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We use aircraft observations from the 1991–2000 Cape Grim Overflight Program and the 2009–2011 HIAPER Pole-to-Pole Observations (HIPPO), together with output from four chemical transport and chemistry-climate models, to better understand the vertical distribution of carbon monoxide (CO) in the remote Southern Hemisphere. Observed CO vertical gradients at Cape Grim vary from 1.6 ppbv km⁻¹ in austral autumn to 2.2 ppbv km⁻¹ in austral spring. CO vertical profiles from Cape Grim are remarkably consistent with those observed over the southern mid-latitudes Pacific during HIPPO, despite major differences in time periods, flight locations, and sampling strategies between the two datasets. Using multi-model simulations from the Southern Hemisphere Model Intercomparison Project (SHMIP), we find that observed CO vertical gradients in austral winter-spring are well-represented in models and can be attributed to primary CO emissions from biomass burning. In austral summer-autumn, inter-model variability in simulated gradients is much larger, and two of the four SHMIP models significantly underestimate the Cape Grim observations. Sensitivity simulations show that CO vertical gradients at this time of year are driven by long-range transport of secondary CO of biogenic origin, implying a large sensitivity of the remote Southern Hemisphere troposphere to biogenic emissions and chemistry. Inter-model variability in summer-autumn gradients can be explained by differences in both the chemical mechanisms that drive secondary production of CO from biogenic sources and the vertical transport that redistributes this CO throughout the Southern Hemisphere. This suggests that the CO vertical gradient in the remote Southern Hemisphere provides a sensitive test of the chemistry and transport processes that define the chemical state of the background atmosphere.

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1 Introduction

Carbon monoxide (CO) plays multiple fundamental roles in tropospheric chemistry, in particular serving as a major reactant of the hydroxyl radical OH (Logan et al., 1981) and as an indirect greenhouse gas (Myhre et al., 2013). A product of incomplete combustion, CO has large primary sources from fossil fuel and biomass burning (BB) as well as secondary sources from oxidation of methane (CH₄) and non-methane volatile organic compounds (NMVOCs), with a typical tropospheric lifetime of 1–2 months. In the Southern Hemisphere (SH), the distribution of CO is strongly impacted by emissions from BB (Edwards et al., 2006; Gloudemans et al., 2006) and biogenic sources (Williams et al., 2013), while anthropogenic emissions play only a minor role due to an inter-hemispheric transport barrier caused by the Inter-Tropical Convergence Zone (Hamilton et al., 2008). Much of the SH is characterized by very low CO emissions, and in these remote regions CO is largely controlled by the balance between long range transport and chemical removal via reaction with OH. Seasonal variability in CO sources, transport pathways, and loss processes leads to a complex seasonal cycle that is different in the free troposphere than at the surface (Pak et al., 2003). The ability of large-scale global atmospheric models to represent the processes driving this seasonality has been difficult to evaluate due to a paucity of measurements in the SH free troposphere. Particularly rare are observations of the CO profile in the SH, despite the importance of such measurements for testing model processes including source attribution and vertical transport (Liu et al., 2013, 2010). Here, we use simulations from four global chemical transport and chemistry-climate models conducted for the Southern Hemisphere Model Intercomparison Project to interpret a unique 9 year record of airborne CO vertical profiles in the remote SH from the Cape Grim Overflight Program (Langenfelts et al., 1996).

Evaluation of CO distributions in atmospheric models has largely focused on the Northern Hemisphere where observations are more widely available, with some limited evaluation in the SH as part of global comparisons (e.g., Shindell et al., 2006). The

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Southern Hemisphere Model Intercomparison Project (SHMIP) was devised to provide a more focused evaluation of current large-scale atmospheric chemistry models in the SH. A central goal of SHMIP is to quantify model ability to represent the seasonal and spatial distributions of trace gases including CO. An overview of SH CO distributions in the four SHMIP models is provided by Zeng et al. (2014), who compare simulated CO to observations from surface in situ and ground-based total column measurements at selected SH sites. They show that using different biogenic emission inventories leads to marked differences in modeled CO at these sites and that accurate representation of biogenic emissions is critical to reproducing observed SH background CO. They also find that the underlying chemical and transport characteristics of each model greatly impact model ability to reproduce background SH CO. In some cases, the inter-model differences are larger than those associated with uncertainties in biogenic emissions, especially for locations further from tropical biogenic and BB sources. Detailed analyses of these uncertainties are addressed by Zeng et al. using column and surface observations; here we expand on this analysis using in situ observations from the remote free troposphere.

As in the SHMIP model evaluation of Zeng et al. (2014), previous model comparison to observations in the SH has generally been limited to in situ surface data (e.g., Duncan et al., 2007; Wai et al., 2014) and ground- or satellite-based remotely-sensed total column data (e.g., De Laat et al., 2007; Edwards et al., 2006; Gloudemans et al., 2006; Kopacz et al., 2010; Morgenstern et al., 2012; Shindell et al., 2006; Zeng et al., 2012). Total column comparisons provide an advantage over in situ surface comparisons for model validation in the free troposphere (Deutscher et al., 2010). However, neither surface nor total column data are able to constrain the vertical structure of CO, which is still poorly understood in the SH mid-latitudes. For example, Shindell et al. (2006) showed that a 26-model ensemble mean was able to reproduce mid-tropospheric CO measurements from the MOPITT satellite instrument in the extratropical SH, but the same models uniformly overestimated the upper-to-lower troposphere ratio seen by the satellite (as well as the seasonal cycle of the ratio). This comparison relied on qualitative differ-

ences between MOPITT upper and lower tropospheric retrievals (Shindell et al., 2006), as MOPITT sensitivity was different at these two altitudes in the version 3 data used (the newer versions 5 and 6 provide more sensitivity to the lower troposphere). More generally, remote-sensing instruments typically display different sensitivities at different altitudes, making it difficult to use these data to study vertical structure. For quantitative evaluation of vertical gradients, independent in situ data from the free troposphere are essential.

To date, in situ observations of CO in the SH remote free troposphere are sparse. Aircraft campaigns carried out in the SH over the last two decades have largely taken place near major emission sources (e.g., BARCA and GABRIEL in South America, SA-FARI in southern Africa, ACTIVE/SCOUT in northern Australia) or their outflow regions (e.g., TRACE-A in the South Atlantic). More remote sampling of SH CO has occurred over the South Pacific during NASA's PEM-Tropics A (1996) and B (1999) campaigns (Chatfield et al., 2002; Staudt et al., 2001). These campaigns provided detailed characterization of free tropospheric distributions during austral spring and fall but were temporally limited and unable to capture a full annual cycle. More recently, the HIPER (High-performance Instrumented Airborne Platform for Environmental Research) Pole-to-Pole Observations (HIPPO) traversed the South Pacific during multiple seasons over the period 2009–2011 (Wofsy, 2011), offering a previously inaccessible view of seasonal variability in the remote SH free troposphere. However, with only one set of flights in each season (including 4–6 individual flights in the SH), it remains difficult to quantify the seasonal and interannual representativeness of these data, complicating their interpretation.

The 9 year record of aircraft data from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Cape Grim Overflight Program (Langenfelds et al., 1996) provides a unique dataset to quantify seasonal variability at altitudes from the surface to 8 km in the remote SH. With monthly flights over the Southern Ocean during clean air conditions, this record contains significant information on the seasonal and vertical structure of CO in the SH free tropospheric background. We use this record

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CO data meeting these criteria included: 18, 20, 23, 26, 28 January 2009 (HIPPO-1); 7, 9, 11, 14 November 2009 (HIPPO-2); 2, 5, 8, 10 April 2010 (HIPPO-3); 22, 25, 28 June 2011 (HIPPO-4); 24, 27, 29 August and 1, 3 September 2011 (HIPPO-5). Sampling locations meeting these criteria are shown in Fig. S1 in the Supplement.

