Atmos. Chem. Phys. Discuss., 5, 3747–3771, 2005
www.atmos-chem-phys.org/acpd/5/3747/
SRef-ID: 1680-7375/acpd/2005-5-3747
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Influence of convective transport on tropospheric ozone and its precursors in a chemistry-climate model

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Received: 1 April 2005 – Accepted: 9 May 2005 – Published: 7 June 2005

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Abstract

The impact of convection on tropospheric O_3 and its precursors has been examined in a coupled chemistry-climate model. There are two ways that convection affects O_3. First, convection affects O_3 by vertical mixing of O_3 itself. Convection lifts lower tropospheric air to regions where the ozone lifetime is longer, whilst mass-balance subsidence mixes O_3-rich upper tropospheric (UT) air downwards to regions where the O_3 lifetime is shorter. This tends to decrease UT ozone and the overall tropospheric column of O_3. Secondly, convection affects O_3 by vertical mixing of ozone precursors. This affects O_3 chemical production and destruction. Convection transports isoprene and its degradation products to the UT where they interact with lightning NO_x to produce PAN, at the expense of NO_x. The combined effect of NO_x to PAN conversions and downward transport of lightning NO_x results in UT NO_x decreases. Convective lofting of NO_x from surface sources appears relatively unimportant. Despite UT NO_x decreases, UT O_3 production increases as a result of UT HO_x increases driven by isoprene oxidation chemistry. However, UT O_3 tends to decrease, as the effect of convective overturning of O_3 itself dominates over changes in O_3 chemistry. The changes in tropical UT O_3 are transported polewards resulting in a 15% decrease in the global tropospheric O_3 burden. These results contrast with an earlier study that uses a model of similar chemical complexity. Differences in chemistry schemes – in particular isoprene-driven changes, as well as differences in convection schemes themselves, are the most likely causes of such discrepancies. Further modelling studies are needed to constrain this uncertainty range.

1. Introduction

The parameterisation of sub-grid scale convection is known to be a major uncertainty in both chemistry transport models (CTMs) and general circulation models (GCMs). A substantial element of divergence amongst CTM simulations arises from differences

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in convection parameterisation schemes, which have a particularly large influence on the distributions of short-lived species such as NO_x ($NO+NO_2$), HO_x ($OH+HO_2$), and ozone (O_3) (Prather and Jacob, 1997; Collins et al., 1999; Prather et al., 2001; Gauss et al., 2003). Future emissions projections (e.g., Nakicenovic et al., 2000) indicate strong growth of ozone precursor emissions in the tropics – how these are processed by convection will be an important determinant of future ozone concentrations and the oxidising capacity of the atmosphere. GCM simulations project future regional changes in the distribution of convection over many parts of the globe (Cubasch et al., 2001). Convection is therefore important in the context of understanding how future climate change may affect tropospheric chemistry, via changes in both vertical mixing and the distribution of lightning NO_x (e.g., Stevenson et al., 2005). Quantifying uncertainties on the impact of deep convection on tropospheric trace gas abundances and distributions are also necessary for assessing how shifts in convection on interannual (and longer) timescales associated with the El Niño Southern Oscillation (ENSO) modulate tropospheric chemistry variability (e.g., Peters et al., 2001).

Since O_3, its lifetime and its production efficiency per NO_x molecule all typically increase with height, deep convection strongly affects O_3 and its precursors throughout the tropical tropospheric column (TTC). Considering ozone in isolation, increased vertical mixing tends to lower TTC O_3, as O_3-poor air mixes upwards, to regions where its lifetime is longer, whilst O_3-rich air mixes downwards through mass-balance subsidence, to regions where its lifetime is shorter (e.g., Lelieveld and Crutzen, 1994; Lawrence et al., 2003). However, the effects of convection on ozone precursors also need to be considered. Where there are surface O_3 precursor sources, especially short-lived ones such as NO_x and isoprene (C_5H_8), convection significantly increases these precursor concentrations in the mid- and upper-troposphere (MT and UT) at the expense of lower troposphere (LT). Collins et al. (1999) and von Kuhlmann et al. (2004) identify convective uplifting of isoprene and its degradation products as a major source of tropical UT HO_x. Lawrence et al. (2003) find that lofting of surface NO_x is a significant driver of increases in O_3 production over much of the tropospheric column.

Lightning in the tropics is a major NO_x source directly associated with convection, with most NO_x added to the UT (Pickering et al., 1998). Convection redistributes lightning NO_x emissions downwards at the expense of the UT. There are also potential interactions between isoprene and lightning emissions (e.g., von Kuhlmann et al., 2004). An important isoprene degradation product is the peroxy acetyl radical (CH_3COO_2), which can affect NO_x by promoting PAN formation over land areas where isoprene and lightning NO_x emissions are co-located. The net impact of convective mixing is thus sensitive to the profile of O_3 and its precursors prior to convection, and is a complex balance between transport and a variety of chemical effects. Lawrence et al. (2003) found the effect of convective changes in precursor emissions on the tropospheric O_3 burden to be more important than the convective redistribution of O_3.

In this paper, the role of convective mixing in determining the distribution of O_3 and its precursors is investigated using the STOCHEM-HadAM3 coupled chemistry-climate model. Section 2 describes the model and the experiments. Section 3 describes the influence of convection on O_3 and its precursors, as well as on O_3 production and destruction for tropical land and ocean separately. Changes to the global O_3 budget are then outlined. Section 4 discusses the results of this paper compared to those from other studies, highlights model differences and uncertainties; Sect. 5 presents conclusions.

