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The CO_2 inhibition of terrestrial isoprene emission significantly affects future ozone projections

P. J. Young[1,2,*], **A. Arneth**[3,**], **G. Schurgers**[3], **G. Zeng**[1,2,***], **and J. A. Pyle**[1,2]

[1]Centre for Atmospheric Science, Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, UK
[2]National Centre for Atmospheric Science, UK
[3]Department of Physical Geography and Ecosystems Analysis, Centre for GeoBiosphere Science, Lund University, Sölvegatan, Lund, Sweden
[*]now at: NOAA Earth System Research Laboratory, Boulder, Colorado, USA
[**]currently at: Physics Department, Helsinki University, Helsinki, Finland
[***]now at: National Institute of Water and Atmospheric Research, Lauder, New Zealand

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Abstract. Simulations of future tropospheric composition often include substantial increases in biogenic isoprene emissions arising from the Arrhenius-like leaf emission response and warmer surface temperatures, and from enhanced vegetation productivity in response to temperature and atmospheric CO_2 concentration. However, a number of recent laboratory and field data have suggested a direct inhibition of leaf isoprene production by increasing atmospheric CO_2 concentration, notwithstanding isoprene being produced from precursor molecules that include some of the primary products of carbon assimilation. The cellular mechanism that underlies the decoupling of leaf photosynthesis and isoprene production still awaits a full explanation but accounting for this observation in a dynamic vegetation model that contains a semi-mechanistic treatment of isoprene emissions has been shown to change future global isoprene emission estimates notably. Here we use these estimates in conjunction with a chemistry-climate model to compare the effects of isoprene simulations without and with a direct CO_2-inhibition on late 21st century O_3 and OH levels. The impact on surface O_3 was significant. Including the CO_2-inhibition of isoprene resulted in opposing responses in polluted (O_3 decreases of up to 10 ppbv) vs. less polluted (O_3 increases of up to 10 ppbv) source regions, due to isoprene nitrate and peroxy acetyl nitrate (PAN) chemistry. OH concentration increased with relatively lower future isoprene emissions, decreasing methane lifetime by ∼7 months (6.6%). Our simulations underline the large uncertainties in future chemistry and climate studies due to biogenic emission patterns and emphasize the problems of using globally averaged climate metrics (such as global radiative forcing) to quantify the atmospheric impact of reactive, heterogeneously distributed substances.

Correspondence to: P. J. Young
(paul.j.young@noaa.gov)

1 Introduction

Understanding how the chemical composition of the troposphere will evolve over the coming century is of central importance for climate change projections and for the development of air quality policies. Climate model integrations need to consider possible changes to anthropogenic and biogenic emission patterns, as well as the response of atmospheric chemistry to changes in temperature, humidity and atmospheric transport. Whilst there are commonly applied projections of future anthropogenic emissions (e.g. Nakicenovic et al., 2000; Dentener et al., 2005), atmospheric chemistry modellers have to estimate future biogenic emissions in a variety of ways, using off/on-line emissions models (e.g. Sanderson et al., 2003; Hauglustaine et al., 2005) or by scaling present day emissions (e.g. Zeng et al., 2008). In the case of biogenic isoprene (C_5H_8), a highly reactive compound (Atkinson and Arey, 2003) and the non-methane volatile organic compound (VOC) with the greatest global emission flux (Guenther et al., 1995), models project large increases in the emission by the 2090s (27–70% relative to present day emissions of ∼450–550 Tg C a^{-1}; Sanderson et al., 2003; Lathière et al., 2005; Wiedinmyer et al., 2006; Arneth et al., 2008), due to the combined effect of higher

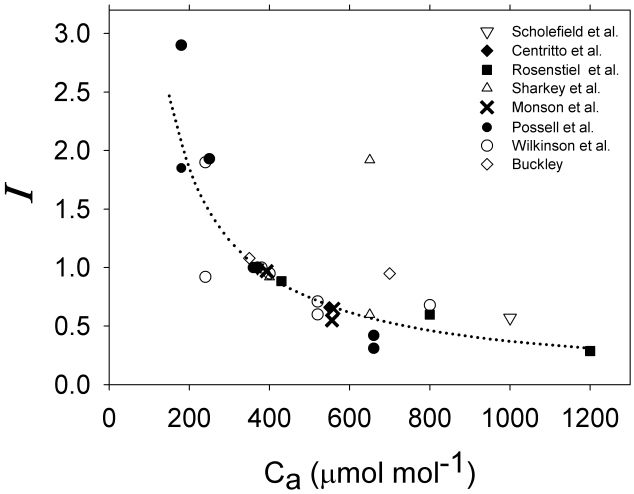

Fig. 1. Field and laboratory observations of leaf isoprene emissions from plants grown in a range of CO_2 concentrations (C_a). Data are normalised to be unity at a CO_2 concentration of 370 ppmv. The dotted line is the simple representation used in Arneth et al. (2007a): I (normalised)=$C_{i\text{-}370}/C_i$, with C_i being the leaf internal CO_2 concentration at non-water-stressed conditions (0.7 C_a), and $C_{i\text{-}370}$=C_i at 370 ppmv. Figure adopted from Possell et al. (2005) and Arneth et al. (2007a); data are from Sharkey et al. (1991), Buckley (2001), Rosenstiel et al. (2003), Centritto et al. (2004), Scholefield et al. (2004), Possell et al. (2004, 2005), Monson et al. (2007) and Wilkinson et al. (2009; their Figs. 1, 2a and c).

surface temperatures, strongly temperature-dependent emissions algorithms (Guenther et al., 1995) and more productive vegetation. However, recent laboratory and field data suggest that higher CO_2 concentrations inhibit isoprene emission (e.g. Rosenstiel et al., 2003; Possell et al., 2005; an overview is provided in Arneth et al., 2007a; see also Fig. 1).

