**Atmospheric
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Improved simulation of isoprene oxidation chemistry with the ECHAM5/MESSy chemistry-climate model: lessons from the GABRIEL airborne field campaign

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Abstract. The GABRIEL airborne field measurement campaign, conducted over the Guyanas in October 2005, produced measurements of hydroxyl radical (OH) concentration which are significantly higher than can be simulated using current generation models of atmospheric chemistry. Based on the hypothesis that this "missing OH" is due to an as-yet undiscovered mechanism for recycling OH during the oxidation chain of isoprene, we determine that an OH recycling of about 40–50% (compared with 5–10% in current generation isoprene oxidation mechanisms) is necessary in order for our modelled OH to approach the lower error bounds of the OH observed during GABRIEL. Such a large amount of OH in our model leads to unrealistically low mixing ratios of isoprene. In order for our modelled isoprene mixing ratios to match those observed during the campaign, we also require that the effective rate constant for the reaction of isoprene with OH be reduced by about 50% compared with the lower bound of the range recommended by IUPAC. We show that a reasonable explanation for this lower effective rate constant could be the segregation of isoprene and OH in the mixed layer. Our modelling results are consistent with a global, annual isoprene source of about $500\,\mathrm{Tg(C)\,yr^{-1}}$, allowing experimentally derived and established isoprene flux rates to be reconciled with global models.

1 Introduction

During the GABRIEL airborne field campaign, conducted over the Guyanas in October 2005, concentrations of OH were measured in excess of those which can be reproduced by models of atmospheric chemistry based on current understanding (Lelieveld et al., 2008, and other papers in this issue). In this study we present detailed comparisons of the measurements taken during GABRIEL with the ECHAM5/MESSy AC-GCM (Atmospheric Chemistry General Circulation Model), and attempt to reconcile our simulations with the measurements.

OH plays an important role in the chemistry of the troposphere, being the oxidising species primarily responsible for the removal of reactive pollutants (e.g. Lelieveld et al., 2004). It is possible to estimate global average OH concentrations using observed distributions of OH precursors (e.g. Spivakovsky et al., 1990, 2000) or compounds in the atmosphere which are removed by reaction with OH, most notably methyl chloroform (e.g. Krol and Lelieveld, 2003; Prinn et al., 2005). OH at regional scales can also be calculated by examining the relative variability of compounds which are removed by OH (e.g. Williams et al., 2001; Bartenbach et al., 2007). Direct measurements of OH in the troposphere are also possible using a variety of techniques (e.g. Heard and Pilling, 2003, and references therein).

OH concentrations measured in polluted urban environments are often lower than predicted by models (e.g. George et al., 1999; Shirley et al., 2006). Such urban environments are characterised by high anthropogenic emissions of non methane hydrocarbons (NMHC) and oxides of nitrogen (NO_x, $NO+NO_2$, with mixing ratios of the order of several

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nmol mol^{-1}). The oxidation of these anthropogenic NMHC by OH radicals leads to production of the HO$_2$ radical, which reacts with NO to recycle OH and form NO$_2$, which then photolyses to form ozone (O$_3$, photolysis of which is responsible for the primary production of OH when the resulting excited O(^{1}D) atoms react with water vapour). The net result of urban photochemistry is maintenance of high OH concentrations during removal of NMHC and production of O$_3$.

Away from the influence of anthropogenic emissions, the atmospheric chemistry of OH-initiated oxidation is quite different. NO$_x$ is typically three to four orders of magnitude less abundant, and NMHC, when present, are usually of biogenic origin. The most abundant biogenic NMHC globally is isoprene (Guenther et al., 2006). Tan et al. (2001) and Carslaw et al. (2001) both report field measurements of OH in regions of low NO$_x$ (<100 pmol mol^{-1}) in the presence of isoprene mixing ratios in excess of 1 nmol mol^{-1}. In both cases the measured OH concentrations are higher than those predicted by models. Thornton et al. (2002) have also noted inconsistencies in the modelled HO$_x$ (OH+HO$_2$) budget in NO$_x$-poor environments in the presence of isoprene. Tan et al. (2001) speculated that ozonolysis of terpenes may be a source of this "missing OH", however Carslaw et al. (2001) measured a comprehensive set of biogenic NMHC, and included their ozonolysis in their model, which was not enough to increase their modelled OH to be in line with the measurements. Ren et al. (2006) also measured OH in a relatively low NO$_x$ (≈100 pmol mol^{-1}) forested area and were able to reproduce their observed OH quite well with a model. In contrast to the studies reported by Tan et al. (2001) and Carslaw et al. (2001), Ren et al. (2006) report low mixing ratios of isoprene (of the order of 100 pmol mol^{-1}) which accounted for an unusually low fraction of the total OH reactivity ($\approx15\%$). Kuhn et al. (2007) and Karl et al. (2007), measuring surface fluxes and mixing ratios of isoprene over Amazonia, also infer concentrations of OH radicals in the presence of isoprene which are higher than calculated from chemical box models.

This tendency of isoprene to deplete the OH concentration in regions of low NO$_x$, especially over tropical continental regions (most notably the Amazon), and thus to lead to higher mixing ratios of isoprene than are measured has also been noted in global three dimensional models of atmospheric chemistry (e.g. Houweling et al., 1998; von Kuhlmann et al., 2003; Folberth et al., 2006; Jöckel et al., 2006). A common solution in global atmospheric chemistry models has been to reduce the flux of isoprene by about one half (e.g. Pozzer et al., 2007). This leads to an inconsistency between isoprene flux estimates based on a multitude of laboratory and field observations (Guenther et al., 1995, 2006) and many of the current state of the art atmospheric chemistry models.

In this paper we examine the hypothesis that the missing OH in NO$_x$-poor, isoprene-rich environments is due to a yet undiscovered OH recycling mechanism present in the isoprene oxidation chain, as proposed by Lelieveld et al. (2008).

We present the results of simulations performed with a global three dimensional AC-GCM using a number of different isoprene oxidation mechanisms, including several with differing degrees of imposed OH regeneration, and compare these with measurements taken during the GABRIEL campaign in order to estimate the degree of OH recycling required for our model to agree with the GABRIEL measurements.

Section 2 describes our methodology, including our modelling approach, in Sect. 3 we compare the results of our model runs with the GABRIEL measurements before examining the global implications in Sect. 4, and we conclude with Sect. 5.

2 Methodology

We use the ECHAM5/MESSy global three dimensional AC-GCM. This model has been developed and evaluated by Jöckel et al. (2006). The chemical submodel, MECCA (Sander et al., 2005), used in this evaluation includes a treatment of isoprene oxidation known as the Mainz Isoprene Mechanism (MIM) which was originally developed by Pöschl et al. (2000) and modified by von Kuhlmann et al. (2004). For this study we select only reactions relevant to the troposphere, and we omit halogen chemistry. Throughout the text we refer to this chemical mechanism as the "MIMvK" mechanism. The other submodels used in this study are CONVECT (Tost et al., 2006a), EMDEP (Ganzeveld et al., 2006), LNOX (Tost et al., 2007), OFFLEM (Kerkweg et al., 2006), SCAV (Tost et al., 2006b), TNUDGE (Kerkweg et al., 2006), as well as CLOUD, CVTRANS, JVAL, RAD4ALL, and TROPOP (Jöckel et al., 2006). We use offline emissions from the OFFLEM submodel, and online emissions and dry deposition from the EMDEP submodel. Turbulent vertical transport and boundary layer mixing processes are treated using an eddy diffusion method (Roeckner et al., 2003). The online photolysis module JVAL contains additionally to the reactions given in Jöckel et al. (2006) the photolysis of MVK, MACR, glyoxal and glycolaldehyde based on Sander et al. (2006). We run the model at T42 horizontal resolution (about 2.8×2.8 degrees), and with 31 levels up to 10 hPa in the vertical, in "free running" mode, forced only by AMIP sea surface temperatures, with no additional nudging of the model meteorology. In order to study the effects of changes in the chemical mechanism in a consistent way, we have turned off all feedbacks in the model between our simulated trace gases and the climate model. This ensures that all of our model runs are performed with identical meteorology, and that our comparisons only examine the effect of our changes to the chemical mechanism.