2. Model and experiments

The STOCHEM-HadAM3 coupled CTM-GCM model has been described in detail in previous studies (Sanderson et al., 2003a, b; Stevenson et al., 2004, and references therein), so a limited description of relevant model processes is presented here. HadAM3 (Pope et al., 2000) is the atmospheric component of the HadCM3 atmosphere-ocean general circulation model (GCM). In this study, HadAM3 was driven by prescribed monthly sea-surface temperatures (SSTs) for 1980–2002 and was run at standard resolution of 3.75° longitude by 2.5° latitude and 19 vertical levels. These

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levels are concentrated at the surface and extend to 10 hPa. Meteorological fields are passed to the CTM every 3 h.

STOCHEM is a Lagrangian tropospheric CTM, first described by Collins et al. (1997), with subsequent major updates to the chemistry (Collins et al., 1999), convection (Collins et al., 2002) and deposition schemes (Sanderson et al., 2003a). Its atmosphere is divided into 50 000 equal mass air parcels that are advected by HadAM3 winds. Air parcels are mapped onto a 5° longitude by 5° latitude horizontal grid with 9 equally spaced vertical levels, which extends from the surface to ~100 hPa. Stratospheric ozone influx is calculated from a present-day stratospheric ozone climatology (Li and Shine 1995) distributed into the troposphere by HadAM3 vertical winds at 100 hPa. Stratospheric input of HNO_3 is modelled similarly assuming a fixed N:O_3 ratio of 1:1000 (Murphy and Fahey, 1994). In this study, the chemical fields from STOCHEM are not fed back into the radiation scheme in HadAM3.

STOCHEM uses the Collins et al. (2002) Lagrangian convective mixing scheme. This mixing scheme uses 3-D convective updraught mass fluxes generated from HadAM3 (Gregory et al., 1997). It represents rapid convective updraughts, entrainment and detrainment of air parcels, and slower mass balance subsidence of larger regions of surrounding air. This scheme simulates radon (^{222}Rn) profiles that compare favourably with observations (Collins et al., 2002). The generation of lightning NO_x is linked to the convection scheme following Price et al. (1997). Convective precipitation from HadAM3 is used to identify lightning occurrence, and cloud height and thickness used to calculate the number of flashes for marine and continental clouds. The profiles of Pickering et al. (1998) are used to vertically distribute the lightning NO_x emissions for three regimes: midlatitude continental, tropical continental and tropical marine; midlatitude marine regions are treated like tropical marine regions. For these three regimes most lightning NO_x (55–75% depending on regime) is emitted in the UT above 8 km. Although 20% of lightning NO_x mass is emitted in the lower troposphere (LT) between 0–1 km in midlatitude continental regions, this amount is relatively small compared to surface anthropogenic and natural (soils and biomass burning) NO_x emissions over

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these regions (Labrador et al., 2004). Using this lightning NO_x scheme and these distribution profiles the ratio of lightning NO_x emissions in the UT over tropical land regions compared to oceanic regions is about 20:1 in these model simulations.

Two experiments were performed for the period 1980–2000: a "control" experiment with normal convective mixing of ozone and its precursors, and a "convection off" experiment with no convective mixing of ozone or its precursors, although convection in the climate model – HadAM3 and lightning NO_x emissions still occur. Also, water vapour comes from HadAM3 and does not change between the two experiments. The effect of convective mixing of trace gases can be investigated from these experiments.

Anthropogenic and natural emissions of global trace gases in both experiments are identical. Anthropogenic emissions come from the SRES A2 scenario (Nakienovi et al., 2000) for the present-day period. Note that emissions from all the different SRES scenarios are similar over this period. Natural emissions are as given in Stevenson et al. (2004). For analysis, a chemical tropopause is defined using the 150 ppbv ozone isopleth, the definition used by Prather et al. (2001).

3. Results

The main region of deep convection, with strong up-draughts that reach the tropopause, occurs in the tropics mainly along the inter-tropical convergence zone (ITCZ) (Fig. 1). Shallower convection that extends up to the mid-troposphere also occurs in the tropics and in mid-latitudes typically associated with frontal activity (Fig. 1).

3.1. Influence of convection over tropical land and ocean

Figure 2 depicts annual zonal mean tropical ozone and NO_x concentrations for tropical land and ocean regions separately (Fig. 2a–d) for the control experiment (i.e. normal convective mixing) and the impact of switching on convective mixing (Fig. 2e–h). Both species are generally higher over land, where the main NO_x surface and UT lightning

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sources are located. The ozone lifetime and production efficiency increase with height – these factors, in conjunction with the stratospheric source of ozone – produce the ozone gradient from the surface (25–35 ppb over land, 10–25 ppb over oceans) to the UT (40–60 ppb over land, 30–55 ppb over oceans) (Fig. 2a–b) . The vertical distribution of sources gives NO_x over land its typical 'C' shaped profile (Fig. 2c–d; above 100 ppt in the LT and UT). Over oceans, most of the UT NO_x arises from advection of UT land lightning NO_x emissions (with a small contribution from lightning over the oceans, Sect. 2) and the NO_x lifetime controls the vertical profile (5–20 ppt at the surface, 70–100 ppt in the UT). The shorter NO_x lifetime compared to ozone results in a greater NO_x land-sea contrast relative to ozone.

