ozone precursors on the one hand but also many are able to react directly with ozone at a fast rate, or decrease ozone production by sequestering NO_x (Fiore et al., 2005; Horowitz et al., 2007; Young et al., 2009). Recently, tropospheric halogen chemistry has been postulated as being an important process missing in many models that have attempted to simulate pre-industrial ozone (Parrella et al., 2012; Saiz-Lopez et al., 2012), but such processes were not included in the ACCMIP models. Clearly, more understanding of all these processes is important for simulating past and future tropospheric ozone.

7 Summary and conclusions

This study has analysed tropospheric ozone changes from 1850 to 2100 from the range of chemistry models that contributed to the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), running the latest set of ozone precursor emissions scenarios, and with 14 out of 15 models also including representations of the changing climate. The multi-model mean ozone distribution compares favourably with present day satellite and ozonesonde observations. The seasonal cycle is well captured, except in some locations in the tropical upper troposphere, and there are suggestions of a high bias in the Northern Hemisphere (NH) and a low bias in the Southern Hemisphere (SH), although most model results fall within the range of observed interannual variability.

In agreement with other studies (e.g. Lamarque et al., 2005), the modelled tropospheric ozone burden in 1850 is ∼30 % lower than the present day, with the largest contribution to the change coming from the NH extratropics. Inter-model agreement on the magnitude of this change is reasonably high (98 ± 17 Tg), although modelled surface ozone concentrations are higher than the available pre-industrial measurements (as per Hauglustaine and Brasseur, 2001) suggesting that there may be unresolved issues with correctly modelling pre-industrial ozone levels (Mickley et al., 2001). Modelled ozone also increases somewhat between 1980 and 2000, particularly over industrialised regions in the NH, in agreement with the general picture described by Parrish et al. (2012).

Future changes in tropospheric ozone were considered for 2030 and 2100 time slices, using projections of climate and ozone precursor emissions from four Representative Concentration Pathways (RCPs). Compared to 2000, the relative changes for the tropospheric ozone burden in 2030 (2100) for the different RCPs are: −5 % (−22 %) for RCP2.6, 3 % (−8 %) for RCP4.5, 0 % (−9 %) for RCP6.0, and 5 % (15 %) for RCP8.5. The decreases apparent for most RCPs are due to reductions in precursor emissions, but the increase in ozone for RCP8.5 is in spite of reductions in nitrogen oxide emissions and, as implied by comparison to other studies (Kawase et al., 2011;

Wild et al., 2012), can be attributed to the very large increase (∼ doubling) in methane and increased stratospheric influx of ozone. Inter-model agreement on the magnitude of the total change compared to 2000 is best where the changes are large, such as for RCP 2.6 in 2100 (−55 ± 17 Tg) and RCP8.5 in 2100 (60 ± 22 Tg). While models with higher present day ozone burdens have higher ozone burdens for the other time slices, there is no relationship between burden and burden change, or between burden changes for different periods/scenarios.

For the changes with all RCPs, generally the models are highly spatially correlated with one another, agreeing on where the changes are occurring, if not their magnitude. Notable exceptions are for the models that do not include representation of the changing influence of the stratosphere on the troposphere, highlighting the importance of ozone recovery (Eyring et al., 2010) and climate change-induced circulation strengthening (Butchart et al., 2006, 2010; SPARC-CCMVal, 2010) in this region of the atmosphere.

Overall, we have shown that the multi-model mean of ACCMIP models generally simulates present day tropospheric ozone well, and agrees on the sign of past and future tropospheric ozone changes and how those changes are distributed. Fully establishing the consistency of the chemical and physical processes driving the changes in the different models is missing from this study due to lack of comparable ozone budget statistics. Future studies will require careful thought as to how to make diagnostics comparable across models and we encourage discussion and further study within the chemistry-climate community of how best to manage this. Furthermore, this study highlights the strong influence of stratospheric processes in controlling tropospheric ozone, which may encourage more chemistry-climate modelling groups to move towards full atmosphere simulations.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/21615/2012/acpd-12-21615-2012-supplement.pdf.