Figure 1 shows the grid of ECHAM5/MESSy superimposed over the region of the GABRIEL airborne campaign along with the tracks of the flights. These flights were performed between 5 October and 15 October 2005, with measurements taken between the hours of 10:30 and 20:00 UTC
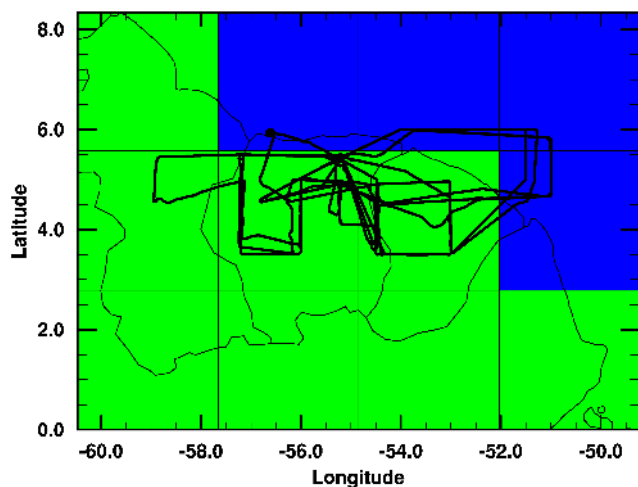
Fig. 1. The Guyanas in ECHAM5/MESSy. Land grid cells are shown in green, and ocean gridcells in blue. GABRIEL flights are shown as solid black lines.

(07:30 and 17:00 local time), from ground level up to an altitude of 11 km. The aircraft was a Learjet 35A belonging to the *Gesellschaft für Flugzieldarstellung* (GFD, Hohn, Germany), and was based at Zanderij International Airport for the duration of the GABRIEL campaign. Most of the data collected during the campaign correspond with the model grid cell directly over Suriname, and the cell immediately to the east. Isoprene was measured with an onboard PTR-MS system (Proton Transfer Reaction Mass Spectrometer, Eerdekens et al., 2008), while OH and HO_2 were measured with a wing-mounted LIF instrument (Laser Induced Fluorescence, Martinez et al., 2008). Chemical weather forecasting support for the campaign was provided using the MATCH-MPIC (Model of Atmospheric Transport and CHemistry, Max Planck Institute for Chemistry version) forecasting system (Lawrence et al., 2003). A more general description of the campaign is provided by Lelieveld et al. (2008), and Stickler et al. (2007) includes further details of other species measured during the campaign.

As we perform a large number of simulations, the results of which we only wish to compare with the measurements taken during the GABRIEL campaign in October 2005, we initialise the model with tracer fields from the evaluation S1 simulation (Jöckel et al., 2006), allow the model two months (August and September 2005) to spinup, and then average the results for October 2005. We use an output frequency of 5 h, and our averaging method preserves the diurnal variability of the model output. For comparison with the GABRIEL measurements in Sect. 3, we perform virtual flythroughs of our model by interpolating our model output spatially and temporally along the flight paths shown in Fig. 1. When presenting the global implications of our modified chemical mechanisms in Sect. 4, we allow three months of spinup time (October, November and December 2004) and present annual averages for 2005.
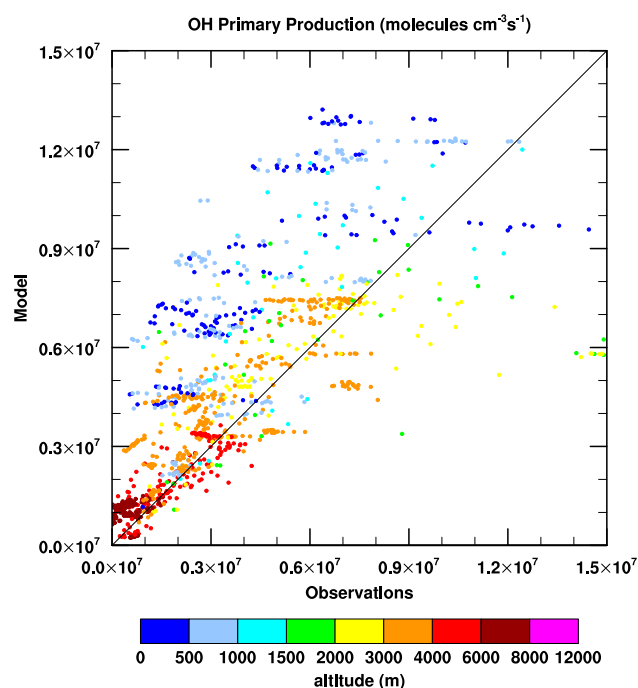

Fig. 2. Primary OH radical production as simulated by ECHAM5/MESSy, compared with GABRIEL measurements.