Both land and ocean regions show large decreases in UT O_3 (10–30 ppb) and NO_x (100–300 ppt over land; 50–200 ppt over the ocean) due to convection (Fig. 2e–h). LT O_3 and NO_x also decrease over land regions (1–3 ppb and 10–100 ppt respectively, Fig. 2e, g), but show divergent behaviour over the ocean, where O_3 increases slightly (0–3 ppb), whilst NO_x decreases slightly (5–10 ppt), (Fig. 2f, h). Conversely, MT O_3 and NO_x generally increase over land (by 0–5 ppb and 2–50 ppt, Fig. 2e, g), and over the oceans north of 10° S. Over the remote oceans, south of 10° S, MT O_3 decreases (0–5 ppb) and MT NO_x increases slightly (0–5 ppt), (Fig. 2f, h).

Figure 3 displays vertical changes in tropical ozone chemical production and destruction when convective mixing is switched on. Since NO is the main species involved in O_3 production (through the $NO+HO_2$ reaction), the changes in ozone chemical production with convective mixing are generally similar to that of NO_x changes (compare Fig. 3a–b, Fig. 2g–h). However there are some differences. In particular, UT O_3 production increases over land, whereas NO_x decreases. O_3 chemical destruction is primarily determined by water vapour concentrations and the O_3 vertical distribution (mainly through the $H_2O+O(^1D)$ reaction). As water vapour concentrations do not change between experiments, the changes in O_3 chemical destruction are similar to the changes in ozone (compare Fig. 3c–d, Fig. 2e–f), although again there are some differences. For example, UT O_3 chemical destruction increases slightly over equatorial land and

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in some parts of the MT over ocean south of 10° S, despite decreases of O_3 in these regions.

The effects of convection on NO_x can partly be understood in terms of a flattening of the 'C' shaped profile over land, and advection of this effect over the oceans. This occurs as UT NO_x from lightning emissions is displaced to lower altitudes, and surface NO_x emissions are lifted to higher altitudes, which results in higher NO_x concentrations in the MT (Fig. 2g–h). However, the UT NO_x decreases over land are larger by an order of magnitude, suggesting that mixing of NO_x is not the only factor influencing NO_x concentrations (Fig. 2g–h). As discussed in Sect. 1, convection also affects non-methane hydrocarbons (NMHCs) including isoprene, lifting these gases and their degradation products into the UT (Collins et al., 1999). Isoprene has a very short lifetime (<1 h; Seinfeld and Pandis, 1997), and is emitted in substantial quantities from tropical vegetation (Guenther et al., 1995; Sanderson et al., 2003b). The natural source of isoprene is much larger than the mainly anthropogenic sources of other NMHCs in the tropics. Here, the prevalence of isoprene, together with its short lifetime, mean that its distribution is strongly affected by convection. Figure 4a shows that convection increases MT and UT isoprene at the expense of surface; these changes are largest over equatorial land. Convective lifting of isoprene brings the peroxy acetyl radical (CH_3COO_2), an isoprene degradation product, into contact with lightning NO_x. This leads to significant PAN formation in the cold UT over equatorial land at the expense of NO_x (Fig. 4c, Fig. 2g), and this effect is advected across the oceans (Fig. 4d). PAN acts as a reservoir for NO_x, and its breakdown to release stored NO_x is strongly temperature dependent – in the cold UT PAN is relatively stable and has a lifetime of the order of months. Thus the impact of convection on NO_x is through convective transport of NO_x itself in combination with isoprene-PAN-NO_x chemistry in the UT.

For O_3, as discussed above for NO_x, upward transport of LT air over land and ocean displaces UT ozone-rich air, which subsides downwards. Over land, similar to NO_x, O_3 is lifted away from its source region and the MT has higher O_3 concentrations. Therefore vertical mixing of the ozone profile itself as well as changes in NO_x distribution are

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responsible for the changes in the O_3 distribution over polluted land. However, changes in UT NO_x over land contrast with changes in UT ozone production over land. Despite a large reduction in UT NO_x (Fig. 2g) with convective mixing, UT ozone production increases (Fig. 3a). The role of isoprene is again important here, as its oxidation generates peroxy radicals (HO_2 and RO_2), which are required for O_3 production. Ozone production in the tropical UT tends to fall due to the reduction in UT NO_x, but this effect is more than offset by an increase in UT HO_2 produced from isoprene (Fig, 4e, f). As HO_2 also destroys O_3, the HO_2 increases explain the small equatorial land UT ozone destruction increases (Fig. 3c). Despite an overall increase in net chemical production in the UT, ozone decreases. This indicates that vertical transport of ozone itself is more important than changes in chemistry in determining the outcome of convective mixing in the UT. Over the remote southern oceans, MT O_3 decreases and surface O_3 increases in contrast to NO_x and ozone production changes. This also implies that over remote tropical locations vertical transport of ozone itself is more important than changes in NO_x chemistry.

Convection therefore influences modelled O_3 distributions by a combination of vertical transport of O_3, as well as by affecting the vertical distribution of its precursors, especially NO_x and HO_2 and the resultant chemical production of O_3. Vertical transport appears to be the dominant process in clean air, over the remote oceans in the MT and LT, and in polluted land regions in the UT. Elsewhere both convective transport and chemistry changes contribute significantly to the overall impact of convection on the O_3 distribution.