These observations are puzzling: they indicate a decoupling of isoprene production from photosynthesis, although one of the chief isoprene precursors (glyceraldehyde-3-phosphate, G3P) is provided by the Calvin Cycle and chemical reduction of the precursors to isoprene is achieved with energy provided from photosynthetic electron transport rate (Niinemets et al., 1999). One hypothesis argues for a changed cell-internal competition for a second isoprene precursor molecule, pyruvate, as a possible metabolic control (Rosenstiel et al., 2003). Phosphoenolpyruvate, the pyruvate precursor, is directed away from the chloroplast (the location of isoprene synthesis) towards other reaction pathways, which are stimulated by increasing CO_2 concentration. In future climate change scenarios, including the declining leaf isoprene emission to increasing CO_2 concentration counters the stimulation of emissions by the warmer temperatures that accompany the CO_2 increase. Globally, emissions have been found to remain relatively unaltered over the 21st century as these two responses tend to balance each other (Arneth et al., 2007b).

This CO_2-isoprene effect, thus far omitted from chemistry/climate modelling studies, has possible ramifications for projected tropospheric ozone and OH levels (and hence methane lifetime), as both are sensitive to the magnitude and spatial distribution of isoprene emission (e.g. Wang and Shallcross, 2000; Sanderson et al., 2003; Fiore et al., 2005; Hauglustaine et al., 2005; Wu et al., 2007; Zeng et al., 2008). Here, we use a chemistry/climate model with isoprene emissions calculated from a recently developed vegetation-isoprene emission model (Arneth et al., 2007a) to investigate the impact of this isoprene/CO_2 effect on tropospheric composition projections for the late 21st century. Further discussion on the impact of isoprene chemistry in the model and the interaction of isoprene and anthropogenic emission changes can be found in Young et al., 2007).

2 Model descriptions

2.1 LPJ-GUESS and isoprene emission

Isoprene emissions were calculated using the dynamic global vegetation modelling framework LPJ-GUESS, used here in global ("DGVM") mode (Smith et al., 2001; Sitch et al., 2003), with a mechanistic leaf isoprene model adapted from Niinemets et al. (1999). Photosynthesis is calculated in a process-based way, adopted from the well established model developed by Farquhar and colleagues (Farquhar et al., 1980; Collatz et al., 1991; Haxeltine and Prentice, 1996). LPJ-GUESS accounts for stimulation of NPP to increasing CO_2 concentration, giving a similar response to the observations from the Free-Air Carbon Enrichment (FACE) experiments (Hickler et al., 2008).

Vegetation isoprene emission calculations combine a mechanistic representation in response to light and temperature that arises from the metabolic pathway of isoprene being linked leaf photosynthesis, while the long-term CO_2 inhibition follows an empirical parameterisation reflecting the as-yet not fully understood cellular process. Connecting photosynthesis and isoprene production ensures that global vegetation carbon cycle and total isoprene calculations and isoprene emissions are performed in a coherent modelling framework that also accounts for effects of vegetation productivity to increasing CO_2 (Hickler et al., 2008). Leaf isoprene production is calculated from photosynthetic electron transport rate, which provides the energy that is required to chemically reduce the C_3-isoprene precursors along the DOXP (1-Deoxyxylulose 5-phosphate) pathway (Lichtenthaler, 1999; Niinemets et al., 1999). One of the two initial precursors (G3P) is the initial product of photosynthetic carbon fixation; the second (pyruvate) is synthesized in the cytosol and transported (as phosphoenolpyruvate) across the chloroplast membrane. As isoprene amounts to only few percent of assimilation in terms of leaf carbon loss (Guenther, 2002) the model assumes that, over periods from minutes to few days,

carbon supply is non-limiting for isoprene production. It has been demonstrated that the short-term temperature and light response, as well as today's global emission patterns, are comparable with other isoprene model estimates (Arneth et al., 2007a, b; Arneth et al., 2008).

Over longer periods, for instance past or future climate change scenarios, the model includes a representation of the observed decreasing leaf emissions as CO_2 concentration increases (and vice versa). Arneth et al. (2007a) showed that the calculated change in leaf internal CO_2 concentration (C_i), when expressed inversely proportional to the internal CO_2 concentration at 370 ppmv (under non-water stressed conditions), successfully reproduced the leaf isoprene response observed in most experimental studies in which plants were grown in a range of CO_2 environments (Possell et al., 2005). Figure 1 illustrates the relationship described by Arneth et al. (2007a), updated to include a larger range of field and laboratory studies. Whilst the cellular mechanism behind the isoprene inhibition is not yet fully understood, the simple expression as a function of changing C_i conceptually fits well with the hypothesis of changing competition for pyruvate as leaf internal CO_2 concentration changes (Rosenstiel et al., 2003). Nonetheless, while most of the studies follow the suggested response it is clear that the sensitivity of the isoprene-CO_2 response may vary between experimental treatments or between plant species, most visibly in a study of *Quercus rubra* where emissions actually increased with CO_2 (Sharkey et al., 1991).