3 Results

Figure 2 shows the comparison between model and measurements of the primary production of OH radicals due to photolysis of O_3 followed by reaction of the resulting excited $O(^1D)$ atoms with H_2O. We plot the values based on the measurements taken during all GABRIEL flights on the x-axis, and each corresponding point from the virtual flythrough of our model output on the y-axis. The model-measurement comparison for the individual terms involved in the calculation of OH primary production (mixing ratios of O_3, the photolysis frequency $O_3 \rightarrow O(^1D)$, and mixing ratios of H_2O) are shown along with the model/measurement comparison for mixing ratios of NO in Fig. 1 of the Electronic Supplement http://www.atmos-chem-phys.net/8/4529/2008/acp-8-4529-2008-supplement.pdf to this article. Our model reproduces the photolysis rate of O_3 fairly well, and slightly underestimates the observed mixing ratio of H_2O at lower altitudes. Our overestimation of OH primary production at low altitudes compared with the GABRIEL measurements (Fig. 2) is due to our overestimation of O_3 mixing ratios at low altitudes. Observations of NO, important for OH recycling (Sect. 1), are characterised by mostly quite low mixing ratios (0–50 pmol mol^{-1}) and occasionally by intense plumes, which are associated with emissions from ships in the Atlantic Ocean to the east of French Guyana and localised anthropogenic activity over the Guyanas. The highest simulated NO mixing ratios over the GABRIEL domain are due
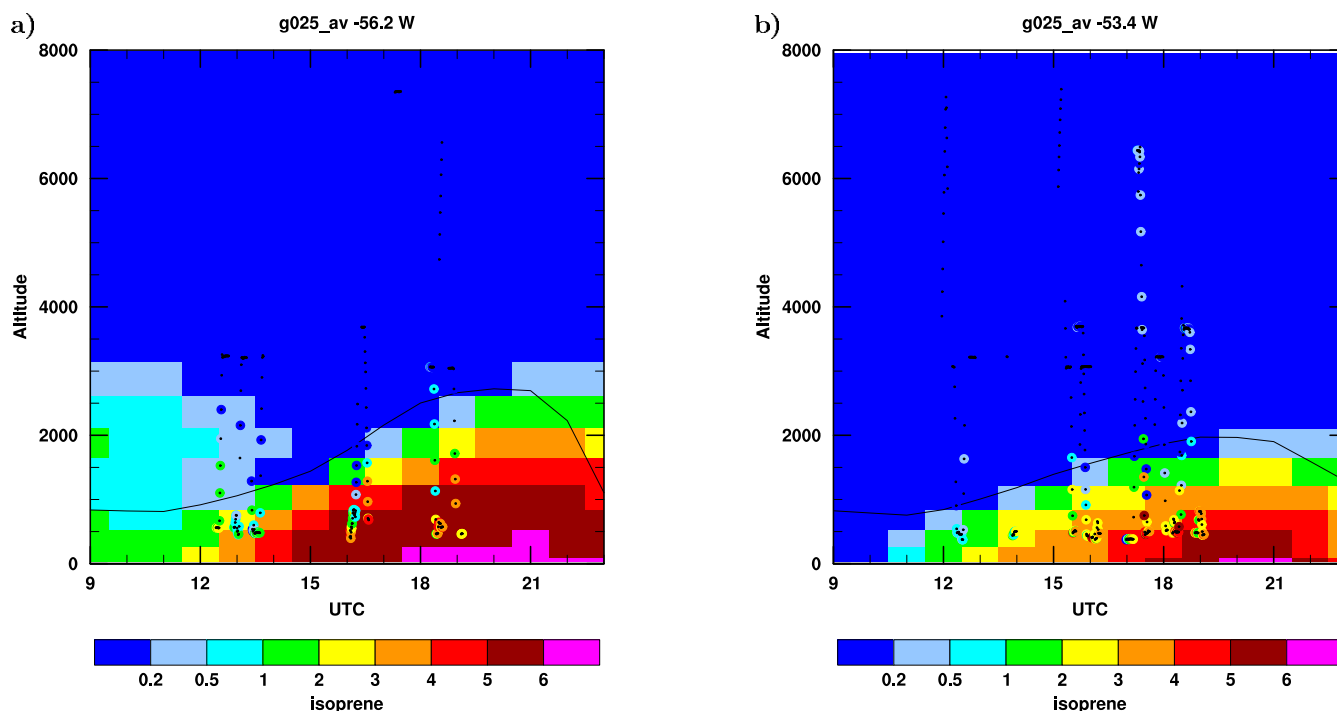
Fig. 3. GABRIEL isoprene measurements (coloured points) superimposed on the modelled diurnal evolution of the October average isoprene mixing ratios from the MIMvK model run (nmol mol^{-1}), along with the model diagnosed mixed layer height (solid line) for the grid cell corresponding with **(a)** Suriname and **(b)** French Guyana.

to ship emissions. Observed NO mixing ratios over land are generally only slightly overestimated by the model.

Isoprene is also an important term in the OH budget over tropical forests, being potentially one of the largest sinks. The vertical profile, including the diurnal variability of isoprene from the model run performed with the MIMvK chemical mechanism is shown in Fig. 3, which also shows the diurnal evolution of the diagnosed height of the mixed layer from our model (solid line) and the GABRIEL isoprene measurements (coloured points). While this model run has too much isoprene in comparison with the measurements, it seems that model does well in simulating the vertical extent of isoprene mixing over both Suriname and French Guyana. Our model calculates the flux of isoprene to the atmosphere online using the algorithm of Guenther et al. (1995), with a global annual flux of isoprene of about 500 Tg(C). Over the Suriname grid cell, this corresponds to an integrated daily flux of 70 mg(isoprene)/m^2/d, which peaks at 9.4 mg(isoprene)/m^2/h around midday. The isoprene flux over the Guyanas during the GABRIEL campaign has been estimated at about 8 mg(isoprene)/m^2/h (Eerdekens et al., 2008).

Figure 4 shows the comparison between the measurements of OH and isoprene, and the corresponding points from the virtual flythrough of the MIMvK model run. The model overestimation of isoprene mixing ratios, seen previously in Fig. 3, and typical for global model simulations of this region

(Sect. 1) is again visible in Fig. 4. OH concentrations in the model mixed layer are severely underestimated despite our overestimation of the OH primary production rate (Fig. 2).

In Fig. 2 of the Electronic Supplement http://www.atmos-chem-phys.net/8/4529/2008/ acp-8-4529-2008-supplement.pdf to this paper, we also show similar comparisons for other species measured during the GABRIEL campaign (HO$_2$, OH/HO$_2$ ratio, total organic peroxides, the sum of MACR and MVK (methacrolein and methyl vinyl ketone), CH$_3$CHO (acetaldehyde) and HCHO (formaldehyde). The model clearly has difficulty in simulating the observed measurements of both OH and HO$_2$ in the mixed layer. The small number of points in Fig. 4 for which good model-measurement agreement is observed correspond with measurements taken over the ocean to the East of French Guyana, where no isoprene is present. Not only are the concentrations of both OH and HO$_2$ severely underestimated, but the HO$_2$/OH ratio is also not reproduced. Similar problems are also seen in chemical weather forecast output[1] from the MATCH-MPIC forecasting system. The simulated mixing ratios of the sum of MACR and MVK, both intermediate products of isoprene oxidation which are themselves oxidised by OH, are too high in comparison with the measurements. This is most

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[1]available via the world wide web at: http://www.mpch-mainz.mpg.de/~lawrence/forecasts.html.
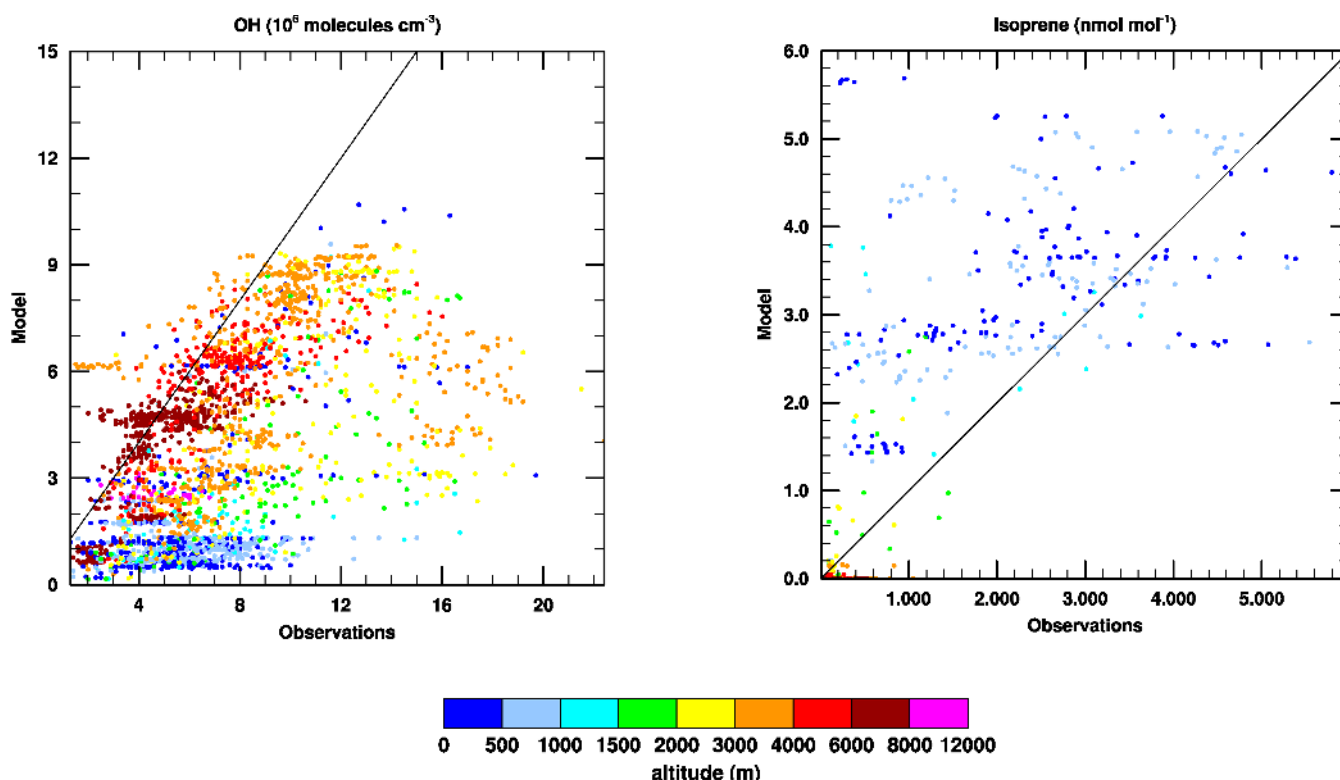
Fig. 4. Model-measurement comparison for OH and isoprene observed during GABRIEL for the MIMvK model run.