To assess the influence of vertical transport on ozone distribution the relationship between the ozone gradient in the convection off experiment and the change in TC ozone due to convection was examined over the tropics (Fig. 5). A strong correlation was found (r=0.7). For each 10 ppb steepening in the ozone gradient between the UT (~150 hPa) and surface, convection reduces TC ozone by 1.5 DU (Fig. 5). The relationship is stronger if the change in UT ozone alone is considered (r=0.9, not shown). This also suggests that vertical transport of ozone plays a major role in the resultant

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O_3 distribution after convection, particularly in the UT.

3.2. Influence of convection in the extra-tropics

Deep convective mixing in the tropics has a global effect on O_3 distributions as a result of hemispheric transport (Fig. 6a). UT ozone not only decreases in the tropics but also decreases by similar amounts in the midlatitudes and polar regions (10–30 ppb). Since convection is relatively shallow and less intense in the midlatitudes (Fig. 1) compared to the tropics, the extra-tropical O_3 decreases can be inferred to mainly emanate from the tropical UT reduction, whereby there is less tropical UT ozone available to be transported polewards. Slightly lower O_3 stratospheric influx (Table 1) may also contribute to lower extra-tropical UT O_3. Convective mixing also influences NO_x distributions well outside the tropics (Fig. 6b). The changes are highly skewed towards the northern hemisphere reflecting the large surface NO_x emissions in this region. Tropical UT NO_x decreases (100–200 ppt) are transported towards the midlatitudes; however the strong negative anomaly changes to a positive anomaly polewards of about 45°, especially in the Northern Hemisphere. This reflects the shorter NO_x lifetime compared to O_3 and the larger hemispheric differences in the levels of NO_x.

In northern midlatitudes, convection generally reduces surface O_3 and NO_x (except for O_3 around 60° N), mainly reflecting enhanced venting of polluted continental NO_x and ozone-rich air by shallow convection (Fig. 6a, b). The increase of O_3 accompanied by a large decrease of NO_x (100–200 ppt) around 60° N is the titration effect. This effect occurs under very high NO_x levels predominantly in winter (low UV levels for NO_2 photodestruction) whereby NO reacts with ozone to form NO_2. Thus with convective mixing, surface air low in ozone and high in NO_x is replaced by air with higher ozone and lower NO_x concentrations. In the polar regions, large-scale subsidence of UT air, that is less rich in ozone due to hemispheric transport, results in lower surface ozone. At northern polar latitudes, where winter NO_x levels are high, weak mixing lifts NO_x upwards from the LT and MT. This effect combined with mid-latitudinal anomaly transport generates negative LT/MT NO_x anomalies in the northern pole (Fig. 6b). In

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the southern midlatitudes as in the southern tropics, where precursor emissions are lesser, surface O_3 increases and NO_x decreases slightly.

MT O_3 increases in the northern mid-latitudes up to around 40° N, as in the northern tropics, but decreases elsewhere in the midlatitudes and polar regions as large scale subsidence of large UT anomalies dominates the vertical O_3 distribution (Fig. 6a). Shallow convection produces strong MT NO_x increases (10–50 ppt) in the northern midlatitudes at the expense of the surface (Fig. 6b). These mid-latitudinal MT NO_x increases are transported to the remote troposphere.

In the column average, convective overturning leads to TC O_3 decreases almost everywhere (Fig. 6c). Decreases are largest (up to 8 DU) over the clean southern ocean regions, stemming from hemispheric transport of lesser amounts of tropical UT O_3. Over equatorial land regions, where MT O_3 increases are greatest, TC O_3 decreases are smallest (0–2 DU) and in small areas above strong NO_x source regions (e.g., S.E. Asia) TC O_3 increases slightly (0–1 DU). Tropospheric column-average NO_x also decreases (strongly) over tropical land regions (50–100 ppt, Fig. 6d) and outflow oceanic regions. The northern mid-latitudes show increases over land and Pacific regions with the largest changes (10–50 pptv, Fig. 6d) over western Eurasia, reflecting upward mixing in shallow convective regions.

Overall, for O_3 deep convective mixing in the tropics is the most important driver of global changes in O_3, whereby tropical changes are propagated polewards. However, deep convection in the tropics and mid-latitude shallow convection are both important drivers of global NO_x changes.

3.3. Influence of convection on the global O_3 budget

Global budgets for O_3 with and without convective mixing are calculated in Table 1. Chemical production increases globally by 3.8%, mainly due to tropical and northern mid-latitudinal MT NO_x increases (Figs. 6b, 3a). Global chemical destruction also increases (by 3.0%) as a result of MT ozone increases (Fig. 6a, 3c). Changes in chemical production and destruction are small outside the tropics and northern mid-latitudes and

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tropics, respectively (not shown). Because net chemical production is the small residual of two large budget terms it has a relatively large increase of 11.3%. Dry deposition (which increases with surface ozone) globally increases by 3.5%. Stratospheric ozone influx decreases by 5.6% with convective mixing. Although the relative changes in dry deposition and stratospheric influx are modest, the absolute changes are small. Despite increased global net chemical production due to tropical MT increases, the global ozone burden decreases by 14.8%, mainly due to UT decreases outside of the tropics. This illustrates the very strong role of hemispheric transport in modifying ozone concentrations in areas where net chemical production of ozone is low. Likewise, the ozone lifetime decreases globally from 22.4 to 18.5 days (17.3%). The global NO_x burden also decreases globally by 22.3% and PAN increases by a similar amount (not shown).