Acknowledgements. ACCMIP is organized under the auspices of the International Global Atmospheric Chemistry (IGAC) and Stratospheric Processes And their Role in Climate (SPARC) projects under the International Geosphere-Biosphere Project (IGBP) and World Climate Research Program (WCRP). The authors are grateful to the British Atmospheric Data Centre (BADC), which is part of the NERC National Centre for Atmospheric Science (NCAS), for collecting and archiving the ACCMIP data. For CESM-CAM-superfast, DB and PC were funded by the US Dept. of Energy (BER), performed under the auspices of LLNL under Contract DE-AC52-07NA27344, and used the supercomputing resources of NERSC under contract No. DE-AC02-05CH11231. The CICERO-OsloCTM2 simulations were done within the projects SLAC (Short Lived Atmospheric Components) and EarthClim funded by the Norwegian Research Council. DP would like to thank the Canadian Foundation for Climate and Atmospheric Sciences for their long-running support of CMAM development. For EMAC, the work of VE and MR was funded by the DLR Earth System Model Validation (ESMVal) project and used the supercomputing resources of the German Climate Computing Center (DKRZ) and the Leibniz Supercomputing Centre (LRZ), and the work of IC was funded by the ENEA National Integrated Model to support the international negotiation on atmospheric pollution (Minni) project. The GEOSCCM work was supported by the NASA Modeling, Analysis and Prediction program, with computing resources provided by NASA's High-End Computing Program through the NASA Advanced Supercomputing Division. VN and LWH acknowledge efforts of GFDL's Global Atmospheric Model Development Team in the development of the GFDL-AM3 and Modeling Services Group for assistance with data processing. For the GISS models, support is acknowledged from the NASA MAP and ACMAP programs. For HadGEM2, WJC, GAF, FO'C and STR were supported by the Joint DECC and Defra Integrated Climate Programme (GA01101). The LMDz-OR-INCA simulations were done using computing resources provided by the CCRT/GENCI computer center of the CEA. The MOCAGE simulations were supported by Météo-France and CNRS. Supercomputing time was provided by Météo-France/DSI supercomputing centre. The MIROC-CHEM calculations were performed on the NIES supercomputer system (NEC SX-8R), and supported by the Environment Research and Technology Development Fund (S-7) of the Ministry of the Environment, Japan. The CESM project, including NCAR-CAM3.5, is supported by the National Science Foundation and the Office of Science (BER) of the US Department of Energy. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under sponsorship of the National Science Foundation. The STOC-HadAM3 work was supported by cross UK research council grant NE/I008063/1 and

used facilities provided by the UK's national high-performance computing service, HECToR, through Computational Modelling Services (CMS), part of the NERC National Centre for Atmospheric Science (NCAS). For UM-CAM, GZ acknowledges NIWA HPCF facility and funding from New Zealand Ministry of Science and Innovation.

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Table 1. Tropospheric ozone burdens (Tg) for the individual models and the ACCMIP mean. Also shows which simulations and time slices are available from each model for this study. Not all relevant variables are available for each model/time slice.

Model	Hist			RCP2.6		RCP4.5		RCP6.0		RCP8.5	
	1850	1980	2000	2030	2100	2030	2100	2030	2100	2030	2100
CESM-CAM-superfast	192	288	302	278	230	–	–	289	252	328	384
CICERO-OsloCTM2[a]	206	287	308	296	247	312	274	–	–	326	343
CMAM	239	310	323	–	–	330	293	–	–	342	371
EMAC	259	352	378	–	–	379	342	–	–	–	441
GEOSCCM	250	333	346	–	–	–	–	–	–	–	–
GFDL-AM3	264	370	378	367	317	389	356	390	359	410	484
GISS-E2-R[b]	252[c]	337	344[e]	341	304[e]	352	321[e]	352	339[e]	379	417[e]
GISS-E2-R-TOMAS	261	350	359	–	–	–	–	–	–	–	–
HadGEM2	227	289	307	–	262	–	295	–	–	–	377
LMDz-OR-INCA[b]	247[c]	322	339[d]	321	278[e]	342	310[e]	329	306[e]	351	374[e]
MIROC-CHEM	239	321	341	325	283	–	–	338	304	356	374
MOCAGE	272	322	327	323	299	–	–	333	318	358	400
NCAR-CAM3.5	221	318	336	317	263	336	294	322	285	349	386
STOC-HadAM3	234	332	348	329	272	–	–	–	–	367	385
UM-CAM	226	304	322	323	293	338	322	–	–	351	397
Mean	244	322	332	321	281	341	310	336	317	353	396
Sdev	39	30	22	29	40	25	30	34	51	28	43
(% of mean)	(16 %)	(9 %)	(7 %)	(9 %)	(14 %)	(7 %)	(10 %)	(10 %)	(16 %)	(8 %)	(11 %)