likely due, at least in part, to the fact that in MIM, the species MVK is a lumped species which includes MVK, MACR, and other carbonyl compounds formed during isoprene oxidation (Pöschl et al., 2000).

Mixing ratios of CH_3CHO and HCHO, both intermediate products in isoprene oxidation which also have non-isoprene related chemical sources as well as surface sources, are respectively underestimated (CH_3CHO) and overestimated (HCHO) in the MIMvK simulation, when compared with the GABRIEL measurements. The disagreement between model and measurements is especially interesting for the total mixing ratio of all organic peroxides. Whereas our model simulates high mixing ratios of organic peroxides at low altitudes (which are mostly peroxides formed during isoprene oxidation), and low mixing ratios of organic peroxides at higher altitudes (which are mostly CH_3OOH formed during oxidation of CH_4), the organic peroxide measurements taken during the GABRIEL campaign show a much smaller vertical gradient, with lower mixing ratios in the mixed layer and higher mixing ratios in the free troposphere than we simulate in our model. The precise nature of these organic peroxides measured at high altitudes during the GABRIEL campaign is unknown.

The MIMvK mechanism has a number of problems in its treatment of isoprene oxidation. Taraborrelli et al. (2008) describe a new isoprene oxidation mechanism, MIM2 (Mainz Isoprene Mechanism, version 2). This mechanism has been shown to agree closely with the much more detailed MCM (Master Chemical Mechanism, Saunders et al., 2003). Improvements in the representation of isoprene oxidation chemistry include more explicit representation of intermediate oxidation products, such as the peroxy radicals (and associated peroxides) formed from reaction of isoprene with OH, explicit representation of MVK and MACR, which had been lumped together along with other carbonyl species in the previous MIM (as used in MIMvK), and the inclusion of previously neglected production pathways of CH_3CHO.

In Fig. 5 we show the effect of using this new isoprene oxidation mechanism on the comparison between our model and the GABRIEL measurements of OH and isoprene. Despite the many revisions to the chemical mechanism and concomitant improvements in the comparison of modelled species with observations, on the whole our simulation of the atmospheric chemistry over the Guyanas still compares poorly with the measurements. The agreement between modelled and measured OH and is only slightly improved, although the approximately 50% increase in mixed layer OH compared with the MIMvK run does lead to a decrease in the modelled isoprene, which now appears, at least on average, to be well simulated by our model. We do not simulate the high variability present in the isoprene observations.
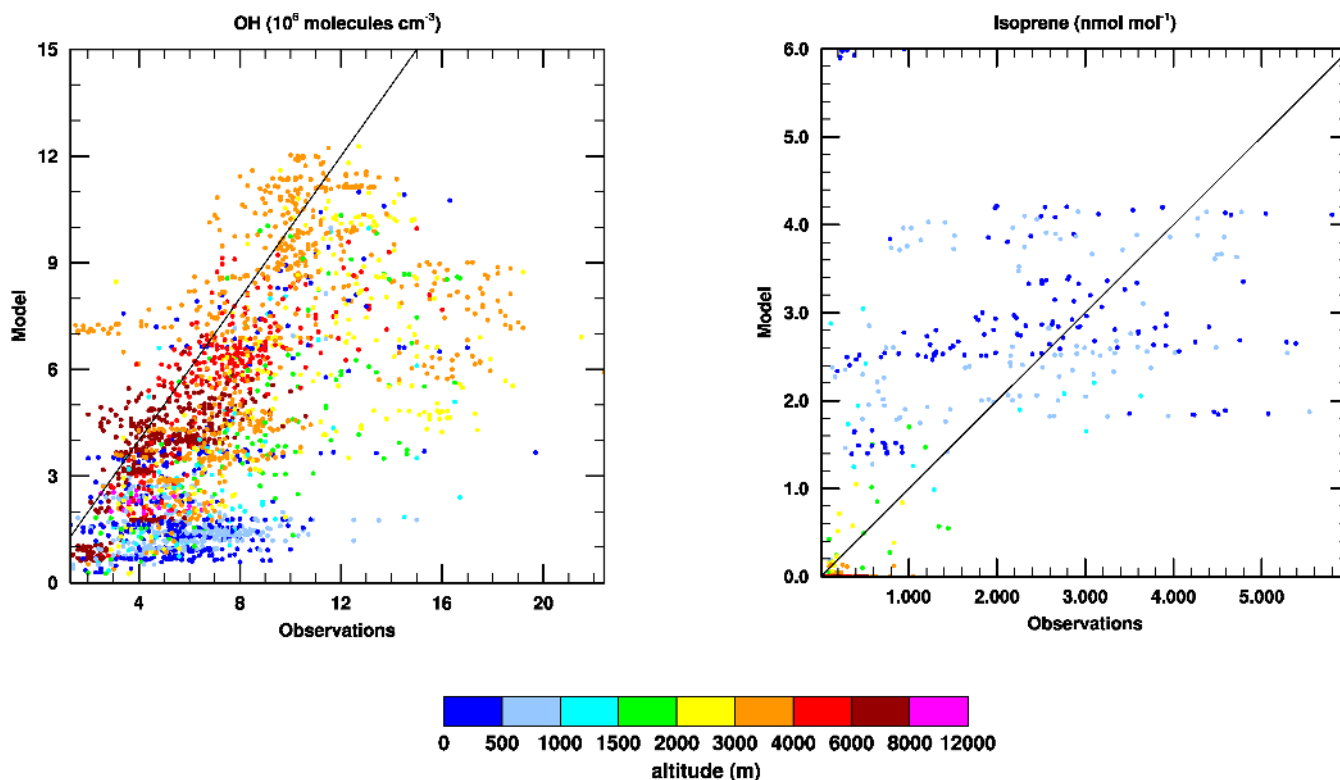
Fig. 5. Model-measurement comparison for OH and isoprene observed during GABRIEL for the MIM2 model run.