Recently, Wilkinson et al. (2009) proposed a sigmoidal, Hill-reaction type isoprene-CO_2 response, that was based on isoprene measurements taken in parallel with short-term CO_2-response curves at young aspen trees grown in four different CO_2 concentrations (between 400 and 1200 ppmv). The parameterisation of this algorithm differed between the CO_2 treatments, as the sensitivity of the short-term CO_2-isoprene response varied between growth environments. By pooling the normalised isoprene aspen data, the authors proposed a common parameterisation to apply the observed short-term Hill-response also to the long-term isoprene-CO_2 response. For above-ambient CO_2 concentration this algorithm projects a mildly lower inhibitory effect compared to the empirical fit and C_i-dependent relationship as used by Possell et al. (2005) and Arneth et al. (2007a) respectively. This small difference is unlikely to change the results in our study substantially. However, the study draws attention to the uncertainty of the below-ambient isoprene-CO_2 response. Wilkinson et al. (2009) found a large increase in leaf isoprene emissions for Eucalypt grown at 240 ppmv CO_2, but not for Sweetgum (see also Fig. 1). Clearly, a larger number of studies are needed to establish the CO_2-response more firmly. But, based on our current knowledge, when the CO_2-inhibition of isoprene emission is included in models, it has the potential to counter the stimulating effects of higher temperature and vegetation CO_2 fertilization in a range of climate and CO_2 scenarios (Arneth et al., 2007b).

Studies on isoprene-CO_2 interactions have been performed on a limited number of species, mostly from temperate growth environments. Initial experimental evidence obtained on Acacia indicates that the overall trend between three CO_2 treatments (sub-ambient, ambient and elevated) observed by Possell et al. (2005) may also hold for tropical tree species; but as the experiment is still ongoing these observations must be considered to be preliminary (M. Possell, personal communication, 2009). Incidentally, since monoterpene production occurs along the same chloroplastic pathway it is likely that a similar response takes place. Whilst the effects of growth CO_2 concentration on monoterpene emissions have not been the focus of intensive study, an inhibition of monoterpene emissions at elevated CO_2 has been observed (Loreto et al., 2001; Rapparini et al., 2004).

2.2 UM_CAM chemistry-climate model

Chemistry-climate integrations were conducted using the latest version of UM_CAM (fully described by Zeng et al., 2008), which has been used previously for both contemporary (Zeng and Pyle, 2005) and future (Zeng and Pyle, 2003) chemistry-climate simulations. Briefly, the climate model is based on the atmosphere-only version of the UK Met Office Unified Model (v4.5, HadAM3, Pope et al., 2000), using prescribed sea-surface temperatures (SSTs) and sea-ice distribution. The horizontal resolution is $2.5° \times 3.75°$ (latitude/longitude) and 19 hybrid sigma-pressure vertical coordinates extend from the surface to 4.6 hPa. The radiation code (Edwards and Slingo, 1996) includes long and short wave absorptions by water vapour, CO_2 and O_3, with additional absorption by methane, nitrous oxide, CFC-11 and CFC-12 in the long wave only. Note, we used an ozone climatology in this experiment (Li and Shine, 1995) and concentrations of radiatively active chemical species as calculated by UM_CAM were not used in the radiation code.

Photolysis, wet and dry deposition, and the non-isoprene part of the chemical mechanism are similar to the offline chemical transport model TOMCAT (Law et al., 1998), including a full description of inorganic O_x-NO_x-HO_x chemistry and near-explicit oxidation mechanisms for methane, ethane, propane and acetone. For isoprene oxidation we use the Mainz isoprene mechanism (MIM) (Pöschl et al., 2001), which is also implemented in the MATCH model (von Kuhlmann et al., 2003) and is of comparable complexity to isoprene oxidation schemes used in other global models (Folberth et al., 2006; Horowitz et al., 2007).

The role of isoprene in reactive-nitrogen (NO_y) chemistry has received particular attention in atmospheric chemistry modelling studies (e.g. Horowitz et al., 1998; von Kuhlmann et al., 2004; Horowitz et al., 2007) and it is therefore important to clarify the parameterisations of NO_y chemistry used in UM_CAM. In the MIM a single lumped species (ISON) is used to represent both stabilised hydroxy alkyl nitrates ("isoprene nitrates"), a minor product from the reaction of

Table 1. Simulation emission fluxes and tropospheric ozone budget terms, PAN burden, OH concentration and methane lifetime[a].