2.3 Southern Hemisphere Model Intercomparison Project (SHMIP)

We compare the Cape Grim and HIPPO aircraft observations to output from a suite of model runs conducted for SHMIP. A detailed overview of the initiative is given in Zeng et al. (2014). SHMIP included two chemical transport models (GEOS-Chem and TM5) and two chemistry-climate models (NIWA-UKCA and CAM-chem), with different tropospheric and tropospheric–stratospheric chemical schemes employed across models. Aerosol effects included in the models vary in levels of complexity. Of particular relevance is loss of HO₂ on aerosol particles, which has been shown to increase CO mixing ratios by 4–7 ppbv in the remote SH (Mao et al., 2013a). This effect is included in GEOS-Chem with aerosol uptake coefficient $\gamma = 0.2$; in other models aerosol uptake of HO₂ is not included or results in HO_x recycling rather than net loss. Additional details of the model configurations and major differences between models are given in Table 1 and described in more detail in Zeng et al. (2014). Simulations spanned 2004–2008 (following a one-year spin-up) using the same emissions across models for anthropogenic, BB, and biogenic sources. Anthropogenic emissions were taken from the REASv2.1 inventory (Kurokawa et al., 2013) between 60–150° E and 10° S–70° N, nested within the global MACCity inventory (Granier et al., 2011; Lamarque et al., 2010). BB emissions were from the GFEDv3 inventory (van der Werf et al., 2010). Biogenic emissions were from the MEGANv2.1 inventory (Guenther et al., 2012), computed offline using the Community Land Model (CLM; Oleson et al., 2010) for each year of simulation (referred to here as MEGAN-CLM). Figure 1 shows the mean seasonal cycle of primary CO emissions and biogenic isoprene emissions (a proxy for secondary CO production) in the SH tropics and extra-tropics used in the standard SHMIP simulations. In addition, a set of sensitivity simulations was performed using biogenic emis-

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sions of isoprene and monoterpenes taken from LPJ-GUESS (Arneth et al., 2007a, b; Schurgers et al., 2009) (with all other species from MEGANv2.1 as in the standard runs). For methane, an important chemical loss term for OH and an indirect chemical source of CO, different approaches were used in each model as described in Table 1.

5 The models also included global and regional idealized CO-like tracers with the same emissions as CO but with different lifetimes, as described below.

Zeng et al. (2014) provide a detailed analysis of SH CO distributions simulated by the four SHMIP models as well as the models' varied abilities to reproduce surface and total column CO observations from selected SH sites. Here, we provide an additional test of
10 the models' abilities to represent vertical structure in the SH free troposphere (and the associated inter-model differences) using observed vertical profiles representative of SH mid-latitudes clean background air. Because of the temporal offset between CGOP (1990s), HIPPO (2009–2011), and the SHMIP simulations (2004–2008), we do not compare individual flights or profiles but instead focus on average behavior seen across
15 multiple years in the observations and models. For comparison with observations from CGOP, which measured only clean background air, we sample each model over the Southern Ocean southwest of Tasmania. We reduce the influence of model spatial variability on the comparisons by averaging each model over four representative grid squares in this region. Differences in model resolution and grid spacing result in slightly
20 different regions being sampled in each model. Coordinates of the relevant grid squares (referred to hereafter as the Cape Grim background region) are given in Table 1 and their spatial extent shown in Fig. 2.

Figure 3 shows the median observed seasonal cycle of CO at Cape Grim averaged over 0–2, 2–5, and 5–8 km altitude bins (black line). The observations show increasing
25 CO mixing ratios with altitude in all months, as previously reported by Francey et al. (1999) in an analysis of five years of the same dataset. Peak mixing ratios were observed in austral spring during the tropical BB season, with a 1 month offset between altitudes below 2 km (peak in October) and those above (peak in September), indicating the importance in the free troposphere of long-range transport of BB plumes

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(Francey et al., 1999). The colored lines in Fig. 3 show the simulated seasonal cycles in the Cape Grim background region for the four individual SHMIP models. Despite large differences in absolute mixing ratios (discussed below), the models are generally able to reproduce the shape of the observed seasonal cycle especially above 2 km, as expected from previous studies (e.g., Shindell et al., 2006). Model ability to match seasonal changes in the relationship between different altitudes is varied and is the subject of further discussion in Sect. 3.

The inter-model and model-observation differences near Cape Grim shown in Figs. 2 and 3 are sizeable, consistent with the detailed analysis of the simulations by Zeng et al. (2014). Annual mean mixing ratios in surface air in this region range from less than 50 ppbv in CAM-chem to nearly 65 ppbv in TM5 (compared to 53 ppbv observed; Fig. 2). GEOS-Chem CO is artificially enhanced as the model does not include a CO sink from dry deposition. A sensitivity test including dry deposition over all vegetated surfaces led to a 1–2 ppbv decrease in GEOS-Chem CO at all altitudes (equivalent to $\sim 50 \text{ Tgyr}^{-1}$ or 2% of the total global CO sink) but did not substantially change the vertical, horizontal, or seasonal distributions. The TM5 overestimate is consistent with the high bias in surface CO identified previously using monthly mean surface CO measurements at Cape Grim from the year 2000 (Williams et al., 2013). The CO differences between models persist with similar magnitude at all altitudes (Fig. 3). These differences in background CO are influenced by a number of factors including grid resolution, meteorological drivers, and chemical mechanisms as discussed in detail by Zeng et al. (2014). A major component of the mean difference between models is the difference in the simulated mean OH background, shown in Table 1. As our focus here is on relative rather than absolute vertical and seasonal gradients, we remove the influence of consistent differences in the CO background from our comparisons by showing CO mixing ratios expressed as ΔCO , the deviation (in ppbv) from a specific baseline value, as done previously for CGOP data by Francey et al. (1999). We use as baseline value the median mixing ratio in surface air (below 1 km) in a given season, computed separately for each model and each set of observations. Expressing the vertical gradients as de-

viations rather than absolute values also allows us to compare the CGOP and HIPPO observations, which are on different absolute scales due to different sampling locations and strategies.

3 Observed and simulated vertical gradients

3.1 Cape Grim and HIPPO observations

The median climatological vertical gradients of CO from CGOP are shown as black lines in Fig. 4. For each season, medians were computed after binning observations from all years into 1 km altitude ranges. Observed variability in each 1 km altitude bin was estimated using the median absolute deviation (MAD) statistic for all observations in the bin, shown as the thin horizontal lines. Profiles are expressed as ΔCO , the deviation in ppbv from the observed median value in surface air (0–1 km) for each season, as described in Sect. 2. Observations were grouped seasonally to increase the number of data points used to construct each profile, with seasonal groupings selected based on inspection of seasonal cycles in the data. In particular, observed behavior in June showed more similarity to that in the preceding months than in July–August in terms of both magnitude and interannual variability, especially at higher altitudes (Fig. 3). This reflects variability in the onset of the SH BB season, which typically occurs sometime in July or August (Edwards et al., 2006). We therefore grouped June data with austral autumn (MAMJ) rather than austral winter (JA) and retained austral spring (SON) as a definitive season.

Figure 4 shows moderate seasonal variability in observed CO vertical gradients of a few ppbv km^{-1} , with larger gradients during the winter-spring burning seasons (JA, SON) than during the rest of the year. As reported previously by Pak et al. (1996) using the first four years of this dataset, the observations show an increase in gradient above 2 km, with the suppressed gradient at lower altitudes indicative of mixing throughout the local boundary layer (Pak et al., 1996). We quantify the observed CO vertical gradients

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using a linear fit to the median profiles for each season. Calculated gradients are given in Table 2 and show a minimum in autumn (1.6 ppbv km^{-1}) and maximum in spring (2.2 ppbv km^{-1}) that are significantly different from one another.