Comparisons of our MIM2 model run with other species measured during the GABRIEL campaign are shown in Fig. 3 of the Electronic Supplement http://www.atmos-chem-phys.net/8/4529/2008/ acp-8-4529-2008-supplement.pdf to this paper. There is considerable improvement in the model/measurement comparison of the sum of MACR and MVK (which are treated as separate species in MIM2). Modelled mixing ratios of both CH_3CHO and HCHO increase using MIM2, which improves the model-measurement agreement for CH_3CHO and worsens the agreement for HCHO. The MIM2 mechanism does not reproduce the high mixing ratios of organic peroxides observed in the free troposphere over the Guyanas, but their mixing ratios in the mixed layer over the Guyanas are reduced compared with the MIMvK run, improving the agreement with the GABRIEL mixed layer measurements.

Kubistin et al. (2008), using a box model, find that they are best able to simulate the GABRIEL OH measurements by simple omission of the isoprene oxidation chemistry. From a chemical budget analysis of our model (using both the MIMvK mechanism and the MIM2 mechanism), we find that globally, each molecule of isoprene emitted to the atmosphere ultimately forms about three molecules of carbon monoxide. In order to examine the effect of omitting isoprene from our global model, we switch off the isoprene flux,

and replace it with a mass of 60% equivalent carbon as CO. Global average CO mixing ratios are not changed significantly by this, although there are differences in the vicinity of isoprene source regions. Similarly, the OH concentration is increased over previously isoprene-emitting regions and decreased elsewhere.

We show the effect of this change on the comparison with the GABRIEL OH measurements in Fig. 6. Without the large sink of OH due to reaction with isoprene, the model now significantly overestimates the OH concentration in the lower part of the mixed layer, as we might expect given our overestimation of OH primary production in this region (Fig. 2). Model-measurement comparisons for other species measured during the campaign are shown in Fig. 4 of the Electronic Supplement http://www.atmos-chem-phys.net/8/ 4529/2008/acp-8-4529-2008-supplement.pdf to this paper. HO_2 is still underestimated in the model, and the modelled HO_2/OH ratio, which is greater than the measured ratio in the two runs involving isoprene, becomes lower than the measured ratio in the run with isoprene replaced by CO. These changes to OH and HO_2 are most pronounced in the mixed layer. The mixing ratio of all organic peroxides at low altitudes is reduced considerably in this simulation due to the lack of higher-order peroxides produced during isoprene oxidation. Our representation of HCHO has improved in this simulation, suggesting that our isoprene oxidation mecha-

nisms are producing too much HCHO. CH_3CHO mixing ratios in this simulation, on the other hand, do not change so much compared with the isoprene-containing simulations.

Ozonolysis of highly reactive as-yet unidentified NMHC has been suggested as a possible source of OH in the atmosphere (Kurpius and Goldstein, 2003; Di Carlo et al., 2004), although these compounds are also likely to be removed efficiently within the forest canopy (Ciccioli et al., 1999), and their impact on the atmosphere is likely to be restricted to the formation of aerosol particles (Goldstein and Galbally, 2007). As these as-yet unidentified NMHC are also likely to be highly reactive toward OH radicals, it is unclear whether they would represent a net source or a net sink of OH radicals. While we cannot rule out the possibility of an as-yet unidentified source of OH from unknown, highly reactive NMHC, we do note that the OH chemistry of the Guyanas, as simulated by our model, is highly sensitive to the treatment of isoprene.

3.1 Artificially enhanced OH recycling

Following the hypothesis of Lelieveld et al. (2008), that isoprene oxidation in nature recycles more OH radicals than the isoprene oxidation mechanisms currently in our model, we look within the isoprene oxidation mechanism itself for the missing OH. From a chemical budget analysis of our model, in which we calculate every possible isoprene degradation pathway from our chemical mechanisms based on globally averaged reaction rates, keeping track of side-effects and end products along the way, we find that globally, for October, the MIMvK mechanism recycles approximately 5% of all OH radicals consumed during the isoprene oxidation chain. MIM2 recycles about 10%. We define this OH recycling as the total number of OH radicals produced during all steps of the oxidation of isoprene to longer lived end products (mostly CO), divided by the total number of OH radicals consumed during this process, expressed as a percentage.

In order to estimate the amount of additional OH production required to match the GABRIEL measurements, we introduce an artificial source of OH into our isoprene oxidation mechanism. The first generation products of isoprene oxidation due to the OH radical are peroxy radicals. In regions of high NO_x these isoprene peroxy radicals react predominantly with NO to form carbonyl compounds. In regions of low NO_x, these isoprene peroxy radicals react more frequently with HO_2 to form isoprene peroxides, as shown in Eq. (1), where ISO_2 and ISOOH respectively represent all isoprene peroxy radicals and isoprene peroxides.

$$ISO_2 + HO_2 \rightarrow ISOOH \qquad (1)$$

In order to simulate an additional production of OH radicals in low NO_x regions, we add an artificial production of OH to these reactions between first generation peroxy radicals of isoprene and HO_2 radicals, as shown in Eq. (2).

$$ISO_2 + HO_2 \rightarrow nOH + ISOOH \qquad (2)$$
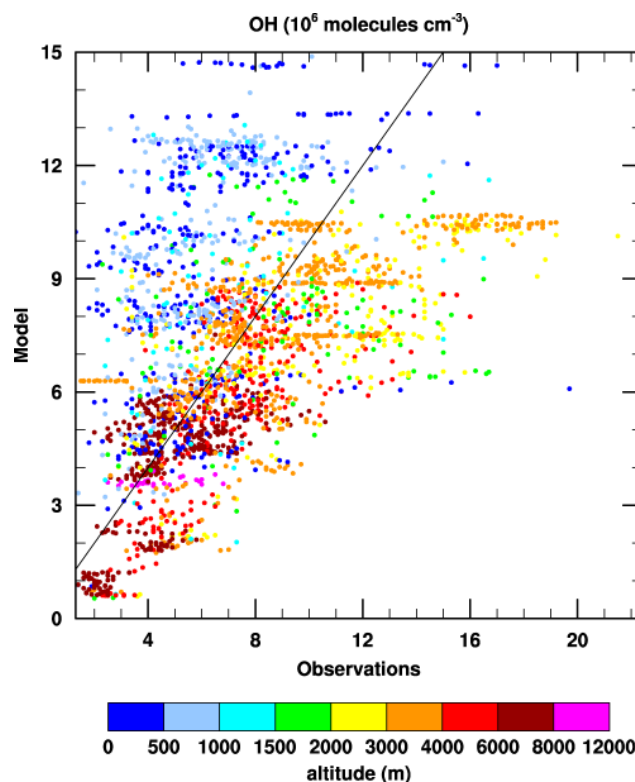

Fig. 6. Model-measurement comparison for OH observed during GABRIEL for the model run performed without isoprene.

We can vary the amount of this artificial OH production by varying the stoichiometric coefficient n of OH in the list of products for each of these reactions.

Figure 5 of the Electronic Supplement http://www.atmos-chem-phys.net/8/4529/2008/ acp-8-4529-2008-supplement.pdf to this paper shows the effect of adding progressively more artificial OH production to the MIM2 mechanism. From left to right we show the cases with one, two, and three OH radicals produced from these reactions. From top to bottom we show the vertical profile of the modelled OH chemical budget over the Suriname grid cell (including the production of artificial OH), the model-measurement comparison for OH, and the model-measurement comparison for isoprene.