4. Discussion

Lelieveld and Crutzen (1994) calculate a 20% decrease in the global ozone burden due to convective mixing, using a global model with no NMHC chemistry. In their model, they found that the effects of mixing O_3 over-rode any chemical effects due to mixing of O_3 precursors. More recently, Lawrence et al. (2003), using a global model with detailed NMHC chemistry (similar to that used in this study), found a global ozone burden increase of 12% from convective mixing. In their study, Lawrence et al. (2003) found the effects of changes in precursor chemistry due to mixing (in particular lifting of surface NO_x emissions) to outweigh the effect of vertical mixing of O_3 itself. In our study, O_3 decreases by 15% due to convective mixing, and the effect of O_3 vertical transport outweighs the effect of precursor mixing changes (Table 1; Fig. 6a). One similarity between the Lawrence et al. (2003) and this study is that MT O_3 increases due to mixing of precursor NO_x emissions. Also, in the Lawrence et al. (2003) study, the changes in tropical UT O_3 are small, thus the effect of hemispheric transport will be less apparent than in this study.

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Lawrence et al. (2003) also report ozone budgets for their simulations. In common with this study, they find that switching on convection results in an increase in production of O_3, although they find a larger percentage increase (Table 1). Another similarity is that convection reduces the ozone lifetime; however the impact on lifetime is much stronger in our study. As a consequence, the tropospheric ozone burden falls in our study, whereas Lawrence et al. (2003) find an increase. The reduction in lifetime in our results arises mainly due to a reduction in UT O_3 concentrations. In our model these UT O_3 reductions are driven mainly by the vertical mixing of ozone (Fig. 5), as they occur despite increases in land UT chemical production (Fig. 3a). An interesting observation is that land UT chemical production increases despite large reductions in NO_x (Figs. 3a, 2g) – this indicates that HO_x increases (Fig. 4e, f) outweigh the NO_x decreases (Fig. g, h). In the Lawrence et al. (2003) study UT O_3 increases, which suggests that UT O_3 production increases are greater than in our study.

A comparison of the emissions used in the two studies shows that NO surface, aircraft and ship emissions are similar but lightning NO_x emissions are higher by 2.1 TgN/yr (~40%) in our study; NMHCs generally are also higher by 5–20 Tg/yr, and isoprene is higher by ~225 Tg/yr (~65%) compared to the MATCH model (von Kuhlmann et al., 2003). The higher isoprene and lightning NO_x emissions in this study may result in greater amounts of PAN formation and consequently a larger UT NO_x reduction, although higher isoprene also suggests higher UT HO_x. Emissions of both lightning NO_x and isoprene from vegetation carry high levels of uncertainty, and it is unclear whether the higher or lower levels of emissions more closely resemble the real world. Both these natural sources are sensitive to climate, and thus likely to respond to changes in climate (Stevenson et al., 2005).

In addition, there may be significant model differences in these two studies in the isoprene degradation schemes which affects the amount of NO_x converted to PAN and amount of HO_x produced, as well as possible differences in locations of lightning NO_x emissions. The isoprene-lightning NO_x interaction in this study leads to significant PAN formation, locking up UT NO_x, and reducing the ability of the UT to produce

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O_3. This mechanism may be much less important in the MATCH-MPIC model used by Lawrence et al. (2003), resulting in larger increases in O_3 production with convection. In STOCHEM, this mechanism limits the effectiveness of convection in promoting chemical production of UT ozone, and consequently the impact of vertical O_3 mixing is the process of overriding importance. In a model sensitivity study, von Kuhlmann et al. (2004) found that isoprene and lightning emissions magnitudes, as well as the details of isoprene degradation schemes, all had important influences on tropical ozone. Differences in isoprene and lightning emissions magnitudes and locations as well as different isoprene chemical schemes may well contribute to differences in ozone sensitivity to convection. Further sensitivity studies are needed to clarify how different emissions and isoprene schemes influence tropospheric O_3 response to convective mixing. If the isoprene emissions or isoprene-lightning interactions are too strong in the STOCHEM model, this may explain its tendency to underestimate O_3 in some parts of the free troposphere; although model estimates are within the uncertainty range of the observations (Stevenson et al., 2004; Dentener et al., 2004). Further validation work is also needed in this area.

Vertical resolution and upper boundary conditions for O_3, as discussed by Lawrence et al. (2003) could be another source of different responses with convective mixing. However, although the vertical grid resolution is lower in STOCHEM than in the MATCH-MPIC model the Lagrangian sampling in STOCHEM is at roughly the same resolution (50,000 air parcels compared to $64\times32\times20=40\,960$ grid cells). Differences in upper boundary conditions may also have some influence.

Finally, differences in the convection schemes themselves (Prather et al., 2001) may be an important, if not the most important cause, of the different effects of convective mixing on the O_3 burden in the two studies. In particular, differences in the efficiency of vertical transport of NO_x and O_3 out of the boundary layer (Beekman et al., 2003), as well as differences in representing the relevant convective processes (e.g. updraughts, entrainment/detrainment, mass-balance subsidence) may be crucial.