	BASE	noCO2	wCO2
NO_x	48.8	124.1	124.1
CO	1077	2327	2327
CH_4	1760	3731	3731
Isoprene	401	764	346
Other VOCs	137	278	278
UM_CAM climate	present	2095–2100	2095–2100
O_3 production	4133	8554	8288
O_3 loss	3338	7444	7183
O_3 influx	387	816	788
O_3 dry deposition	1182	1926	1893
O_3 burden	316.0	457.8	455.5
PAN burden	4.0	6.6	5.0
OH concentration	8.4	8.7	9.3
CH_4 lifetime	10.7	9.1	8.5

[a] NO_x emissions ($Tg\,N\,a^{-1}$) include contributions from surface, aircraft and lightning; CO emissions in $Tg\,a^{-1}$; fixed CH_4 concentrations in ppbv; isoprene in $Tg\,C\,a^{-1}$; and other VOC emissions in $Tg\,C\,a^{-1}$. O_3 budget terms (production, loss, influx and deposition) in $Tg\,a^{-1}$; O_3 and PAN burdens in Tg; OH concentration in 10^5 molecules cm^{-3}; and methane lifetime in years.

isoprene hydroxy-peroxy radicals (ISO_2) with NO, and peroxy alkyl nitrates, from the reaction of isoprene with NO_3. The parameterisation of the kinetics and solubility of ISON is important in determining whether it is a reservoir or sink of NO_x (=NO+NO_2) in the atmosphere. For deposition, we use parameters that aim to account for the expected different physical properties of the constituent species of ISON: hydroxy alkyl nitrates are likely to deposit more quickly than peroxy alkyl nitrates. A Henry's Law constant (K_H (298 K)) of $3.0\times10^3\,M\,atm^{-1}$ is applied, derived from the average of data for 2-nitroxy butanol and 3-methyl-1-butyl nitrate (Staudinger and Roberts, 1996), and the dry deposition velocities are approximately 15% higher than those used for PAN (using data from Giannakopoulos (1998) and refs. therein). For the reaction kinetics, the data from Pöschl et al. (2001) were adopted: ISON is produced in a 4.4% yield from the ISO_2+NO reaction (Chen et al., 1998), whilst the ISON+OH reaction (ultimately recycling NO_x) has a rate constant of $1.3\times10^{-11}\,cm^3\,molecule\,s^{-1}$ (Kwok and Atkinson, 1995). The solubility, dry deposition rate and rate constants are on the lower end of the range of literature estimates (e.g. see the discussion in Horowitz et al., 2007), although sensitivity studies suggest that changing these parameterisations to match the recommendations of Horowitz et al. (2007) result in relatively small perturbations globally (generally <5% effect on boundary layer ozone) (P. J. Young, unpublished results).

3 Experiment descriptions

In this study, we present the results from three UM_CAM model simulations, summarised in Table 1. The set up of the BASE simulation is appropriate to present day conditions, using IIASA anthropogenic emissions (Dentener et al., 2005), LPJ isoprene emissions (average of 1980–1999) calculated with present day climate and CO_2 concentration (Arneth et al., 2007b), and climatological SSTs and sea-ice fields (GISST) (Parker et al., 1995) as the boundary condition for UM_CAM.

The future simulations (noCO2 and wCO2) were designed to simulate a pessimistic 2090s atmosphere consistent with the SRES A2 scenario (Nakicenovic et al., 2000). Emissions of anthropogenic ozone precursors and the concentrations of well-mixed greenhouse gases (see Johns et al., 2003) are greatly enhanced compared to present day, though emissions from biomass burning and biogenic sources other than isoprene are at the same level as BASE. UM_CAM was forced with SST and sea-ice fields calculated for a doubled CO_2 atmosphere for these simulations. We used the SRES A2 scenario in order to assess the sensitivity to a large climate change and increase of ozone precursor emissions. Note, lightning NO_x emissions are parameterised based on convective cloud top height following Price and Rind (1992, 1994), and are therefore sensitive to the model climate. For wCO2 and noCO2, lightning emissions are $3.9\,Tg\,N\,yr^{-1}$, an increase of 26% compared to the emissions in BASE (3.1 Tg N yr-1).

noCO2 and wCO2 differ in terms of their isoprene emission calculated by LPJ-GUESS. In the former, emissions respond to a warmer temperature (an effect of stimulating photosynthesis in many environments and of the high temperature optimum of isoprene production) and enhance vegetation productivity (an effect of CO_2 fertilization of photosynthesis). In the latter, the long-term leaf CO_2-isoprene inhibition is included in addition. The indirect effects of temperature and CO_2 concentration on vegetation productivity were the same in both cases (see Sect. 2.1 and Arneth et al., 2007b). Both vegetation model simulations used CO_2 concentrations following the SRES A2 scenario and a corresponding future climate from the Hadley Centre HadCM3 model to calculate the isoprene emission response (Arneth et al., 2007b). In the calculations LPJ-GUESS simulated potential natural vegetation; additional effects of anthropogenic land-cover change on isoprene emissions were not taken into account. Figure 2 illustrates the differences in yearly total isoprene emission between the three simulations. The difference between the wCO2 and noCO2 simulations reveals the impact of the direct CO_2-isoprene effect in a 2090s atmosphere.

For the wCO2 and noCO2 simulations we report results that are the average of the final 5 years of a 66 month UM_CAM integration, in order to account for the interannual variability between the SSTs for the years 2095–2100.