There is a trade-off in our model between reproducing the isoprene measurements well and reproducing the OH measurements well. We achieve good agreement between the observed and modelled OH concentrations when we add three artificial OH radicals as products to the reactions of first generation peroxides of isoprene with HO_2 (Eq. 2). In this case, however, the modelled isoprene ratios fall below 1 nmol mol^{-1}, which is well below the mean isoprene mixing ratio measured during GABRIEL. The case with two artificial OH radicals increases the simulated OH in the mixed layer over the Guyanas by approximately a factor
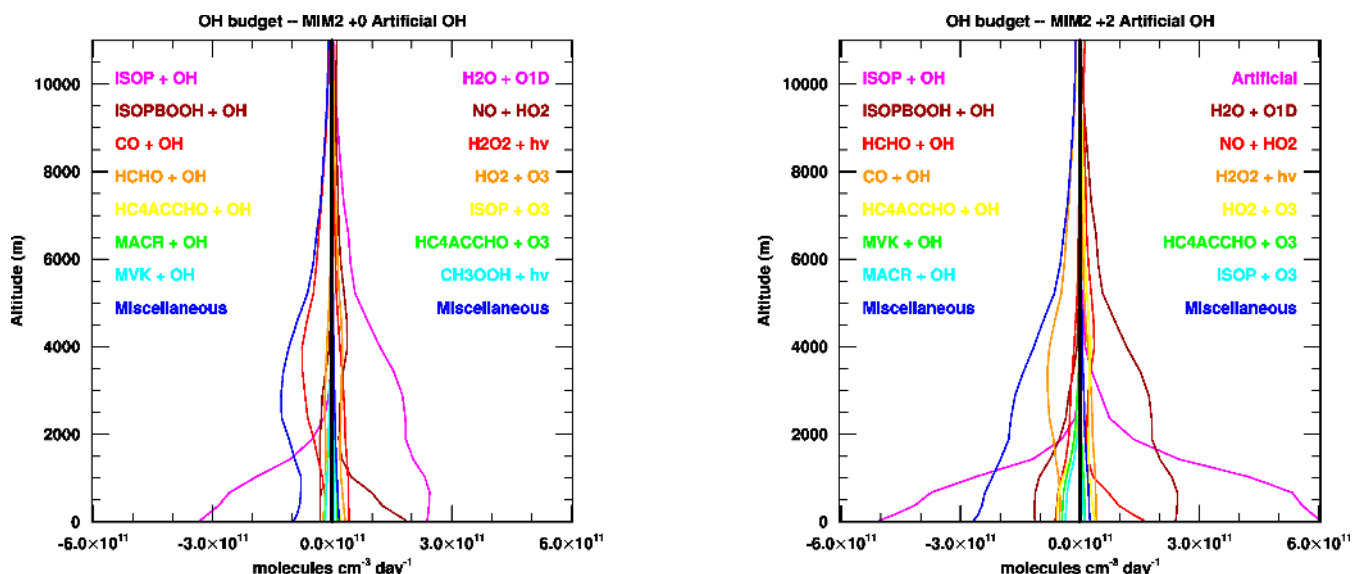
Fig. 7. Diurnally integrated vertical profiles of the modelled OH budget over the Suriname grid cell for the model runs without (left) and with (right) artificially enhanced OH recycling

of two, bringing these modelled OH concentrations closer to the lower bound of the 40% uncertainty in the measurements. This case seems to represent a good compromise between well-simulated OH and well-simulated isoprene, modelled mixing ratios of which are reduced by almost a factor of two compared with the MIM2 case. This corresponds with a global mean October OH recycling efficiency of 40% (increased from 10% in MIM2), and also corresponds to an additional source of two artificial OH radicals for every molecule of isoprene oxidised globally. This can also be expressed as a net cost of OH radicals for the entire global isoprene oxidation chain. The unaltered MIM2 mechanism requires four OH radicals for the oxidation of isoprene to its end products. The addition of two artificial OH radicals in Eq. (2) reduces this net cost of isoprene oxidation to three OH radicals per isoprene molecule, not to two radicals, as might be expected, because the extra OH leads to less photolysis of isoprene oxidation intermediates, which become more likely to react with OH.

We show the vertical profiles of the diurnally integrated OH budget terms in the Suriname grid cell from model runs performed with both $n=0$ and $n=2$ (Eq. 2) in Fig. 7. The new "artificial" source of OH becomes the dominant production term in the OH budget below about 2000 m altitude, and is comparable in magnitude to the OH sink due to reaction with isoprene in this grid cell. We show the comparison of OH and isoprene from this run with the GABRIEL measurements in Fig. 8. Comparisons with other species measured during the campaign are shown in Fig. 6 of the Electronic Supplement http://www.atmos-chem-phys.net/8/4529/2008/ acp-8-4529-2008-supplement.pdf to this paper. The effect on HO$_2$ of adding this artificial source of OH is small com-

pared with the change in OH, but these combined changes are enough to bring the modelled HO$_2$/OH into good agreement. The modelled mixing ratios of the isoprene oxidation intermediates do not change as much as either the modelled OH concentration or the modelled isoprene mixing ratio. Furthermore, they do not all change in the same direction with the addition of artificial OH. Compared with the base MIM2 run (Fig. 5 in this paper, and Fig. 3 of the Electronic Supplement http://www.atmos-chem-phys.net/8/4529/2008/ acp-8-4529-2008-supplement.pdf to this paper), the MIM2 run with artificial OH recycling produces increased mixing ratios of organic peroxides and HCHO, but decreased mixing ratios of CH$_3$CHO and MVK+MACR. This has a mixed effect on the comparison of our model with the GABRIEL observations: MACR+MVK improves, while the model-measurement comparison of organic peroxides, HCHO and CH$_3$CHO gets worse.

3.2 Isoprene chemistry and mixing

The problem remains that even with this relatively modest amount of extra OH (our simulated OH in the mixed layer is still about half of the OH concentration measured over the Guyanas), the model now severely underestimates the isoprene mixing ratio observed over Suriname. Given that we appear to be simulating the vertical mixing of isoprene within the mixed layer well (Fig. 3), possible reasons for this underestimation of the isoprene mixing ratio are that we are underestimating the flux of isoprene to the atmosphere in our model, or that we overestimate the effective rate constant for the reaction of OH with isoprene.
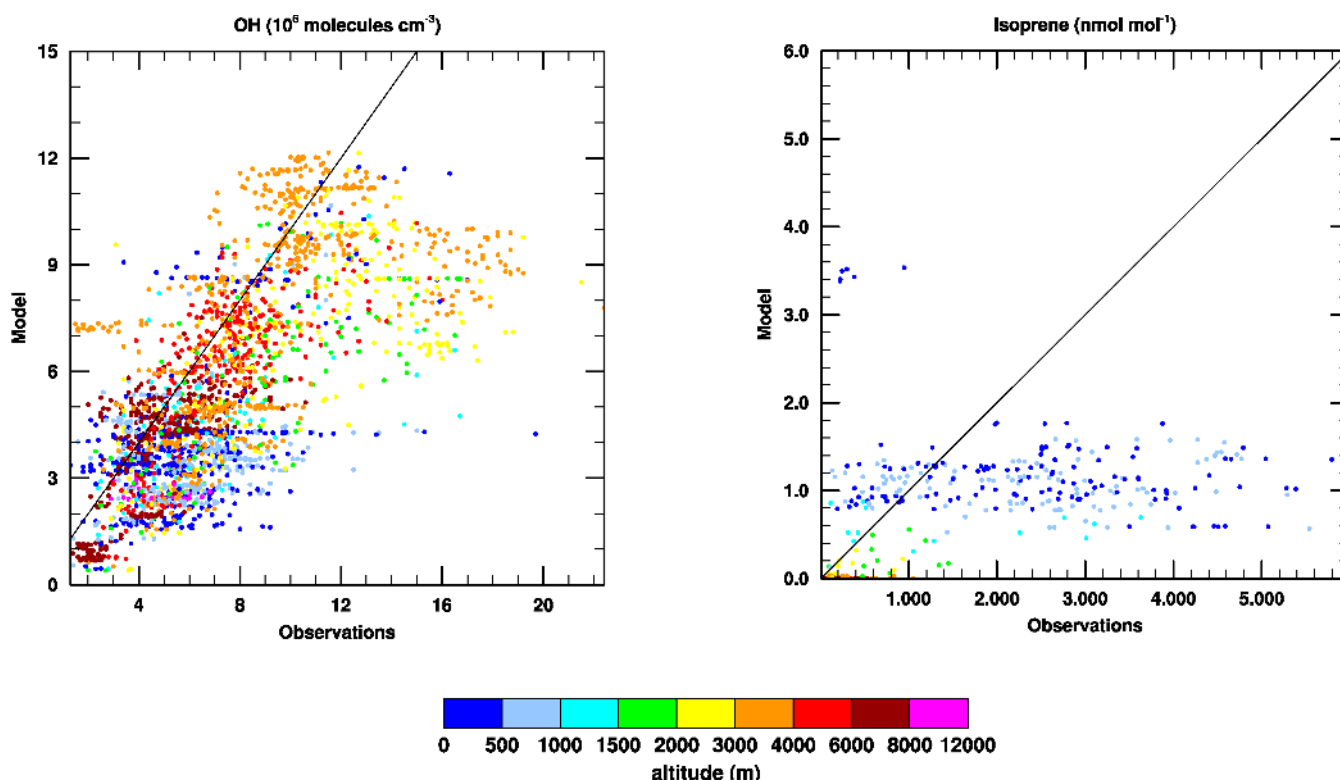
Fig. 8. Model-measurement comparison for OH and isoprene observed during GABRIEL for the run performed with MIM2 and two artificial OH radicals produced from the reaction of HO_2 with peroxides of isoprene.