We evaluate the large-scale spatial representativeness of the CGOP data using dependent HIPPO observations from the South Pacific. Seasonal profiles are shown in gray in Fig. 4 and were constructed from one HIPPO deployment each, with the exception of MAMJ which includes both HIPPO-3 and HIPPO-4 flights. HIPPO-5 profiles for JA also include data from the two flights in early September to increase the data available in that season and to keep all flights from each deployment together. The figure shows that although the relative variability in CO (thin lines) differs somewhat between HIPPO and CGOP, there is generally overlap in the observed ΔCO from each dataset (thick lines). The most notable difference between datasets (although still within the observed variability of both campaigns) is seen above 4 km in JA. We examined this difference using regional BB tracers in the four models (tracers are described below) and found the offset between CGOP and HIPPO in JA is consistent with differences in transport from southern African BB sources to the two different sampling locations. Outflow from Africa is frequently southeastward at this time of year, passing directly over Cape Grim. BB plumes are not well-mixed by the time they arrive at Cape Grim, resulting in large and distinct peaks in observed CO anywhere from 4–8 km (Francey et al., 1999; Pak et al., 2003). In contrast, simulated transport to the southwest Pacific is both less frequent and less direct in JA, leading to more diffuse BB plumes and lower CO mixing ratios. Simulated CO profiles over the Pacific (not shown) display a broad peak of moderately enhanced CO from 2–8 km, consistent in shape with airborne observations of BB-influenced air from PEM-Tropics A (Staudt et al., 2002).

With the exception of the mid-troposphere in JA, the observed CO vertical gradients are very similar between CGOP and HIPPO, despite major differences in flight locations (Southern Ocean vs. Pacific), observation years (1990s vs. late 2000s), and sampling strategies (number of profiles, frequency of flights). This remarkable correspondence lends confidence to our use of vertical gradients derived from the CGOP data as being

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that contribute to background CO in this region since the 1990s (when the observations were collected). This is consistent with a number of recent studies (and with our own analysis of Cape Grim surface flask data) showing observed trends in SH CO are much smaller than interannual variability (Zeng et al., 2012; Wai et al., 2014; Warner et al., 2013; Worden et al., 2013; Yoon and Pozzer, 2014). Significant peaks in BB have been observed for individual years in both periods (in particular, the 1997 and 2006 El Niño years), and these are reflected in the large interannual variability shown for these seasons in Fig. 5 (horizontal lines).

Outside of the burning season, model ability to match observed vertical gradients deteriorates, as does inter-model agreement (Fig. 5). GEOS-Chem and CAM-chem in particular show a sharp drop in gradient from spring to summer/autumn that is unmatched by the observations; the change in NIWA-UKCA and TM5 is more gradual but still too large (Table 2). Across all models, the overall decrease in the vertical gradient from spring to autumn is between 1–2 ppbv km⁻¹, larger than the observed change from CGOP of ~ 0.5 ppbv km⁻¹. In the following section, we evaluate possible reasons for the model-CGOP and inter-model discrepancies in the summer-autumn CO vertical gradients.

4 Drivers of inter-model variability

Model-observation differences can result from model errors in emissions, chemistry, meteorology/transport, or a mix of these. As all SHMIP models used identical emissions (except for parameterized lightning, soil, and volcanic sources with limited impact on CO), the inter-model differences seen here should result primarily from differences in chemistry and meteorology/transport (resolution may also play a small role). Here, we investigate the role of model differences in transport and chemistry on differences in simulated vertical gradients using a set of sensitivity simulations, run for a two-year period (2004–2005) to reduce the influence of interannual variability on the results.

Figure 6a shows the simulated CO vertical gradients from the standard simulations in 2004–2005 as a point of reference for the sensitivity simulations.

4.1 Transport

The first sensitivity simulation uses an idealized CO-like tracer (CO_{25}) designed to quantify the impact of model transport, independent of the influence of model chemistry. The CO_{25} tracer used the same emissions as CO globally with a fixed 25 day lifetime and was not subject to chemical production or chemical loss. In remote regions, the CO_{25} mixing ratio therefore represents the balance between primary emission and long-range transport, with differences between models caused exclusively by differences in transport over the 25 day tracer lifetime. Vertical gradients of the CO_{25} tracer are shown in Fig. 6b. The differences in CO_{25} between models are much smaller than differences in total CO, especially in summer-autumn, suggesting inter-model differences in meteorology and transport are small relative to other drivers of variability. In DJF and MAMJ, all models display a greatly diminished ability to match observed gradients when chemistry is neglected, indicating transported primary emissions play only a small role in driving CO vertical gradients at this time of year. In winter-spring, CO_{25} vertical gradients are only slightly shallower than those of total CO and are within the observed interannual variability, consistent with the gradients being driven by primary BB emissions that are well represented in all four models.

We further investigate the impacts of inter-model transport differences using regional CO_{25} tracers. Figure 7 shows the contribution from six regions (Australia, South America, southern Africa, Southeast Asia, East Asia, and all other sources) to total CO_{25} at Cape Grim in three altitude ranges. Total CO_{25} amounts are highest in GEOS-Chem, indicating more rapid transport to this region than in the other models, and are typically lowest in NIWA-UKCA. In summer, the relative contributions of different sources are largely consistent across the models, with a slight dominance from Australia below 2 km and a slight dominance from South America above. The “other” contribution shown in gray in Fig. 7 represents the difference between the global CO_{25} tracer and

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the sum of the regional CO₂₅ tracers and mainly reflects the contribution from northern Africa. Inter-model differences are larger for this “other” term than for any of the regional CO₂₅ tracers, with in particular NIWA-UKCA showing less influence than the other models. This contribution peaks in austral summer, likely driven by the seasonal source from NH African burning, which is at its annual maximum in DJF (Roberts et al., 2009). In summer-autumn, differences between models are largely constant with altitude and result in very similar vertical gradients, as seen previously in Fig. 6b.

During the tropical BB seasons (JA-SON), inter-model differences in the CO₂₅ sources at Cape Grim are larger, as shown in Fig. 7. In JA, the contribution from southern Africa is dominant and also varies most, responsible for 50–60 % of total CO₂₅ in NIWA-UKCA compared to only 20–30 % in CAM-chem, with the other models falling between these values. Absolute differences in this source of up to 7 ppbv at 8 km can explain much of the difference in the JA CO₂₅ gradient shown in Fig. 6b, suggesting that long-range transport of African BB emissions contributes to inter-model variability during the early BB season. In SON, the South American contribution dominates, reflecting a one-month offset in peak emissions from these regions in 2004–2005 in the GFEDv3 inventory. The southern African contribution is also more consistent across models in SON, with inter-model differences of similar magnitude to those from the South American source (2–3 ppbv).

4.2 Chemical loss

Fixed-lifetime tracers do not account for model differences in chemistry, which for CO include differences in both OH-driven loss and in secondary chemical production. We isolate the impact of the former using a second set of idealized CO-like tracers (CO_{OH}). In this case, the CO_{OH} tracers again have the same primary emissions as CO but with tracer loss driven by each model’s OH fields and CO+OH rate constant. Differences in the rate constant at standard temperature and pressure are of order 10 % (e.g., between the IUPAC recommendation used in NIWA-UKCA and the JPL recommendation used in GEOS-Chem). Differences in OH mixing ratio are of order 5–20 % for the global

tropospheric mean (Table 1) but can be much larger regionally. Like CO_{25} , CO_{OH} tracers are subject to differences in model transport, with differences between CO_{25} and CO_{OH} indicative of the impacts of modeled CO loss rates.

Figure 6c shows the vertical gradients of the global CO_{OH} tracer in the Cape Grim region as simulated by GEOS-Chem, NIWA-UKCA, and TM5 (CAM-chem did not include a global CO_{OH} tracer). Both the relative vertical gradients and the regional contributions are generally similar between the two idealized tracers (regional contributions are shown in Fig. S2 in the Supplement). In DJF, tropospheric OH production leads to a small decrease in mid-tropospheric CO_{OH} relative to surface values in all three models. As for CO_{25} , CO_{OH} gradients in DJF-MAMJ are greatly reduced relative to those of total CO (Fig. 6a), suggesting both transport and chemical loss are insufficient in these seasons to explain the large inter-model variability, which instead must be driven by secondary CO production.