[a] Simulations are a single year.
[b] These models submitted transient simulations. Their "time slice" means represent 10-yr averages about the given decade, except as noted.
[c] Mean of 1850–1859.
[d] Mean of 1996–2000 (when the transient simulation stops).
[e] Mean of 2091–2100.

Table 2. Tropospheric ozone column, bias and spatial correlation for the Hist 2000 simulation of the ACCMIP models vs. a climatology derived from OMI data (Ziemke et al., 2011).

Models	Column (DU)	Bias (DU)	*r*
CESM-CAM-superfast	26.2	−4.9	0.79
CICERO-OsloCTM2	28.3	−2.8	0.84
CMAM	30.3	−0.8	0.87
EMAC	34.8	3.7	0.84
GEOSCCM	32.1	1.1	0.87
GFDL-AM3	35.1	4.0	0.89
GISS-E2-R	33.7	2.6	0.85
GISS-E2-R-TOMAS	34.7	3.6	0.87
HadGEM2	28.6	−2.4	0.83
LMDz-OR-INCA	31.2	0.1	0.87
MIROC-CHEM	31.3	0.2	0.81
MOCAGE	28.8	−2.2	0.60
NCAR-CAM3.5	28.9	−2.2	0.84
STOC-HadAM3	28.7	−2.4	0.81
UM-CAM	29.7	−1.4	0.75
ACCMIP mean (± sdev)	30.8	−0.4 ± 2.7	0.87 ± 0.07

Table 3. Tropospheric ozone column and bias (DU) for the Hist 2000 simulation of the ACCMIP models vs. the OMI climatology for different latitude bands.

	60° S–30° S		30° S–Eq.		Eq.–30° N		30° N–60° N	
	Col	Bias	Col	Bias	Col	Bias	Col	Bias
CESM-CAM-superfast	21.9	−7.8	21.6	−8.4	26.0	−5.0	37.2	3.1
CICERO-OsloCTM2	22.1	−7.6	27.5	−2.5	30.0	−1.0	33.2	−0.9
CMAM	29.1	−0.6	27.5	−2.4	29.3	−1.7	36.5	2.4
EMAC	29.4	−0.3	33.9	3.9	36.7	5.7	38.6	4.5
GEOSCCM	28.4	−1.3	28.8	−1.2	32.0	1.0	40.6	6.5
GFDL-AM3	31.4	1.7	31.8	1.9	35.2	4.2	42.9	8.8
GISS-E2-R	27.4	−2.3	29.0	−1.0	33.5	2.5	46.5	12.4
GISS-E2-R-TOMAS	30.0	0.2	30.5	0.5	33.8	2.8	46.3	12.2
HadGEM2	22.8	−6.9	26.4	−3.6	31.1	0.1	34.2	0.1
LMDz-OR-INCA	25.7	−4.0	29.2	−0.8	31.9	0.9	38.3	4.2
MIROC-CHEM	25.1	−4.6	31.4	1.4	33.8	2.7	34.1	−0.0
MOCAGE	18.9	−10.8	24.5	−5.5	32.3	1.3	40.0	5.9
NCAR-CAM3.5	25.1	−4.7	24.7	−5.3	29.4	−1.6	37.6	3.6
STOC-HadAM3	21.5	−8.3	26.1	−3.8	31.2	0.2	35.8	1.7
UM-CAM	26.2	−3.5	23.8	−6.1	30.4	−0.6	40.4	6.3
ACCMIP mean	25.7 ± 3.7	−4.1	27.8 ± 3.4	−2.2	31.8 ± 2.7	0.8	38.8 ± 4.1	4.7
OMI (obs)	29.7		30.0		31.0		34.1	

Table 4. Differences in the tropospheric ozone burden compared to Hist 2000, using data in Table 1.