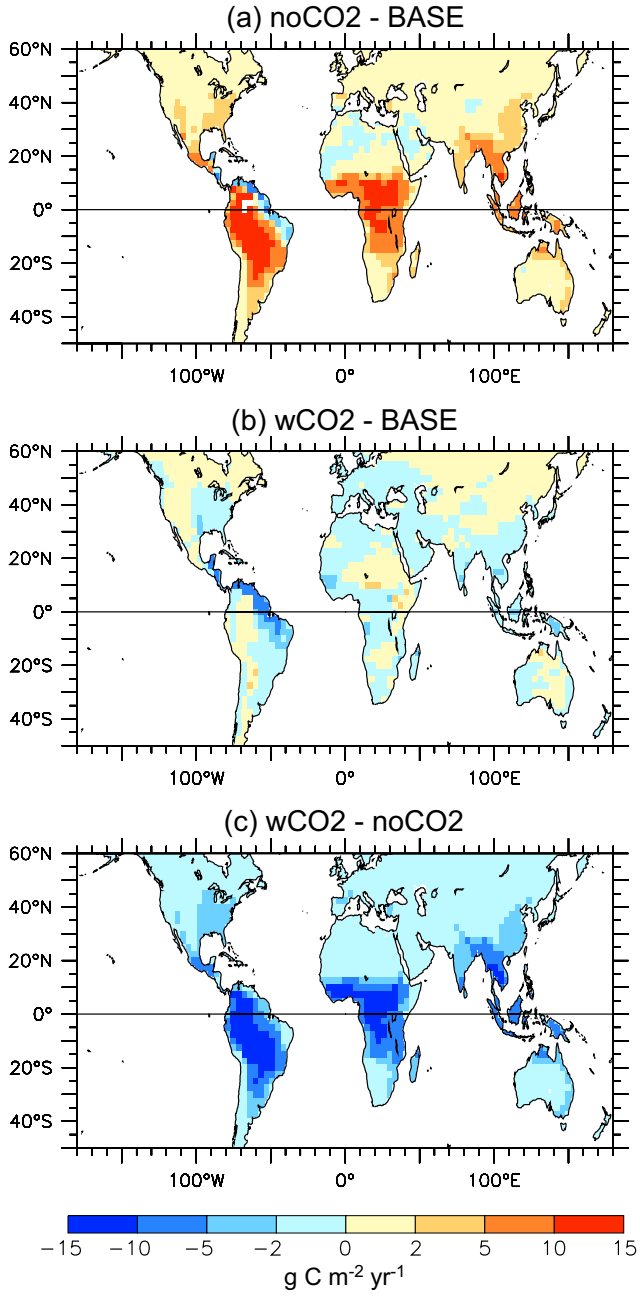

Fig. 2. Difference in the yearly total isoprene emissions ($g\,C\,m^{-2}\,yr^{-1}$) between **(a)** noCO2 and BASE, **(b)** wCO2 and BASE and **(c)** wCO2 and noCO2.

For BASE, we report results that are the average of the final 2 years of a 30 month simulation. We employ a shorter integration here because, as we use climatological SSTs, the differences between simulated years are very much less than the difference between BASE and wCO2/noCO2.

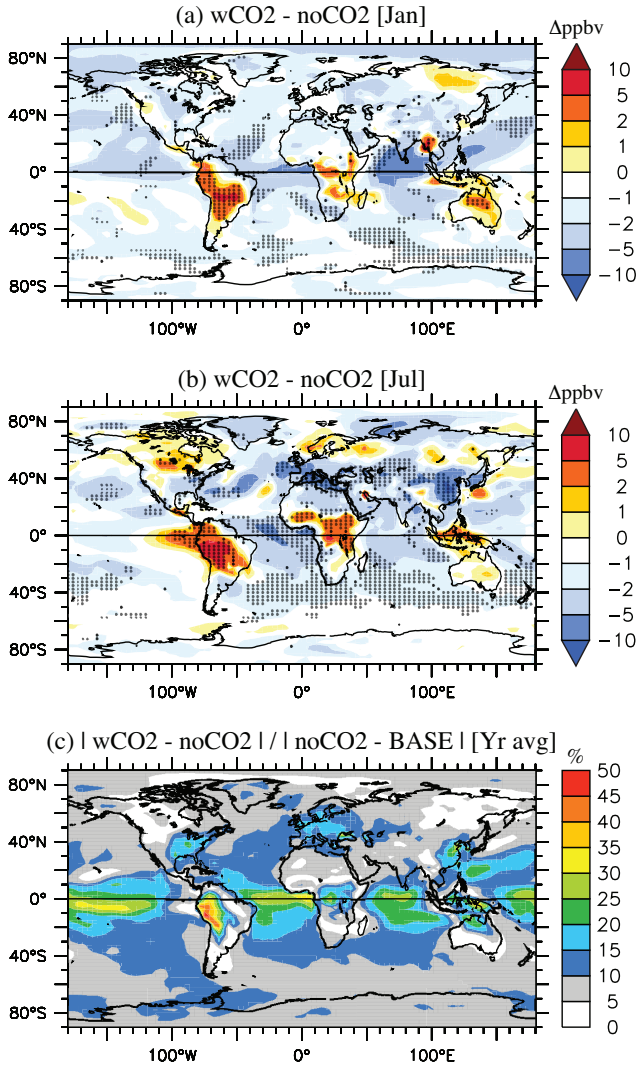

Fig. 3. Difference in monthly mean surface ozone concentrations (ppbv) between wCO2 and noCO2 simulations for **(a)** January and **(b)** July (2090–2095 average). The shading indicates where the difference is significant at the 95% level (student's t-test). And **(c)** Yearly averaged (absolute) difference in surface ozone between wCO2 and noCO2 relative to the yearly averaged (absolute) difference between noCO2 and BASE (%).