5. Conclusions

Model experiments have been performed to examine the role of deep convective mixing in determining the distributions of tropospheric O_3 and its precursors. In contrast to results from an earlier study with a model of similar chemical complexity (Lawrence et al., 2003), convective mixing in this study reduces the O_3 burden, due to vertical O_3 redistribution and associated lifetime changes. Convection of ozone precursors has several competing effects on O_3 chemical production. Over tropical land, convection lofts surface sources of NO_x and NMHCs in particular isoprene, tending to increase their concentrations in the MT and UT at the expense of the LT. However, the subsidence associated with convection mixes downwards UT lightning NO_x. UT NO_x is also converted to PAN by the introduction of peroxy acetyl radicals, an oxidation product of isoprene. The overall effect is a reduction in UT NO_x, together with an increase in UT HO_x; the net effect is a small increase in ozone production. However, this increase in O_3 production is more than counteracted by the effects of convective mixing of ozone itself, and UT O_3 reduces. The features generated over the tropical land are advected over the tropical oceans, although over the remote oceans, the impact of local vertical mixing becomes more dominant. The changes in tropical UT O_3 are transported polewards resulting in a 15% decrease in the global ozone burden despite a 4% increase in chemical production. This apparent contradiction arises because the mean tropospheric ozone lifetime reduces substantially (by 17%); this is mainly because less O_3 resides in the UT, where its lifetime is longest. Differences between this study and that of Lawrence et al. (2003) arise from a combination of variations in chemistry and convection schemes, with possibly slightly differing treatments of lightning NO_x and vegetation isoprene emissions proving important. With such divergent results from two apparently similar models (in terms of resolution and complexity), and the importance of deep convective mixing processes in altering the state of the atmosphere on interannual and longer timescales, further studies with other models are needed to constrain this range of uncertainty.

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Acknowledgements. This work was supported by the NERC UTLS thematic programme (NER/T/S/2000/01041). D. S. Stevenson was supported by NERC/Environment Agency fellowship funding (P4-F02, NER/J/S/2000/00840). The UGAMP project is thanked for computing resources to run the coupled HadAM3-STOCHEM model. Thanks to J. Pyle and G. Zeng for useful discussions.

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Table 1. 20-year average O_3 budget changes (control – convection off).

Budget term ($Tg\ (O_3)yr^{-1}$)	20-year average control (convection on)	20-year average convection off	% change with convective mixing	Lawrence et al. (2003) % change	Lelieveld and Crutzen (1994) % change
O_3 chemical production	4757	4582	+3.8	+16.7	+14
O_3 chemical destruction	4236	4114	+3.0	+15.0	+22
O_3 net chemical production	521	468	+11.3	+81.8	−25
O_3 dry deposition	881	851	+3.5	+7.0	+15
O_3 stratospheric influx	361	383	−5.6	−2.1	
O_3 burden ($Tg\ O_3$)	263	309	−14.8	+11.9	−20
O_3 lifetime (days)	18.5	22.4	−17.3	−2.5	
NO_x burden ($Tg\ N$)	0.156	0.200	−22.3	+14	−30

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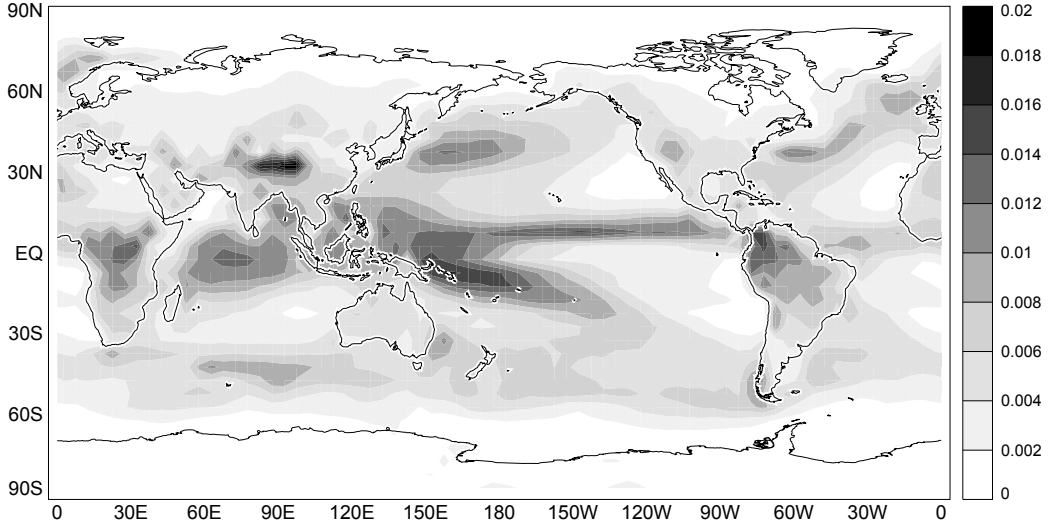

Fig. 1. 20-year average convective updraught flux (kgs^{-1}) at 600 hPa (MT) from the control experiment. Generally only in the tropics do updraught fluxes reach 150 hPa (not shown).