Model	Hist		RCP2.6		RCP4.5		RCP6.0		RCP8.5	
	1850	1980	2030	2100	2030	2100	2030	2100	2030	2100
CESM-CAM-superfast	−110	−14	−24	−72	–	–	−13	−50	26	82
CICERO-OsloCTM2[a]	−102	−21	−12	−61	4	−34	–	–	18	35
CMAM	−84	−13	–	–	7	−30	–	–	19	48
EMAC	−119	−26	–	–	1	−36	–	–	–	63
GEOSCCM	−96	−13	–	–	–	–	–	–	–	–
GFDL-AM3	−114	−8	−11	−61	11	−22	12	−19	32	106
GISS-E2-R	−92	−7	−3	−40	8	−23	8	−5	35	73
GISS-E2-R-TOMAS	−98	−9	–	–	–	–	–	–	–	–
HadGEM2	−80	−18	–	−45	–	−12	–	–	–	70
LMDz-OR-INCA	−92	−17	−18	−61	3	−29	−10	−33	12	35
MIROC-CHEM	−102	−20	−16	−58	–	–	−3	−37	15	33
MOCAGE	−55	−5	−4	−28	–	–	6	−9	31	73
NCAR-CAM3.5	−115	−18	−19	−73	0	−42	−14	−51	13	50
STOC-HadAM3	−114	−16	−19	−76	–	–	–	–	19	37
UM-CAM	−96	−18	1	−29	16	0	–	–	29	75
Mean	−98	−15	−13	−55	6	−25	−2	−29	23	60
Sdev	17	6	8	17	5	13	11	19	8	22
(% of mean)	(17 %)	(39 %)	(66 %)	(31 %)	(86 %)	(51 %)	(536 %)	(64 %)	(36 %)	(37 %)

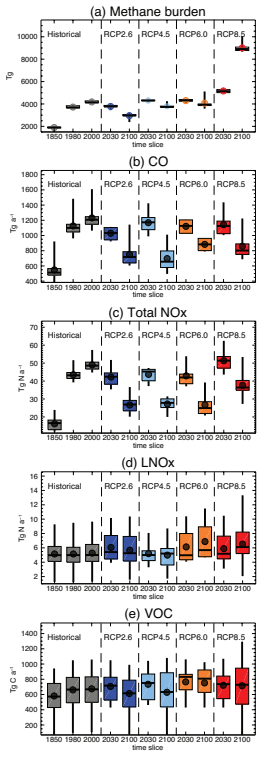

Fig. 1. Burdens and emissions of ozone precursors used in the ACCMIP scenarios and time slices, showing **(a)** the tropospheric methane burden, and yearly total **(b)** CO emissions, **(c)** total NO_x emissions, **(d)** lightning NO_x emissions and **(e)** VOC emissions. The spread of the emissions/burden in each model is indicated for each scenario and time slice, with filled box showing the interquartile range, the whiskers indicating the full range, and the dot and line indicating the mean and median repsectively. Not all models completed all the scenarios.