4 Impact on ozone concentrations

Figure 3a, b shows the difference in (January and July) monthly-mean surface ozone concentrations that were simulated by using the two different future isoprene emission scenarios. Both panels clearly illustrate a significant impact on surface ozone, but with a large degree of spatial heterogeneity. The relatively lower isoprene emissions in wCO2 compared to noCO2 resulted in decreased ozone levels over most oceanic regions in both months. In these areas the major source of NO_x (and hence ozone production) is the thermal degradation of PAN transported from adjacent continents

(Moxim et al., 1996; Horowitz et al., 1998). Isoprene is the major PAN precursor in the model; the tropospheric PAN burden decreased by ∼24% between noCO2 and wCO2 (Table 1). Surface NO_x levels decreased by 10–30% over most oceanic regions in wCO2, and by 50% in continental outflow regions (not shown). This effect becomes visible, for instance, in the North Atlantic Ocean in July, where the wCO2 simulation shows peak ozone reductions of 5–10 ppbv (15–20%) due to reduced export of NO_x from Eastern USA, an area influenced by isoprene emissions from South-Eastern USA (Fiore et al., 2005). A similar pattern was apparent over the Indian Ocean in January, related to reduced NO_x export, due to less isoprene emission, from Asia (Fig. 2). Decreases in ozone in wCO2 were also evident in July over the polluted regions of Eastern USA, Europe and Southeast Asia, with reductions of between 2–10 ppbv (5–10%). Co-located higher NO_x levels in these areas indicate that ozone production is sensitive to the level of VOCs, hence the less isoprene in wCO2 leading to reduced ozone (Sillman, 1999).

Figure 3a, b shows 2–10 ppbv (up to 20–25%) surface ozone increases over the Amazon, tropical Africa and the maritime continent for both months, coincident with a ∼50% decrease in isoprene emission over these major source regions in wCO2 compared to noCO2. The ozone increase resulted from reduced sequestration of NO_x by isoprene oxidation products (isoprene nitrates and PAN) (e.g. Roelofs and Lelieveld, 2000), leading to increased NO_x levels (10–30%) and increased ozone production in these regions, as well as reduced isoprene ozonolysis (as noted by Fiore et al., 2005; Wiedinmyer et al., 2006). The surface ozone increase was most marked in the Amazon (>15% in both months), where the low NO_x levels result in a lower oxidizing capacity increasing the stability of isoprene nitrates and hence their importance as a NO_x sink (Pöschl et al., 2000).

Zonal mean ozone changes (not shown) were largely consistent with the effects of non-methane VOC chemistry described by Wang et al. (1998). wCO2 showed a 1–3 ppbv increase (∼5%) in tropical upper troposphere (UT) concentrations compared to noCO2 in January and July. This resulted from a decrease in isoprene oxidation products in convective plumes, reducing NO_x sequestration in the region (NO_x levels increase by 20–40%) and hence increasing ozone production. In the mid and lower troposphere, ozone decreased by ∼5% in wCO2. In less-polluted regions, such as the tropics, the ozone decrease is attributable to the reduction in NO_x transported by isoprene oxidation products (NO_x levels decrease by 10–15%). Over more polluted regions, where NO_x is more efficiently recycled from isoprene nitrates due to the higher oxidising capacity, the drop in ozone levels is due to lower peroxy radical concentrations in wCO2 compared to noCO2, reducing ozone production.

Overall, Table 1 shows that the tropospheric ozone burdens of noCO2 and wCO2 were almost the same, indicating that increases and decreases in ozone concentration approximately balance. Likewise for the tropospheric ozone budget terms, Table 1 shows that difference between wCO2 and noCO2 for the globally integrated production and loss terms is small, disguising larger regional differences. For instance, the difference in boundary layer ozone production between wCO2 and noCO2 ranges from +/−50%, with the increases and decreases following the pattern outlined for surface ozone above. Further discussion on the relationship between isoprene and the tropospheric ozone budget can be found in Wu et al. (2007), as well as Young (2007) for UM_CAM.

The results from this study can be compared to two other studies that investigated the relationship between late 21st century ozone levels and isoprene emission changes, also using the SRES A2 scenario. The presence of both decreases and increases in future surface ozone, due to the regionally heterogeneous effect of isoprene on atmospheric chemistry, are not reported by Sanderson et al. (2003) or Hauglustaine et al. (2005), who found near universal increases in ozone wherever isoprene increases. Part of the reason for the difference between the simulations may arise from the treatment of isoprene nitrates, which were identified as the major source of systematic difference between chemical mechanisms of different models by Pöschl et al. (2000). The chemical scheme of Sanderson et al. (2003) does not include the formation of isoprene nitrates from the isoprene-peroxy+NO reaction (Collins et al., 1999), excluding this sink for NO_x. The oxidation mechanism of Hauglustaine et al. (2005) recycles NO_x from isoprene nitrates at a 15% faster rate than in our model (Folberth et al., 2006 versus Pöschl et al., 2001), reducing their efficacy as a NO_x sink and potentially leading to higher ozone levels. However, a UM_CAM model integration using 3 times faster NO_x recycling than the BASE simulation (not shown) (as per Horowitz et al., 2007) resulted in <5% increases in ozone. Furthermore, compared to a present-day UM_CAM integration without isoprene emissions included, both this sensitivity simulation and BASE simulation show similar magnitude decreases in ozone over non-polluted tropical regions. Overall, whilst the treatment of isoprene nitrates might explain some of the differences between this model study and that of Hauglustaine et al. (2005), there are clearly other model elements making a contribution. Although both models include wet and dry depositional losses for isoprene nitrates, there are no data presented in Folberth et al. (2006) to compare the UM_CAM parameters against.