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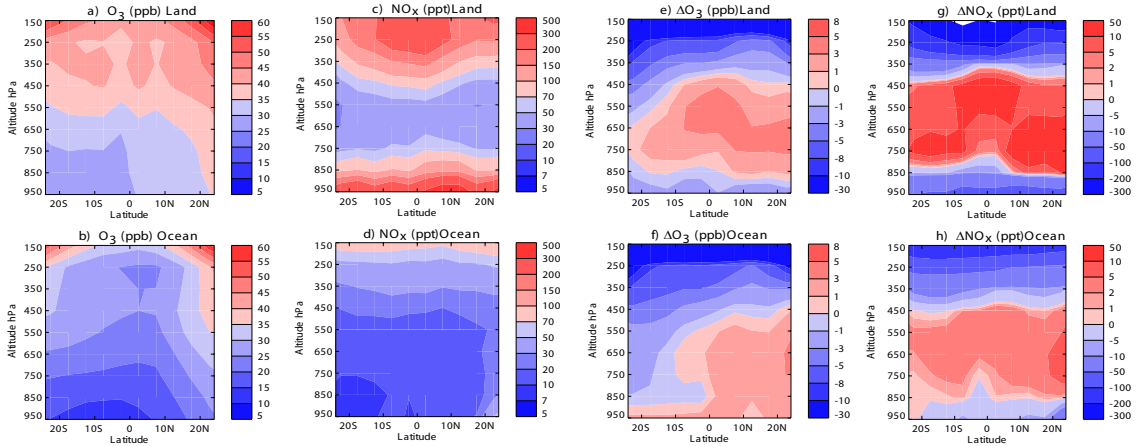

Fig. 2. 20-year average zonal mean tropical land and ocean **(a, b)** O_3 (ppb) and **(c, d)** NO_x (ppt) for the control experiment and 20-year average zonal mean tropical land and ocean **(e, f)** O_3 and **(g, h)** NO_x differences control-convection off.

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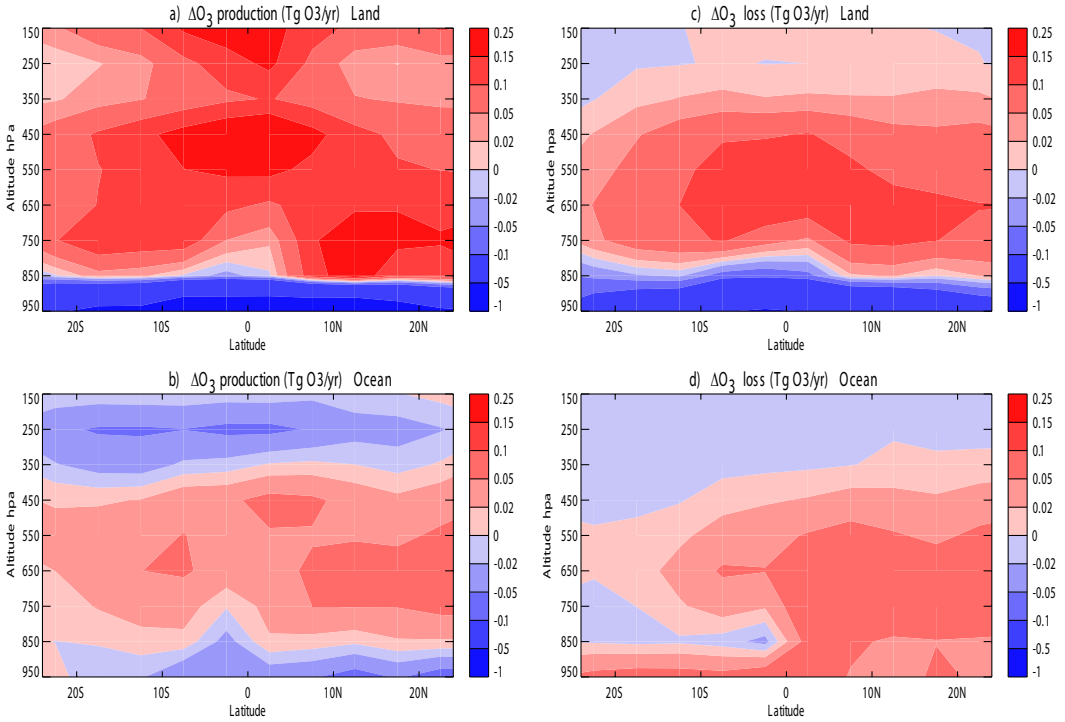

Fig. 3. 20-year average zonal mean tropical land and ocean ozone **(a, b)** production and **(c, d)** loss differences (Tg O_3) control-convection off.

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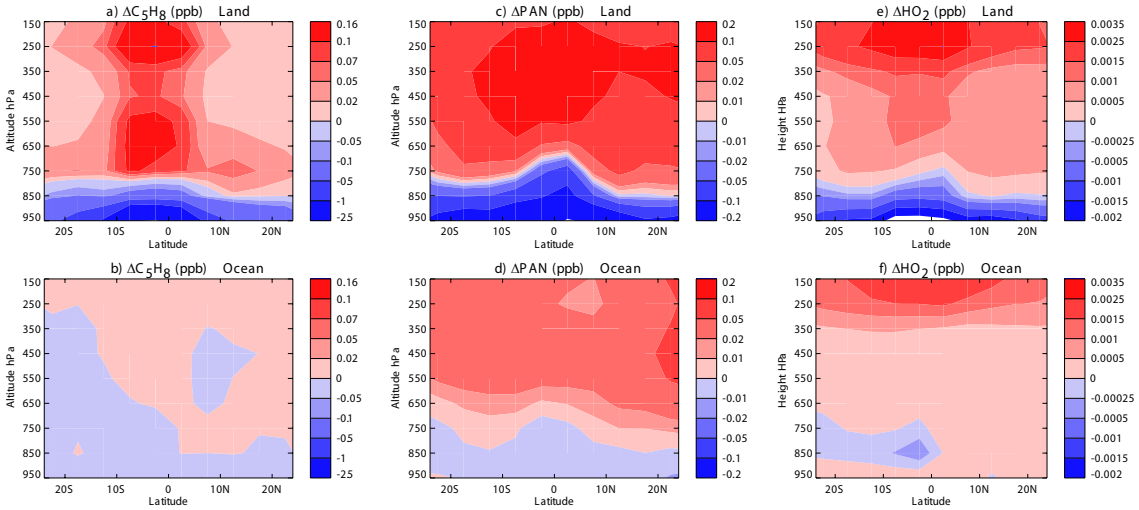

Fig. 4. 20-year average zonal mean tropical land and ocean **(a, b)** isoprene, **(c, d)** PAN and **(e, f)** HO_2 differences (ppb) control-convection off.