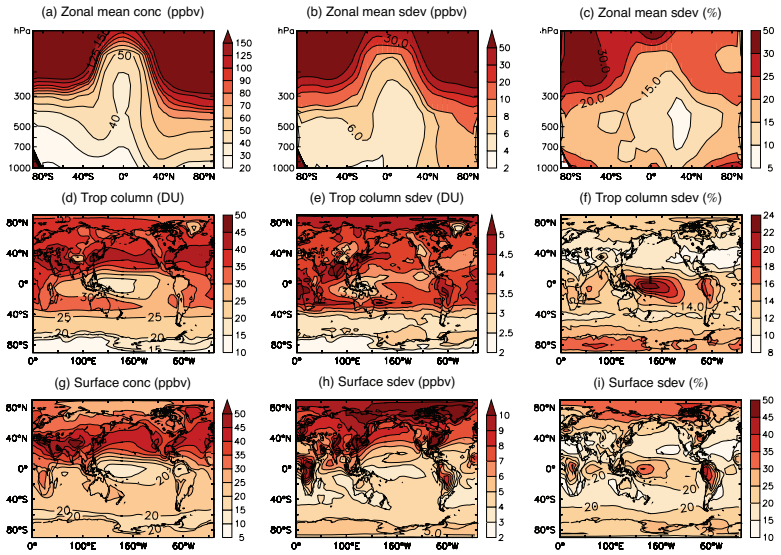

Fig. 2. ACCMIP ensemble mean, annual mean ozone climatologies and their inter-model variability, for the 2000 time slice of the Historical simulation. Top row shows zonal mean ozone, the middle row shows the tropospheric ozone column, and the bottom row shows surface ozone. For each row, the left hand panels show the absolute values of the ozone variable: ppbv for the zonal mean and surface concentrations, and Dobson units (DU) for the tropospheric column. The middle panels show the absolute standard deviations in the same units. The right hand column expresses the standard deviation as a percentage of the ensemble mean value (also known as the coefficient of variation). Note that each panel has a different scale.

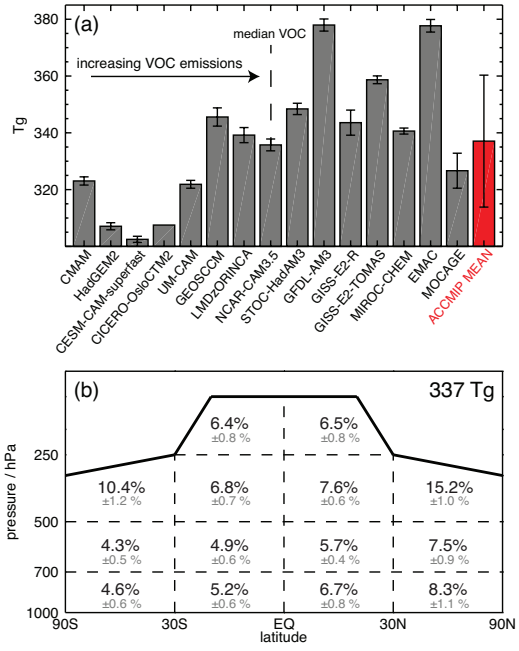

Fig. 3. (a) Tropospheric ozone burdens for the ACCMIP models from the Hist 2000 simulations. Error bars for the models indicate the variability in the burden between different years of a model's time slice (±1 std. dev.). The error bar on the ensemble mean burden indicates the inter-model spread of the burden (±1 std. dev.). Models are arranged in order of increasing VOC emissions. **(b)** Distribution of the mean ozone burden throughout the troposphere for the mean model, using the "boxes" recommended by Lawrence et al. (2001) for reporting OH concentrations. The solid line indicates the tropopause (see text for definition).