4.3 Chemical production

The difference between CO_{OH} and total CO for each model represents the contribution from in situ chemical production, estimated to account for roughly half of the total CO source globally (Jiang et al., 2011; Kopacz et al., 2010) and an even larger proportion in the SH (Pfister et al., 2008). Comparing Fig. 6a and c shows that chemical production plays a dominant role in controlling the simulated CO vertical gradient in DJF and MAMJ but has much less influence during the tropical BB seasons when primary emissions dominate. Chemical production also appears to be the major source of inter-model variability in DJF and MAMJ, and uncertainties in this term may help explain the large underestimates of the observed summer gradient seen in particular by GEOS-Chem and CAM-chem (Fig. 5).

The final sensitivity test shown in Fig. 6 evaluates the role of biogenic emissions in driving the simulated CO vertical gradients by replacing MEGAN-CLM emissions with LPJ-GUESS for isoprene and monoterpenes. Since emissions are the same across models, they cannot explain inter-model variability; however, they can help attribute

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sources of model-observation bias as well as provide insight into the dependence of the simulated vertical gradients on biogenic sources. Figure 6d shows that in summer-autumn the LPJ-GUESS emissions reduce the simulated CO vertical gradient in all models, while in winter-spring the differences are negligible. These results present a picture consistent with the previous sensitivity tests; namely, that observed vertical gradients are driven by primary BB emissions in winter-spring and by secondary CO of biogenic origin in summer–autumn.

Biogenic source regions are located far upwind of Cape Grim, so model error in the Cape Grim background region can result from errors in both model chemistry and the transport of secondary CO. Distinguishing between these factors is not straightforward. Using GEOS-Chem, we performed an additional one-year sensitivity test for 2004 designed to partially discriminate between these terms by replacing the standard GEOS-5 meteorology with GEOS-4. The latter has been shown to have more rapid vertical uplift over tropical source regions (Liu et al., 2013, 2010), where biogenic emissions are also large (Guenther et al., 2006). The same chemical mechanism was used in both simulations, and the CO+OH reaction rate changed by less than 2 % from differences in temperature and pressure, so simulated differences at Cape Grim can be attributed to model transport. Results from this sensitivity simulation (not shown) indicated virtually no impact on the CO vertical gradient in summer-autumn, implying a dominant influence from the chemistry controlling secondary CO production.

5 Chemistry and transport of biogenic-sourced secondary CO

In preceding sections, we have shown that inter-model differences in the vertical distribution of CO in the remote SH are largest in austral summer-autumn, and that these differences cannot be explained by the transport or chemical loss of primary emitted CO; instead, they are clearly driven by differences in CO produced chemically from biogenic emissions. Here we evaluate model differences in the chemistry and transport of secondary CO from biogenic source regions in the context of their impacts on

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SH background CO in summer (DJF), when inter-model variability is largest. We focus our analysis in this section on GEOS-Chem and NIWA-UKCA, the two models that best reproduce absolute CO mixing ratios at Cape Grim (Fig. 3) but with significant differences in the simulated vertical gradient (Fig. 5).

5 Chemical mechanisms differ substantially across the SHMIP models (Zeng et al., 2014), and differences are difficult to interpret due to varying levels of complexity, especially for NMVOC speciation and oxidation. Of particular importance here are differences in the oxidation of isoprene, summarized for all models in Table 3, and monoterpenes. The GEOS-Chem SHMIP simulations use the Caltech isoprene mechanism as implemented in v9-01-03 (http://wiki.seas.harvard.edu/geos-chem/index.php/New_isoprene_scheme_prelim), which includes formation of first and second generation isoprene nitrates under high-NO_x conditions (Paulot et al., 2009a) and formation of isoprene hydroperoxides and subsequently epoxydiols under low-NO_x conditions (Paulot et al., 2009b). Isoprene oxidation in NIWA-UKCA is from the original Mainz Isoprene Mechanism (MIM; Pöschl et al., 2000) but with updated rate coefficients for reactions between OH and isoprene nitrates and between NO and isoprene peroxy radicals from Paulot et al. (2009a, b); still, the NIWA-UKCA mechanism contains a limited number of species and predates many recent advances in isoprene chemistry available in newer mechanisms like the Caltech scheme or MIM2 (Taraborrelli et al., 2009).
20 Monoterpene oxidation is not included explicitly in GEOS-Chem v9-01-03 as used here; instead, monoterpene emissions produce CO with an assumed 20 % molar yield (Duncan et al., 2007). NIWA-UKCA includes simple monoterpene oxidation reactions based on Brasseur et al. (1998). Oxidation products of isoprene and monoterpenes are similar, and we do not distinguish between these two sources in either model.

25 Figure 8 shows mean summertime mixing ratios of CO and key related species (isoprene, formaldehyde, OH, and HO₂) in near-surface air (< 1 km) as simulated by GEOS-Chem and NIWA-UKCA for the tropics and SH extra-tropics. Similar maps for TM5 and CAM-chem can be found in Fig. S3 in the Supplement. At the surface, CO hotspots across the tropics show similar magnitudes in GEOS-Chem and NIWA-UKCA,

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especially in Africa and Southeast Asia where primary emissions dominate (Fig. 8a). Surface isoprene – indicative of biogenic source regions – is also similar across models (Fig. 8b), with maximum values of more than 10 ppbv over South America. Comparison to observations from the October 2005 GABRIEL campaign over the north-east Amazon shows a 40–70 % high isoprene bias in the boundary layer (modeled means of 2.9–3.4 ppbv in the 3–6° N, 50–60° W flight region vs. observed mean of 2.00 ± 0.76 ppbv from Lelieveld et al., 2008). In the free troposphere, mean simulated isoprene ranges from 0.04–0.2 ppbv across models, generally within the variability of the GABRIEL observations (0.07 ± 0.12 ppbv; Lelieveld et al., 2008). The inter-model consistency of the surface overestimate points to a high bias in the MEGAN-CLM emissions, which are common to all SHMIP models.

The models show large discrepancies in surface distributions of formaldehyde (CH_2O), with much higher surface CH_2O in NIWA-UKCA than GEOS-Chem (Fig. 8c). In non-urban continental boundary layers, the dominant source of CH_2O is atmospheric oxidation of NMVOCs, and in particular isoprene (Palmer et al., 2003). The higher mixing ratios simulated by NIWA-UKCA are therefore indicative of more rapid chemical processing following isoprene oxidation. As inter-model differences are small for isoprene mixing ratios (Fig. 8b), OH mixing ratios (Fig. 8d), and the rate of the initial isoprene+OH oxidation reaction (within ~ 1 % at standard temperature and pressure), the differences in surface CH_2O shown in Fig. 8 are likely driven by the chemistry of second and later generation oxidation products. CH_2O oxidation provides a source of CO over short timescales, and the faster production of CH_2O therefore also results in more rapid production of CO in NIWA-UKCA. This is seen in Fig. 8f, which shows that the net balance between CO chemical production (P_{CO}) and CO chemical loss (L_{CO}) is more strongly weighted towards production in NIWA-UKCA, leading to slight enhancements in boundary layer CO over biogenic source regions (e.g., South America, Fig. 8a). These differences in $P_{\text{CO}}-L_{\text{CO}}$ are unlikely to be driven by differences in CO loss rates given the similarity of surface OH between models (particularly over

South America where all models show OH titration; Fig. 8d), and are thus more likely reflective of CO production chemistry.

The implications of these chemistry differences for the broader vertical and horizontal distributions of CO depend on subsequent transport and chemical processing.

Figure 9 shows mean summertime longitude-altitude cross sections (averaged over 15–45° S) for isoprene, CH₂O, and CO (see Fig. S4 for TM5 and CAM-chem). The isoprene cross sections (Fig. 9a) show key differences in vertical transport between models. Relative to NIWA-UKCA, GEOS-Chem shows more deep convective injection of isoprene to the upper troposphere (UT) over Africa and Australia but less over South America, where isoprene mixing ratios are at their maximum. As a result, NIWA-UKCA displays an enhancement of isoprene mixing ratios at roughly 12 km over South America while isoprene is largely depleted at these altitudes in GEOS-Chem. The result is more UT production and therefore higher UT mixing ratios of both CH₂O (Fig. 9b) and CO (Fig. 9c) in NIWA-UKCA than GEOS-Chem. Subsequent zonal transport distributes this additional CO across the SH mid-latitudes UT. Because isoprene emissions are much higher in South America than other SH source regions (Fig. 8), the differences in vertical transport over Africa and Australia play a much more minor role in defining SH UT CO distributions.