Guenther et al. (2006) state an upper estimate on the global isoprene source of 660 Tg(C)/yr. This is 32% higher than the global annual isoprene flux in our model. Although our modelled isoprene flux is comparable to the isoprene flux derived from GABRIEL measurements (Sect. 3), we explore the effect of an increased isoprene flux in our model by performing a run with the global isoprene flux increased by 50%. We show the results of this run in Fig. 9. Compared with the run with the normal isoprene flux and two artificial OH radicals (Fig. 8), we improve the agreement between our modelled isoprene mixing ratios and those measured during GABRIEL when we increase the global isoprene flux in our model. Our modelled OH concentrations, however, which were already at the lower bound of the measurement uncertainty, are reduced to below the lower uncertainty bound for the measurements.

We show the model-measurement comparison for other species measured during the campaign in Fig. 7 of the Electronic Supplement http://www.atmos-chem-phys.net/8/4529/2008/acp-8-4529-2008-supplement.pdf to this paper. Our modelled mixing ratios of CO, which can be considered an end product of isoprene oxidation, are increased in our run with the higher isoprene flux, both in the mixed layer and in the free troposphere, degrading the model-measurement agreement. As the free troposphere over the Guyanas is strongly influenced by global background conditions, this increase in free tropospheric CO over the Guyanas represents the increase in global background CO due to a 50% larger global isoprene flux. The poorer agreement with the GABRIEL measurements when we increase the global isoprene flux indicates that our original global isoprene flux is more consistent with global background CO.

All of our modelled isoprene oxidation intermediates are also increased in this run, degrading the agreement with the measurements for organic peroxides, MACR+MVK and HCHO. It is possible that isoprene oxidation in nature recycles even more OH than the two OH radicals we assume in these runs. If we were to add yet more artificial OH recycling to our mechanism, then we would remove more MACR and MVK, improving our agreement with the measurements, but this extra OH would also remove isoprene, which would degrade our agreement with the measurements. This would then require us to increase the isoprene flux again. Perhaps there is some point at which an increased isoprene flux combined with increased OH recycling could produce agreement with measurements of both OH and isoprene, but we argue that this would also lead to more production of both CO and HCHO, which are already overestimated in this run based on the estimated upper limit of the global annual isoprene flux. We also note that it is currently impossible to explain the true
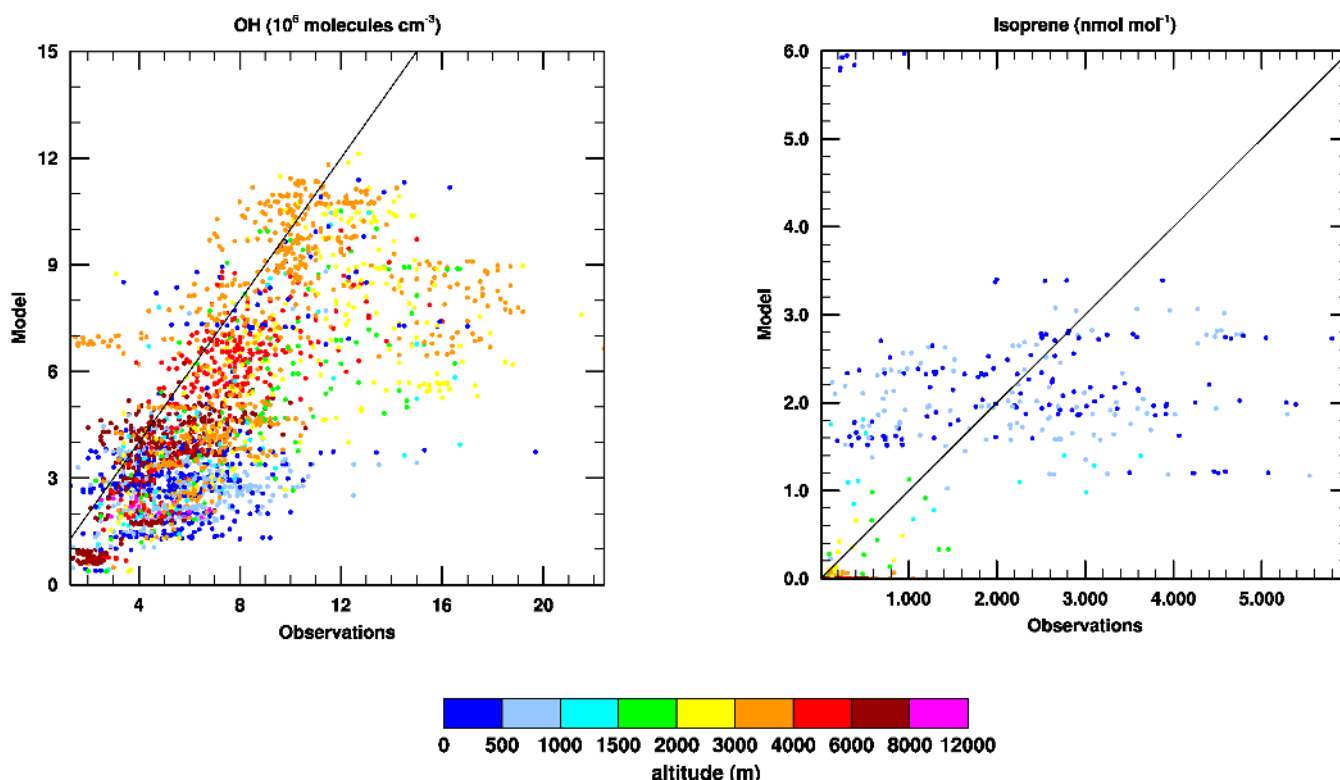
Fig. 9. Model-measurement comparison for OH and isoprene observed during GABRIEL for the run with both artificial OH and a 50% increase in the global isoprene flux.

origin of our artificial OH. If we were to add more of this artificial OH, explaining its origin would become even more difficult. From this we conclude that our original isoprene flux, both globally and from the Guyanas, is more consistent with the GABRIEL measurements than any increased flux.