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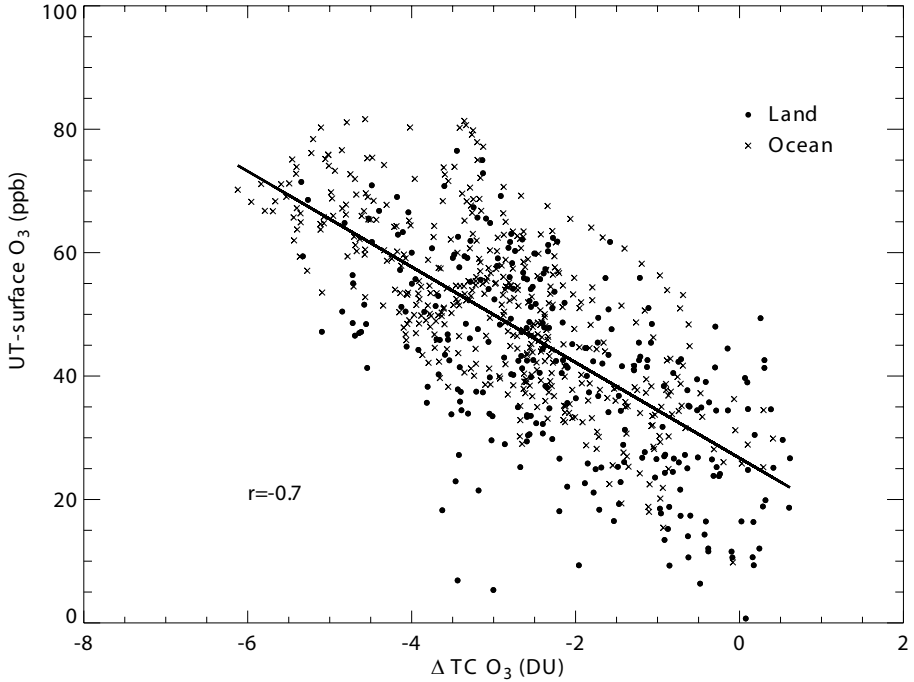

Fig. 5. 20-year average change in TC O_3 (DU) with convective mixing (control-convection off) vs. 20-year average UT-surface O_3 (ppb) (convection off experiment) for combined tropical land and ocean grid boxes.

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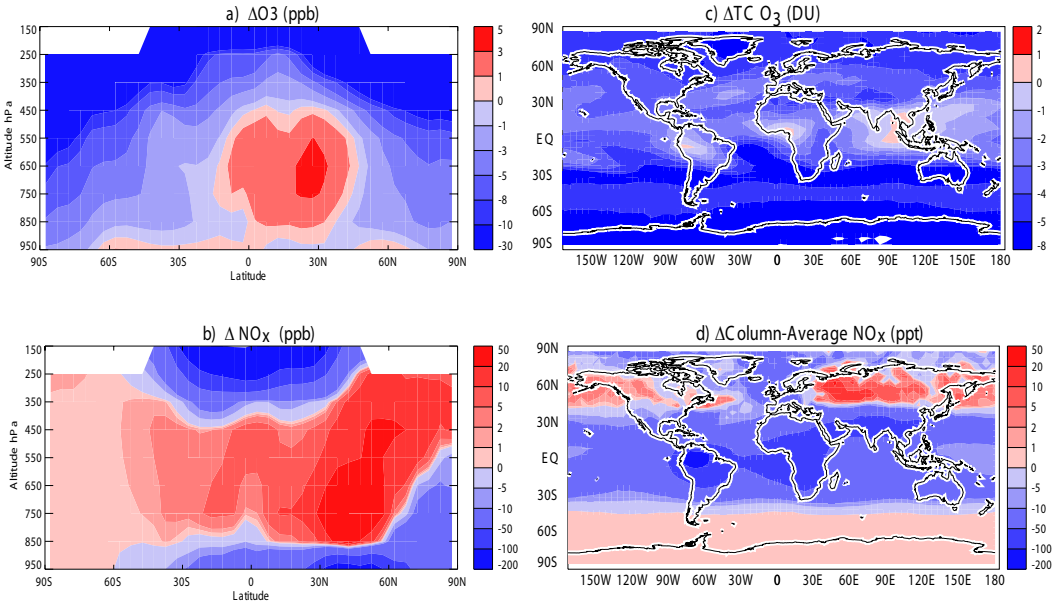

Fig. 6. 20-year average global zonal mean change in **(a)** O_3 (ppb) and **(b)** NO_x (ppt) (control – convection off), and 20-year global average **(c)** TC O_3 change (DU) **(d)** column-average NO_x change (ppt) (control – convection off).

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