The mean location and vertical extent of the profiles from CGOP are shown as the blue lines in Fig. 9. The figure shows that the inter-model differences in CO vertical gradient seen in Fig. 5 are consistent with the combined effects of differences in chemistry and transport. Slower oxidation of isoprene products in GEOS-Chem leads to a horizontal smearing effect in the lower-mid troposphere, resulting in relatively more CH₂O and CO (largely of Australian biogenic origin) reaching Cape Grim below ~ 3 km in GEOS-Chem compared to NIWA-UKCA. Meanwhile, NIWA-UKCA's rapid isoprene uplift and subsequent CO production and UT transport result in relatively more CO (largely of South American biogenic origin) reaching Cape Grim above ~ 6 km in NIWA-UKCA than in GEOS-Chem. Combined, these two factors drive a stronger vertical gradient

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in NIWA-UKCA in the Cape Grim region. Impacts are similar over the western Pacific region sampled by HIPPO.

In austral autumn (MAMJ), inter-model differences in surface mixing ratios and vertical uplift are similar to those shown in Figs. 8 and 9 for austral summer. We have shown previously that biogenic-derived secondary sources continue to drive simulated CO gradients in this season (Fig. 6). Combined, these results suggest that the inter-model variability in autumn is caused by the same differences in model chemistry and transport as seen for summer.

6 Conclusions

We have used a 9 year dataset of monthly airborne observations of CO from the Cape Grim Overflight Program (CGOP) to evaluate CO distributions in the remote Southern Hemisphere (SH) free troposphere as simulated by four global 3-D atmospheric chemistry models using identical emissions. Observations above the surface in this region are rare and are typically limited to a single year and/or season, so interpretation of the Cape Grim data provides a unique picture of climatological CO seasonal cycles and vertical gradients in the remote SH. Our analysis focused on the models' relative abilities to reproduce observed vertical gradients of CO from the surface to 8 km in different seasons. Through model sensitivity analysis and comparison of simulated spatial distributions, we evaluated the importance of primary vs. secondary sources on CO vertical gradients and diagnosed the causes of inter-model divergence.

Observations from both CGOP near Tasmania (1991–2000) and the recent HIPPO campaigns over the SH Pacific (2009–2011) showed similar seasonality, with larger gradients during the austral winter-spring burning seasons (JA, SON) than during the rest of the year. The close correspondence between these two datasets despite differences in location, time period, and sampling strategies suggests the processes driving observed vertical gradients are coherent across much of the remote SH and have not changed significantly over the past two decades. The four models (GEOS-Chem,

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NIWA-UKCA, TM5, and CAM-chem) were all able to reproduce observed vertical gradients during winter-spring, but observed gradients were underestimated in austral summer (DJF) and autumn (MAMJ) by GEOS-Chem and CAM-chem. All models overestimated the seasonal cycle of the vertical gradient to some degree.

Sensitivity analysis showed that transport of primary BB CO is the main driver of the observed gradients in winter-spring, when models and observations agree. Regional tracers with CO-like primary emissions and either fixed (CO_{25}) or OH-driven (CO_{OH}) lifetimes suggested a dominant influence in these seasons from southern African BB in JA and South American BB in SON, with the seasonal offset due to the timing of peak emissions from these two regions. Inter-model variability was relatively small in both seasons and could generally be attributed to variability in the influence of the southern African source. In summer-autumn, model ability to match observed gradients was significantly diminished when secondary CO sources were not included. Inter-model differences in both CO_{25} and CO_{OH} tracers were much smaller than differences in total CO during non-BB seasons, suggesting that neither transport nor CO loss rates are sufficient to explain inter-model variability at this time of year. Instead, simulated gradients and inter-model variability in these gradients are driven by secondary CO of biogenic origin, implying a strong sensitivity of tropospheric composition in the remote SH to long-range transport of biogenic emissions and their products.

We compared simulated austral summer (DJF) horizontal and vertical distributions of CO and related species between NIWA-UKCA and GEOS-Chem (the models with the most realistic CO mixing ratios at Cape Grim) and found significant differences driven by chemical processing and vertical transport. While OH-driven oxidation of isoprene is similar between the models, the ensuing chemistry of isoprene oxidation products appears to proceed faster in NIWA-UKCA than in GEOS-Chem, leading to more rapid production of formaldehyde and CO. The slower chemistry in GEOS-Chem leads to a smearing effect, with CO produced further downwind from source regions, and this effect is particularly pronounced in the lower-mid troposphere near biogenic sources. Inter-model chemistry differences are compounded by differences in vertical transport.

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More rapid uplift over South America in NIWA-UKCA leads to a secondary isoprene maximum at roughly 12 km that is not seen in GEOS-Chem. Subsequent oxidation produces additional CO in the upper troposphere near biogenic source regions, and zonal transport distributes this CO across the SH mid-latitudes. The net effect of the differences in chemistry and vertical transport is less CO at the surface and more at altitude in NIWA-UKCA than GEOS-Chem, resulting in a stronger gradient that is more consistent with CGOP observations.

It is important to note that the simulated summer-autumn CO vertical gradients shown in Fig. 5 reflect the convolved effects of biogenic emissions, model chemistry, and model transport, and the ability to match the observed gradients cannot unambiguously test whether any of these are correct (e.g., the emissions sensitivity test in Fig. 6d). NIWA-UKCA's superior ability to match the observed DJF gradient relative to GEOS-Chem or CAM-chem is achieved despite the fact that its isoprene oxidation scheme (MIM with some updates) is relatively simple and has known deficiencies (Butler et al., 2008; Taraborrelli et al., 2009). Many recent advances in our understanding of isoprene chemistry – including some that are included in the other models' mechanisms – are not yet implemented in NIWA-UKCA (e.g., Crouse et al., 2012, 2011; Paulot et al., 2009a, b; Peeters and Müller, 2010; Peeters et al., 2009; Rollins et al., 2009), although the mechanism does include updated reaction coefficients from Paulot et al. (2009a, b). Simulated agreement therefore cannot be considered an endorsement of the chemical scheme but rather an indication that the chemistry, transport, and emission inventory are well-matched to one another. This has important implications for the use of model inversion studies to correct emission estimates, as the strength of the correction will depend heavily on the chemical scheme and driving meteorology used. Global, satellite-based CO-only inversions in particular may be significantly impacted, as constraints include observations over remote SH scenes such as those studied here, which we have shown to be driven primarily by secondary biogenic sources. Improved quantification of CO sources may require combined inversion of multiple species with

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different lifetimes and different contributions from biogenic vs. fuel sources, such as CO and CH₂O (Jiang et al., 2011; Fortems-Cheiney et al., 2012).

Understanding the clean background atmosphere is essential for accurately attributing the impacts of ongoing anthropogenic and natural global change. With relatively few primary source locations, the remote SH serves as a large-scale testbed for quantifying background processes. Although much of the previous work on SH atmospheric composition has focused on the impacts of tropical burning, we have shown here that the non-BB seasons (austral summer and autumn) provide a more nuanced and critical test of the chemistry of the background atmosphere. We have also shown that the vertical gradient of CO is a particularly sensitive test of this chemistry as it is driven by chemical production in summer and autumn. Regular measurements of CO vertical profiles in the remote SH, such as those conducted during the 1990s under the Cape Grim Overflight Program, would thus provide an extremely valuable dataset for probing the state of the background atmosphere and its response to ongoing change. Current models display varying degrees of fidelity in reproducing observed CO gradients in a way that is consistent with a state-of-the-science understanding of isoprene chemistry, and increasing the complexity of the chemical mechanisms does not necessarily improve simulation of CO gradients. Disentangling the impacts on model biases of uncertainties in emissions from those in chemistry and transport will necessitate broader in situ sampling during non-burning seasons of multiple species with different chemical lifetimes (including CO, NMVOCs, and HO_x), at altitudes throughout the tropospheric column, and in a range of SH environments including near-source, direct outflow, and remote downwind regions.