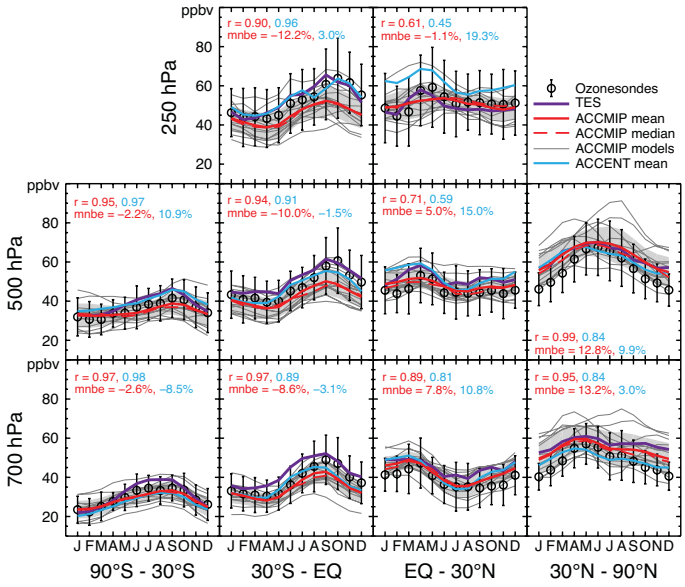

Fig. 4. Comparison of the annual cycle of ozone, between ozonesonde observations (black circles) and the ACCMIP ensemble mean (solid red line), ACCMIP ensemble median (dashed red line) and the ACCENT ensemble mean (blue line) (Stevenson et al., 2006). Ozone concentrations from TES (purple line) are also shown. ACCMIP model data is from the 2000 time slice mean of the Historical experiment. Model and observational data were grouped into four latitude bands (90° S to 30° S, 30° S to 0°, 0° to 30° N and 30° N to 90° N) and sampled at three altitudes (700 hPa, 500 hPa and 250 hPa), with the models sampled at the ozonesonde locations before averaging together. The individual ACCMIP models are represented by the thin grey lines, with the grey shaded area indicating ±1 standard deviation about the ACCMIP ensemble mean, showing the model spread. Error bars on the observations indicate the average interannual standard deviation for each group of stations. The correlation (r) and mean normalised bias error (mnbe) for the ACCMIP (red) and ACCENT (blue) ensemble means versus the observations are also indicated in each panel. This figure is an update of of Stevenson et al. (2006).

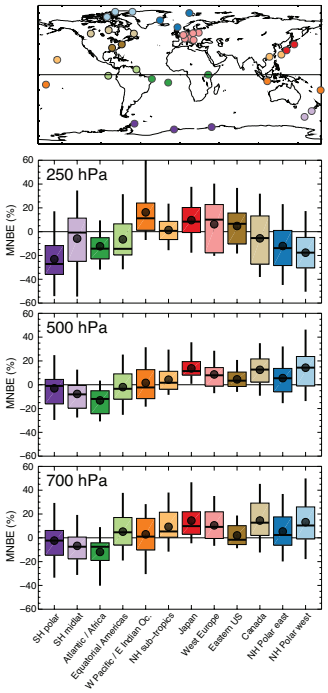

Fig. 5. Normalised biases for the ACCMIP models (Hist 2000 simulation) against the ozonesonde measurements compiled into regions by Tilmes et al. (2012). Each region is colour-coded, and the constituent ozonesonde sites are indicated in the top panel. Biases are show for (bottom to top) 700, 500 and 250 hPa. The box, whiskers, line and dot show the interquartile range, full range, median and mean biases respectively, in a similar style to Fig. 1. The y-axis has the same scale in each panel.

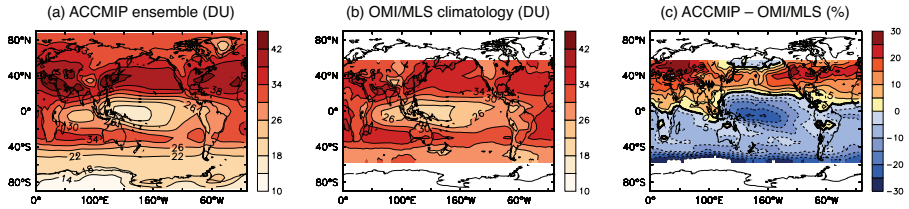

Fig. 6. Comparison of the annual mean tropospheric ozone column between **(a)** the ACCMIP ensemble (different tropopause compared to Fig. 2d) and **(b)** a climatology derived from the Ozone Monitoring Instrument (OMI) and Microwave Limb Sounder (MLS) by Ziemke et al. (2011). **(c)** ACCMIP ensemble bias compared to OMI/MLS (%). See also Tables 2 and 3.