Several other modelling studies that have investigated isoprene chemistry calculate results similar to those reported here for UM_CAM. Using the MOZART-2 model (Horowitz et al., 2003), Wiedinmyer et al. (2006) report both increases and decreases in surface ozone in response to higher isoprene emissions, although for simulations where anthropogenic emissions were held at present day levels. A similar result is found by Fiore et al. (2005), who use the GEOS-CHEM model (Bey et al., 2001) to compare present-day USA isoprene emission inventories. Fiore et al. (2005) calculate ozone increases in response to isoprene decreases in

the South-Eastern USA, which they attribute to decreased isoprene ozonolysis and isoprene nitrate chemistry. Houweling et al. (1998), Roelofs and Lelieveld (2000) and Pfister et al. (2008) all also report tropical ozone decreases (especially over the Amazon) when comparing runs with and without isoprene emissions included. Houweling et al. (1998) assumed no wet depositional loss of isoprene nitrates, as well as a low dry deposition velocity (the same as PAN). But as they used a low rate constant for isoprene nitrates with OH (∼7 times lower than used here), their effectiveness as a NO_x-sink is increased. Roelofs and Lelieveld (2000) assumed that isoprene nitrates quickly react to produce nitric acid, which makes them an effective NO_x-sink (due to the high solubility of nitric acid). Pfister et al. (2008) used an isoprene nitrate+OH rate constant ∼3.5 times faster than used in UM_CAM (as well as including an additional reaction with ozone), and parameterised isoprene nitrate wet deposition by mapping the species onto nitric acid; there is no information on the dry deposition velocity.

Clearly there are many additional differences in both the model chemistry schemes and the underlying climate models/meteorological data (that drive emissions and control chemical reaction rates) that can lead to the range of responses published to date. For instance, von Kuhlmann et al. (2004) investigated the sensitivity of their model results to different isoprene oxidation mechanisms, reporting effects as large as 20–60% on surface ozone over isoprene source regions. The differences between studies underline both the need to investigate sensitivities and constraints of isoprene nitrate chemistry (von Kuhlmann et al., 2004; Horowitz et al., 2007) as well as to conduct multi-model ensemble studies (e.g. Stevenson et al., 2005; Shindell et al., 2006).

Figure 3c compares the yearly average absolute difference between wCO2 and noCO2, with the absolute difference between noCO2 and BASE (i.e. the total change between the 2090s and present day as reported in studies that do not include the CO_2 impact on isoprene emission). As has been observed in a number of previous other model experiments studies (e.g. Johnson et al., 1999; Zeng and Pyle, 2003; Hauglustaine et al., 2005; Zeng et al., 2008) altered anthropogenic emissions (mainly NO_x) dominated the future surface ozone projections overall. However, the difference between wCO2 and noCO2 amounts to >20% of the noCO2-BASE difference in the continental outflows, and it is up to half the effect over the Western Amazon, highlighting the importance of isoprene chemistry in these regions. As well as emission perturbations, climate change also contributes to the impact on ozone. In UM_CAM, the effect of climate change alone on the tropospheric ozone burden is a 3.5% reduction (Zeng et al., 2008), mainly attributable to an increased loss rate with the higher humidity in a warmer climate.

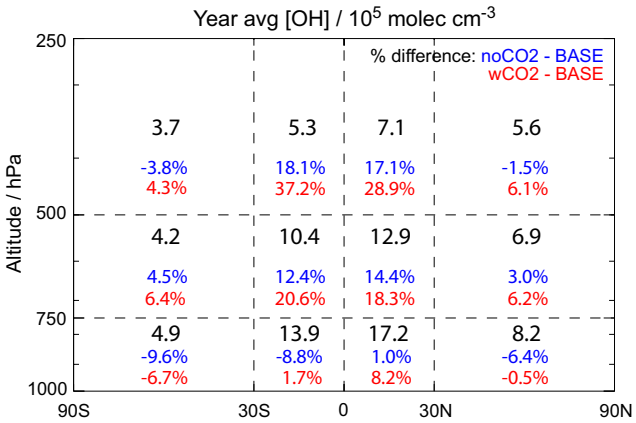

Fig. 4. Air mass weighted, yearly average tropospheric OH concentrations for the BASE simulation (black), calculated for the regions specified in Lawrence et al. (2001). The percentage differences between noCO2 and BASE (blue) and wCO2 and BASE (red) are also shown.