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Table 1. Details of model simulations used in SHMIP^a.

	GEOS-Chem ^b	NIWA-UKCA ^c	TM5 ^d	CAM-chem ^e
Model type ^f	CTM	CCM	CTM	CCM
Horizontal resolution (lon × lat)	2.5° × 2°	3.75° × 2.5°	3° × 2°	2.5° × 1.9°
Vertical levels: total & (< 8 km) ^g	47 (26)	60 (20)	34 (16)	56 (27)
Meteorology ^h	GEOS-5, GEOS-4	Forced by SSTs & sea ice	ERA-interim	MERRA
Emission injection heights ⁱ	Surface	Surface	Up to 6 km (fires) or surface	Surface
Methane mixing ratios ^j	Prescribed from observations	Prescribed from hemispheric gradient	Simulated	Prescribed from observations
Global mean tropospheric OH ^k (molec cm ⁻³)	10.1 × 10 ⁵	10.6 × 10 ⁵	8.6 × 10 ⁵	9.1 × 10 ⁵
Cape Grim background region ^l	138.75–143.75° E,	136.875–144.375° E,	138.0–144.0° E,	138.75–143.75° E,
Cape Grim background region ^l	41.0–45.0° S	41.24–46.25° S	42.0–46.0° S	41.7–45.5° S

^a A full description of the models including references is provided in Zeng et al. (2014)

^b GEOS-Chem (www.geos-chem.org) was modified from the standard version 9-01-03 with Caltech isoprene mechanism (Paulot et al., 2009a, b) to include HO₂ uptake by aerosols with $\gamma = 0.2$ (Mao et al., 2013b), add methanol as an interactive tracer based on the offline simulation of Millet et al. (2008), and use pre-computed biogenic emissions with imposed diurnal variability tied to solar zenith angle.

^c NIWA-UKCA comprises a coupled stratosphere–troposphere chemistry scheme (Morgenstern et al., 2013). The background climate model for NIWA-UKCA is HadGEM3-A (Hewitt et al., 2011). The updated version used here includes C₂H₄, C₃H₈, CH₃OH, isoprene, and monoterpene in addition to those described in Morgenstern et al. (2013). The isoprene oxidation is based on Pöschl et al. (2000) and the monoterpene oxidation is as described in Brasseur et al. (1998).

^d The TM5 version used here employs the modified CB05 mechanism (Williams et al., 2013) using the configuration outlined in Williams et al. (2014). The isoprene and monoterpene oxidation schemes are taken from Yarwood et al. (2005) subsequently modified according to Archibald et al. (2010).

^e CAM-chem is described in Lamarque et al. (2012). CESM-1.1.1 is used here, with tropospheric (MOZART-4) chemistry.

^f Chemical transport model (CTM) or chemistry-climate model (CCM).

^g Altitudes are approximated from model pressure levels. The number of levels below 8 km is for the Cape Grim background region, with bounds given below.

^h Goddard Earth Observing System (GEOS) fields are from the NASA Global Monitoring and Assimilation Office (GMAO). GEOS-5 was used for the base simulations, and GEOS-4 was used for a one-year sensitivity study. NIWA-UKCA sea surface temperatures (SSTs) are from the Program for Climate Model Diagnostic and Intercomparison (PCDMI). ERA-interim fields are from the European Centre for Medium-Range Weather Forecasts (ECMWF). Modern Era Retrospective-analysis for Research and Applications (MERRA) fields are from the NASA GMAO.

ⁱ With the exception of the aircraft source, emissions are generally injected at the surface or in the first few model layers. Aircraft emissions are introduced throughout the troposphere depending on aircraft location and flight paths. In TM5, isoprene emissions between 20° S and 20° N are introduced into the first two layers of the model to represent canopy height. Also in TM5, fire emissions are distributed over different altitude regimes depending on fire type following Dentener et al. (2006), except in the tropics where injection heights are increased from 1 to 2 km based on recent satellite observations (Labonne et al., 2007).

^j Surface observations from the NOAA Global Monitoring Division (GMD) are used to prescribe methane mixing ratios in GEOS-Chem (all altitudes) and CAM-chem (surface only). NIWA-UKCA assumes methane mixing ratios of 1812 ppbv in the Northern Hemisphere and 1707 ppbv in the Southern Hemisphere. TM5 simulates methane interactively using emissions from the Emission Database for Global Atmospheric Research (EDGARv4.1) and the Lund–Potsdam–Jena Wetland Hydrology and Methane Dynamic Global Vegetation Model (LPJ-WhyMe).

^k Multi-year mean air density-weighted OH below the climatological tropopause defined as $p = 300 - 215(\cos(\text{lat}))^2$ hPa (Lawrence et al., 2001).

^l Cape Grim background region is the region in each model used for comparison with clean air observations from the Cape Grim Overflight Program, as described in the text and shown in Fig. 2.

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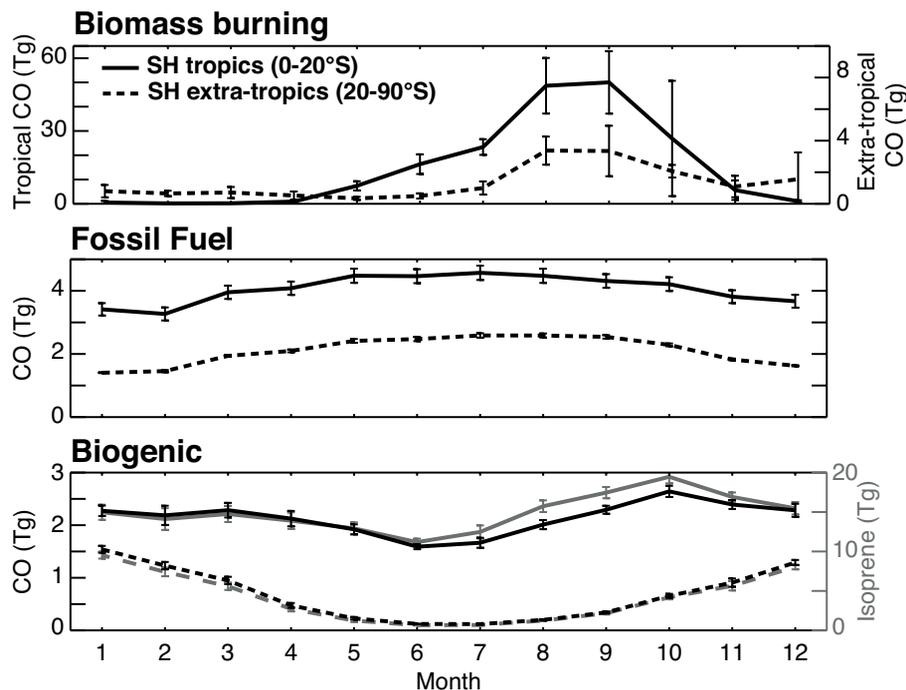


Figure 1. 2004–2008 mean primary CO emissions used in the SHMIP simulations for the Southern Hemisphere tropics (solid) and extra-tropics (dashed). Biogenic isoprene emissions are shown in gray in the bottom panel as a proxy for secondary CO. Error bars represent the interannual standard deviations. Emissions are from GFEDv3 for biomass burning (top), MAC-City and REASv2.1 for fossil fuels (middle), and MEGANv2.1 computed using CLM for biogenic sources (bottom), as described in the text.