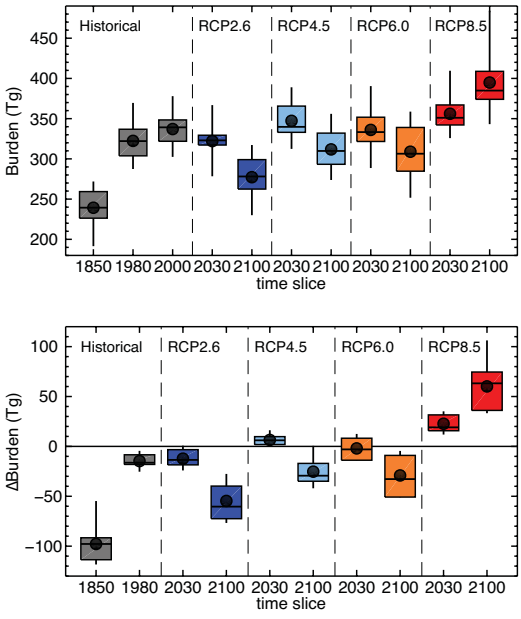

Fig. 7. (a) Modelled tropospheric ozone burdens for the different scenarios and time slices. **(b)** Change in the tropospheric burden, relative to the Hist 2000 simulation. The box, whiskers, line and dot show the interquartile range, full range, median and mean burdens and differences, in a similar style to Fig. 1.

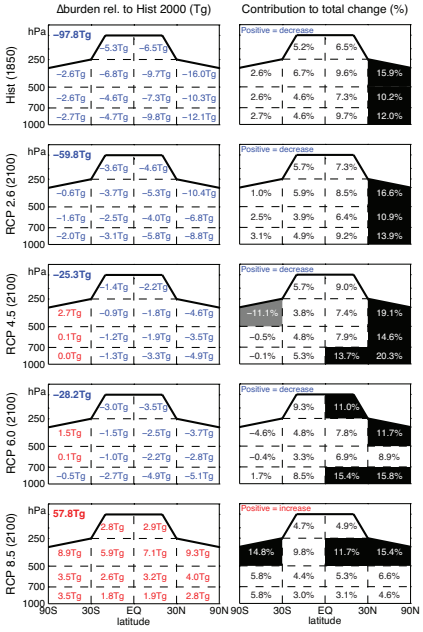

Fig. 8. ACCMIP ensemble mean change in the tropospheric ozone burden relative to the Hist 2000 simulation viewed in Lawrence et al. (2001)-style boxes (see also Fig. 3b), for (top to bottom) the Hist 1850, RCP2.6 2100, RCP4.5 2100, RCP6.0 2100 and RCP8.5 2100 simulations. The left hand column shows the absolute difference in ozone burden for the different boxes (red/blue for increase/decrease), with the tropospheric total change indicated in top left of each panel. The right hand column shows the fractional (%) contribution of each box to the overall change in the tropospheric burden. A positive value indicates that the box's change is the same sign as the overall change. Boxes with a fraction larger than 10 % are highlighted.

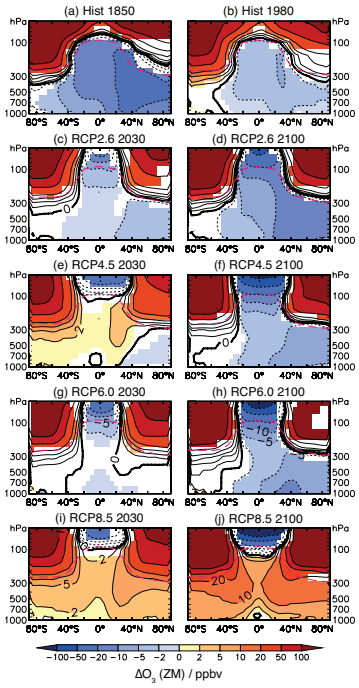

Fig. 9. Absolute change in annual zonal mean ozone for the ACCMIP ensemble mean compared to the Hist 2000 simulation (ppbv). Top row shows the difference for the Hist 1850 and 1980 time slices. The next four rows show the difference for the 2030 and 2100 time slices of the RCP simulations. Non-white regions indicate where the change is significant at the 5 % level, based on the spread of the differences between the models. The dashed red line indicates the position of the annual zonal mean 150 ppbv ozone contour from the Hist 1850 simulation.