5 Impact on OH concentrations

OH is the most important oxidizing agent in the troposphere, determining the rate of removal of many reduced gases, including methane. Tropospheric OH levels are uniformly higher in wCO2 compared to noCO2 (Fig. 4), as the relatively lower isoprene emission in the former reduced the OH sink (e.g. see also Spivakovsky et al. (2000) and Pfister et al., 2008). Figure 4 shows that the largest relative difference between wCO2 and noCO2 OH levels was simulated in the tropical upper tropopause (UT), where, when averaged over 30 S–30 N and for 500–250 hPa, there was a 13% increase. Two reasons underlie this result (cf. zonal mean ozone): firstly, in wCO2 there was a decreased OH sink in the UT due to relatively lower concentrations of isoprene oxidation products in the convectively lifted air masses; and secondly, less lightning-produced NO_x was sequestered by isoprene oxidation products in wCO2 (tropical UT NO_x levels were 20–35% higher in wCO2 compared to noCO2), increasing the efficiency of HO_2 to OH conversion (Spivakovsky et al., 2000). There was also a large increase in the tropical lower troposphere OH concentrations in wCO2 (8%), mostly due to a decrease in the reaction rate of isoprene with OH. Globally, the average tropospheric OH concentration was 7.2% higher in wCO2 which reduced the tropospheric chemical lifetime of methane by ∼7 months (Table 1), illustrating the indirect role in radiative forcing attributable to isoprene (Collins et al., 2002).

As for ozone, OH differences between BASE and noCO2 or BASE and wCO2 are the product of both climate change and changes in anthropogenic and isoprene emissions. Changes in emissions have antagonistic effects, with NO_x increases tending to increase OH (through increased production of ozone) and VOC increases tending to decrease

OH (by increasing the OH sink). In previous simulations with the UM_CAM model, anthropogenic emission increases in the SRES A2 scenario have led to an overall 17% increase in OH (Zeng et al., 2008). A warmer climate increases OH production, due to increased humidity. In the present simulations the signal of climate on OH was calculated from two wCO2 runs, one with SSTs, sea-ice and well-mixed greenhouse gas concentrations as in BASE (wCO2_p) and the other as described in Sect. 3 (wCO2). Comparing these simulations showed that climate change led to a 7.6% increase in the average OH concentration (wCO2 – wCO2_p). This is comparable to the difference calculated between wCO2 and noCO2; in fact the signal from the change in isoprene emissions was similar in magnitude to the climate change signal throughout most of the lower troposphere and the tropical UT. Of course, the result of climate change is regionally heterogeneous and influences many other reaction rates and meteorological parameters relevant to atmospheric chemistry.

6 Conclusions

Biogenic emissions are important uncertainties in future atmospheric chemistry and climate even in a scenario with strong anthropogenic emission changes. The direct isoprene-CO_2 interaction significantly alters surface ozone concentrations, especially in the tropics, which is important for future air quality projections. The projected tropospheric OH levels are also significantly affected, with the relatively lower isoprene emission, in simulations that accounted for the inhibitory effect of increasing CO_2 concentration, reducing the methane lifetime notably. However, whether the ozone burden increases or decreases depends on the region, illustrating the problems of expressing climate effects of reactive traces gases based on global total burden or global radiative forcing. In our calculations the overall ozone radiative effect presumably would be small, but the global totals hide a possible cooling effect in some areas and a warming in others (although not necessarily geographically aligned with the changes in ozone, Shindell et al., 2007). Other regional impacts due to long-range transport of reaction products (e.g. PAN) or the indirect climate effect on methane lifetime are also difficult to take into account with existing climate change metrics. Ways forward may be to break global warming potentials (GWPs) into distinct regional values and/or to use novel calculations like global temperature change potentials (GTPs) (Rypdal et al., 2005; Shine et al., 2005) of short-lived species that may also be compared relative to that of CO_2 (Boucher and Reddy, 2008).

Our results have demonstrated the different response of atmospheric chemical models to isoprene emissions, namely that the globally averaged response of UM_CAM to less isoprene emissions is an increase in ozone, rather than the decrease noted by some other studies (Sanderson et al., 2003; Hauglustaine et al., 2005). Whilst we have tried to rationalise the differences by appealing to differences in the model isoprene schemes, there is a need to better quantify the differences between atmospheric chemical models and their constituent parts. Initial work in this direction has been completed by studies such as Mallet and Sportisse (2006), who conducted an ensemble simulation of ozone by substituting different values for parameters such as turbulent closure and the model resolution, though further work is needed to expand this effort to different model systems. Clearly, the models are also limited in their ability to represent isoprene chemistry accurately and new mechanisms (e.g. Butler et al., 2008) need to interface with new laboratory measurements for evaluation

In this experiment, we only highlight one of the many uncertainties in the overall response of future BVOC emissions, atmospheric chemistry and climate. A number of additional factors will also affect future BVOC emissions. Firstly, future land use and land cover change is likely to alter emissions substantially, particularly in tropical ecosystems where conversion of rainforest, woodlands and savannahs into agricultural ecosystems will decrease isoprene and monoterpene emissions (Lathière et al., 2006). Furthermore, the net effect of interactions between BVOC emissions, tropospheric ozone and plant productivity are as yet unresolved. Ozone is phototoxic and reduces photosynthesis and net carbon uptake (Sitch et al., 2007). However, some studies have shown that isoprene and monoterpene emissions may help plants to withstand the phytotoxic effects (Loreto and Velikova, 2001; Fares et al., 2008). How these additional interactions affect biogenic emission projections and atmospheric chemistry remains to be tested.

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