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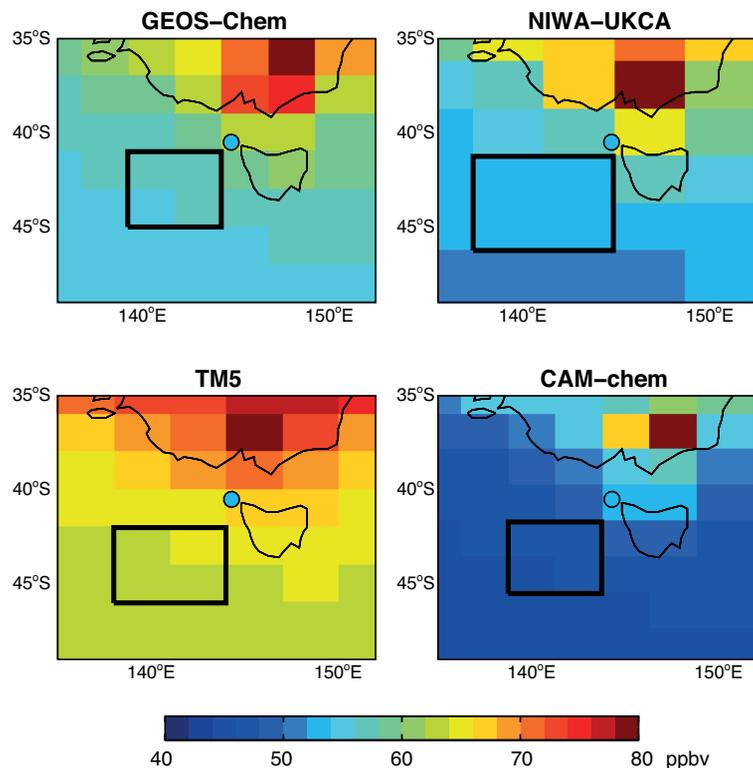


Figure 2. 5 year (2004–2008) mean surface CO mixing ratios from the four SHMIP models in the vicinity of Cape Grim. The circle shows the multi-year (1991–2000) mean observed CO below 500 m from CGOP, plotted at the location of typical vertical profiling. Black boxes indicate the four grid squares of the clean air “Cape Grim background region” sampled in each model for comparison with the aircraft observations, as described in the text.

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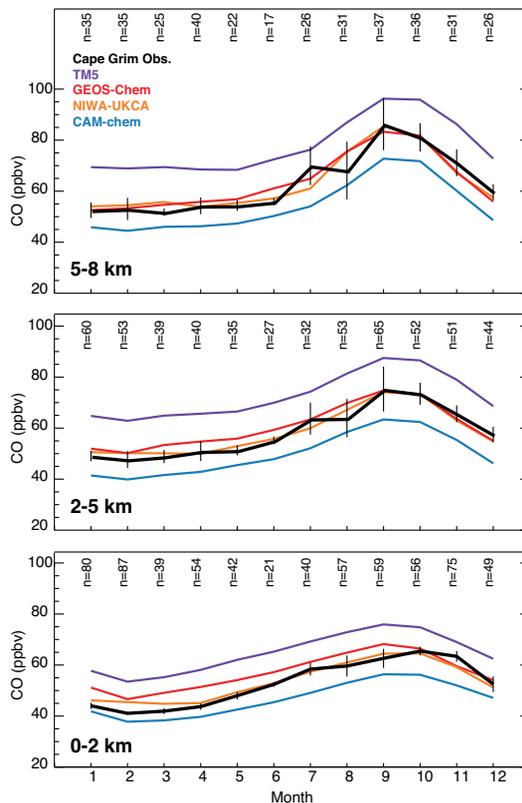


Figure 3. Median monthly CO observed near Cape Grim (1991–2000; black) and simulated for 2004–2008 in the Cape Grim background region (see Fig. 2) by TM5 (purple), GEOS-Chem (red), NIWA-UKCA (orange), and CAM-chem (blue). Seasonal cycles are shown for 0–2 km altitude (bottom), 2–5 km (middle), and 5–8 km (top). Thin black vertical lines show the observed median absolute deviation across all years of measurement. The number of observed data points in each monthly altitude bin is given at the top of each plot.

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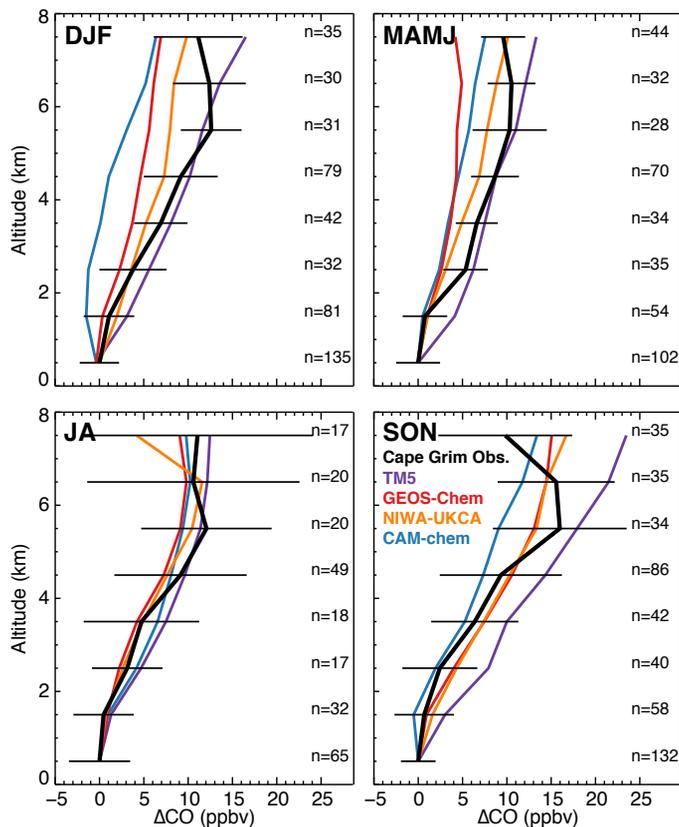
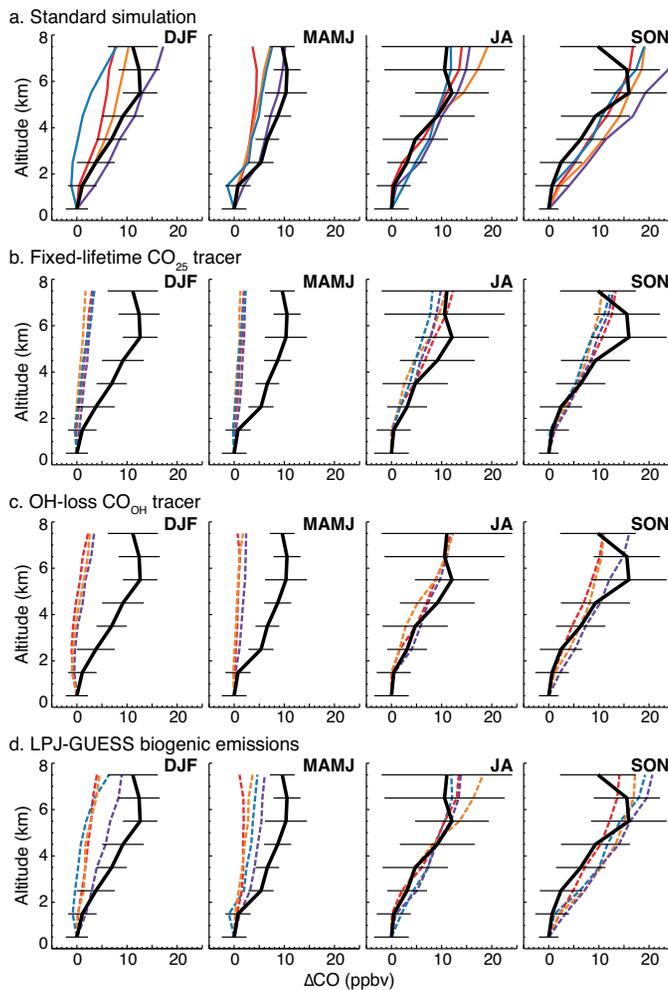


Figure 5. Median CO vertical profiles observed from 1991–2000 during CGOP (black) and simulated for 2004–2008 by TM5 (purple), GEOS-Chem (red), NIWA-UKCA (orange), and CAM-chem (blue) in the Cape Grim background region (see Fig. 2). Profiles are shown as ΔCO , the deviation (in ppbv) from the observed or modeled value in surface air in each season. Thin horizontal lines show the observed median absolute deviations across all years. The number of observed data points in each seasonal altitude bin is given at the right of each plot.