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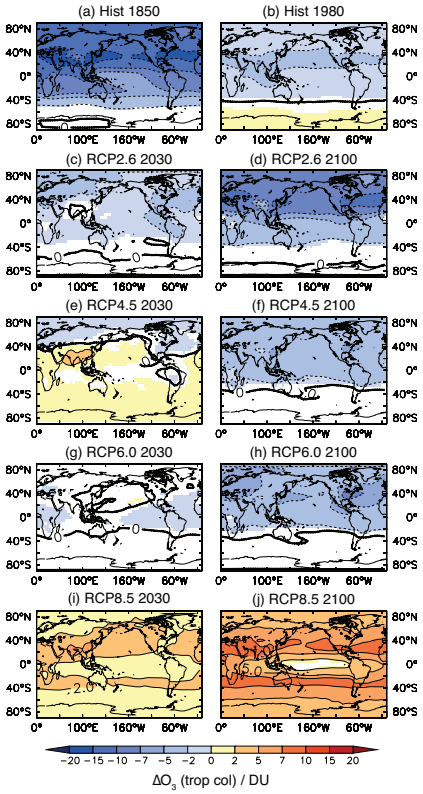

Fig. 10. As Fig. 9, but for the absolute change in the tropospheric ozone column (DU).

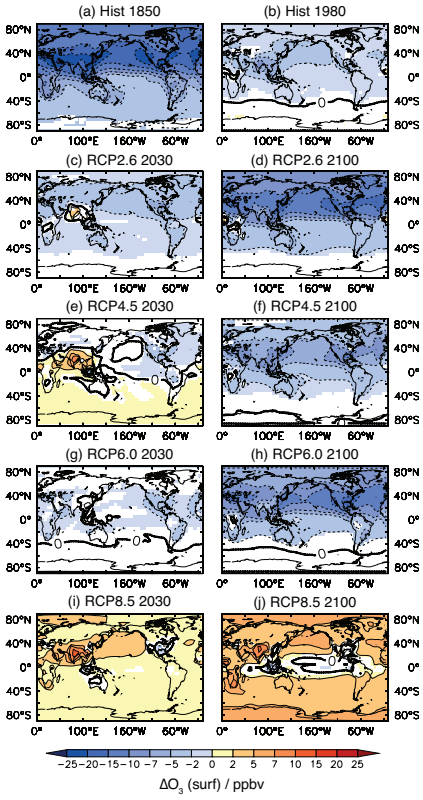

Fig. 11. As Fig. 9, but for the absolute change in surface ozone (ppbv).

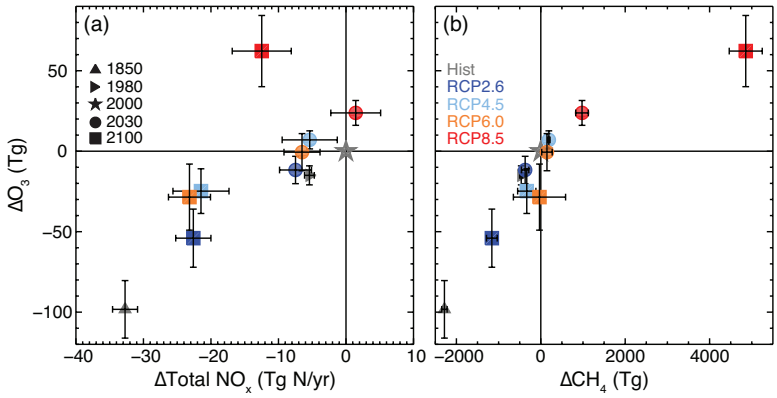

Fig. 12. ACCMIP ensemble mean change in the tropospheric ozone burden compared to the Hist 2000 simulation as a function of **(a)** changes in total NO_x emissions and **(b)** changes in the tropospheric methane burden. Error bars indicate ±1 std. dev. of the changes in ozone, NO_x emissions and methane burdens, calculated from the spread of the models. Different colours represent the different scenarios, whereas different symbols represent the different time slices.