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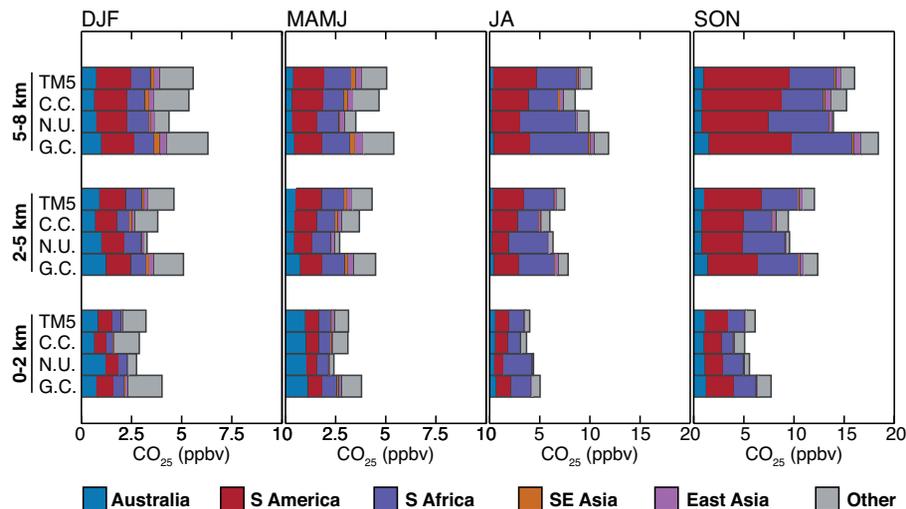


Figure 7. Contributions to CO₂₅ in the Cape Grim background region from sources in Australia (111–156° E, 11–44° S), South America (34–84° W, 57° S–1° N), southern Africa (9–44° E, 5–37° S), Southeast Asia (94–156° E, 11° S–7° N), East Asia (91–144° E, 7–44° N), and elsewhere, as simulated by GEOS-Chem (G.C.), NIWA-UKCA (N.U.), CAM-chem (C.C.), and TM5 for different altitude bands and seasons in 2004–2005. Note the difference in scale between DJF-MAMJ and JA-SON.

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Southern Hemisphere carbon monoxide profiles

J. A. Fisher et al.

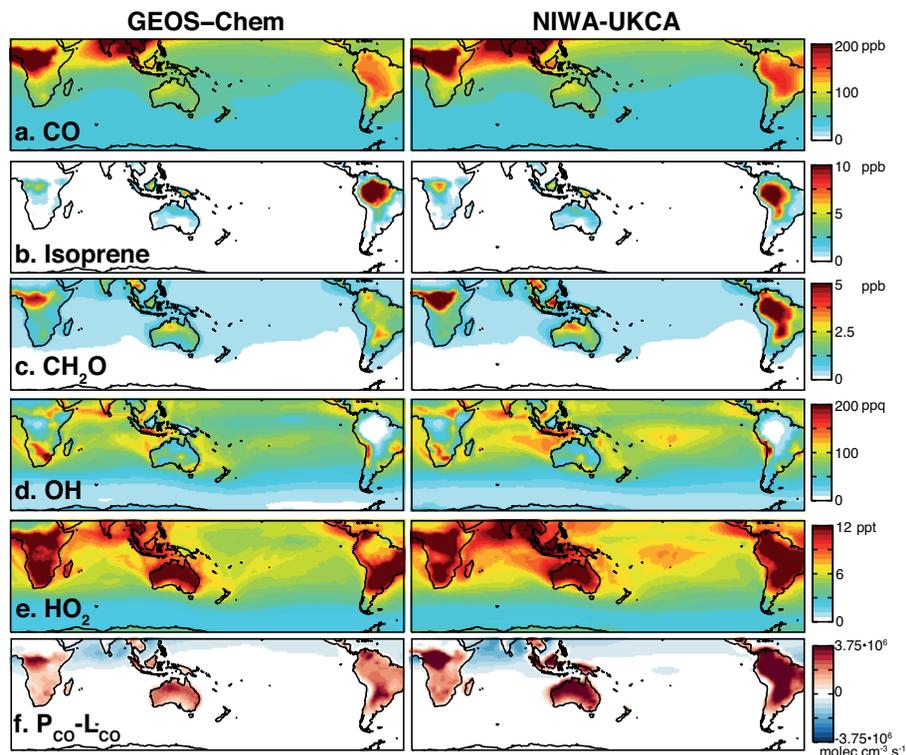


Figure 8. 5 year mean DJF mixing ratios in near-surface air (< 1 km) of **(a)** CO, **(b)** isoprene, **(c)** CH₂O, **(d)** OH, and **(e)** HO₂ as simulated by GEOS-Chem (left) and NIWA-UKCA (right). **(f)** The bottom row shows the difference between rates of CO chemical production (P_{CO}) and CO chemical loss (L_{CO}) in molecules cm⁻³ s⁻¹ for DJF 2004 only. Regions where production outweighs loss are shown in red and the inverse in blue.

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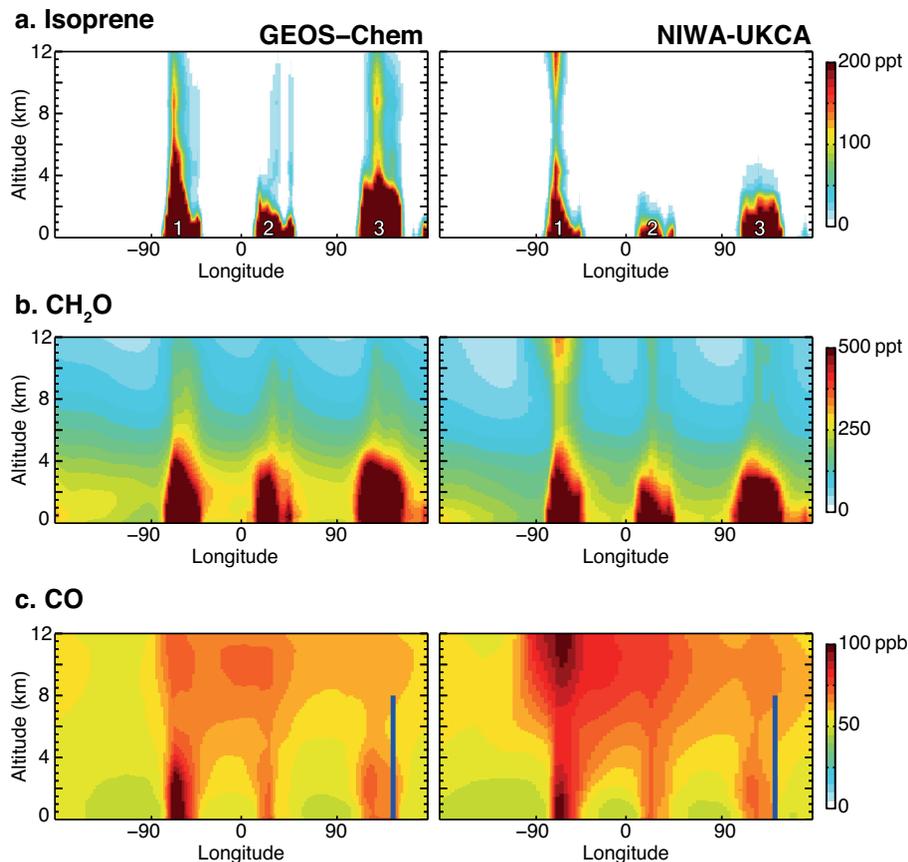


Figure 9. 5 year mean DJF longitude-altitude cross sections averaged over 15–45° S of (a) isoprene, (b) CH₂O, and (c) CO as simulated by GEOS-Chem (left) and NIWA-UKCA (right). Numbers in (a) correspond to locations of continental source regions: 1 = South America, 2 = Africa, 3 = Australia. The blue lines in (c) show the location and vertical extent of the CGOP aircraft profiles.