The current IUPAC recommendation quotes a lower limit for the rate constant of isoprene+OH which is about 20% lower than the rate constant we use in our model. This lower value for the rate has also recently been confirmed by Campuzano-Jost et al. (2004). We have done a model run with this rate reduced by 20%, and noticed a 20% increase in isoprene mixing ratios, with negligible effect on OH.

Krol et al. (2000) show that effective rate constants for reactions of hydrocarbons with OH can be reduced by up to 30% compared with box model simulations of the mixed layer (where perfect mixing is implicitly assumed) when a heterogeneously distributed surface flux combined with inefficient mixing in the mixed layer leads to segregation of these reactive hydrocarbons from OH. This effect is largest when the chemical lifetime of the reactive hydrocarbon (τ_{chem}) is comparable to the turbulent mixing timescale (τ_{mix}), or $Da \approx 1$, where Da is the Damköhler number, defined as

$$Da = \frac{\tau_{\mathrm{mix}}}{\tau_{\mathrm{chem}}} \tag{3}$$

For the case shown in Fig. 8, our model calculates an isoprene lifetime of about half an hour in the mixed layer over the Guyanas. Recall that the OH concentration measured in the mixed layer during GABRIEL is approximately double what we simulate in this model run, implying an even shorter bulk lifetime for isoprene. Eerdekens et al. (2008) calculate a convective mixing timescale of about between 8 and 16 min during the GABRIEL campaign, which is similar to the 10 min "eddy turnover timescale" used in the Large Eddy Simulation (LES) modelling literature (Agee and Gluhovsky, 1999; Anfossi et al., 2006). It seems that we have a Damköhler number for isoprene of the order of unity over the Guyanas.

Verver et al. (2000) studied the isoprene+OH system and noticed no significant segregation effects, however their modelled OH concentrations were quite low ($\approx 5 \times 10^5$ molecules/cm^3, or an order of magnitude lower than those measured during the GABRIEL campaign), leading to substantially lower values of the Damköhler number for isoprene than we calculate for our model. Our model generally contains about eight resolved levels in the mixed layer over Suriname during the afternoon when the height of the mixed layer is at its greatest, but is not capable of resolving the turbulent eddys which are responsible for mixing in the mixed layer. This is clearly an issue which deserves future attention with more resolved models.
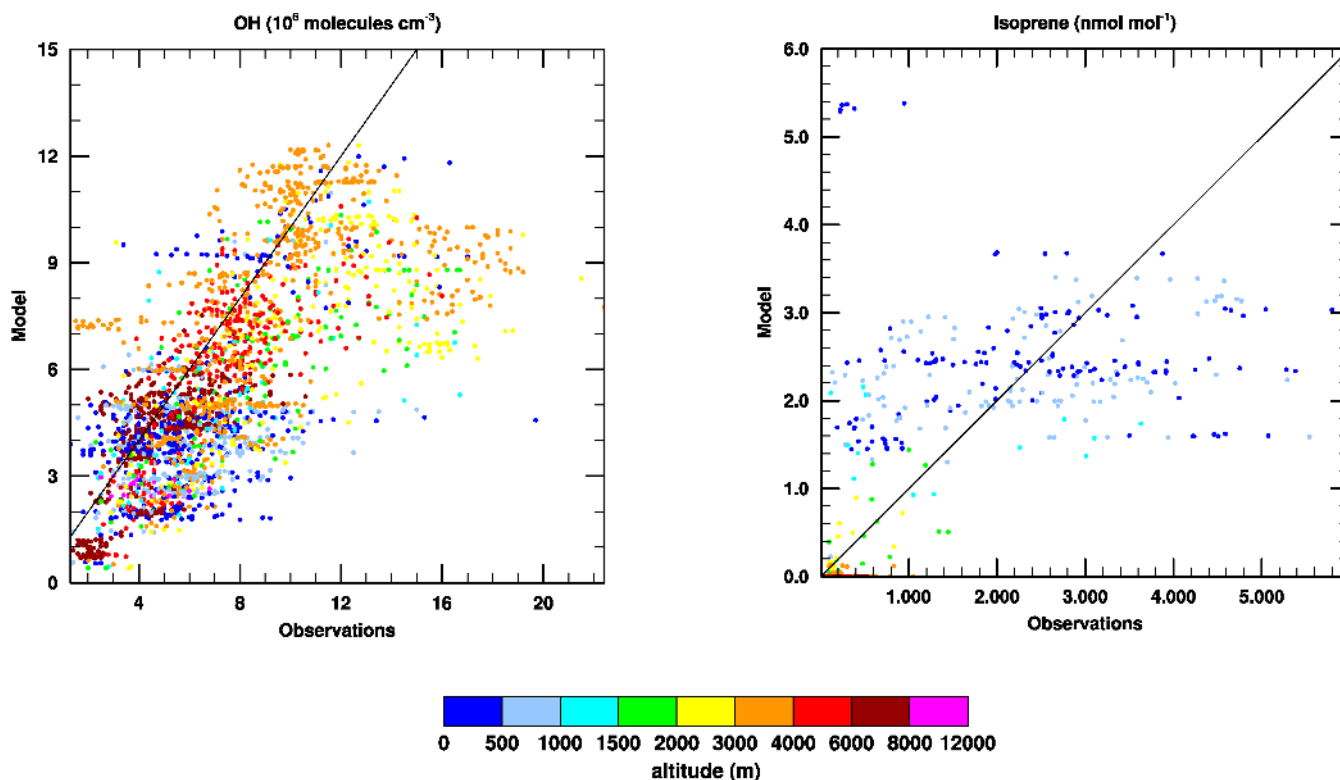
Fig. 10. Model-measurement comparison for OH and isoprene observed during GABRIEL for the run with both artificial OH and the reduced rate constant for isoprene+OH.

We have calculated the intensity of segregation between isoprene and OH from the GABRIEL measurements of OH and isoprene using the formula

$$< I_{s,A+B} >= \frac{< A'B' >}{< A >< B >} \qquad (4)$$

where A and B are the concentrations of isoprene and OH, primes represent deviations from the average, and angle brackets represent averages over all of the GABRIEL measurements for which valid measurements of OH and isoprene coincide. The intensity of segregation influences the volume-averaged effective reaction rate constant $<k_{A+B}>$ according to the formula

$$< k_{A+B} >= k_{A+B}(1+ < I_{s,A+B} >) \qquad (5)$$

where k_{A+B} is the laboratory rate constant. Positively correlated deviations of A and B lead to a higher effective rate constant, while anticorrelated deviations reduce the effective rate constant. Based on 5 s average OH measurements, and approximately 2 s average isoprene measurements falling inside these 5 s OH measurement windows, we calculate an intensity of segregation between OH and isoprene of -0.13, which corresponds to a reduction in the effective rate constant of 13%. Due to this 5 s averaging time combined with the high speed of the aircraft in the mixed layer ($>100\,\mathrm{ms}^{-1}$), these measurements can not be expected to capture the fine

structures involved in mixing. These measurements represent averaged conditions over larger spatial scales than the scales over which we expect reactants to be segregated. We expect, therefore, that the intensity of segregation between isoprene and OH in the mixed layer over the Guyanas in October 2005 will have been more negative than the -0.13 which we calculate from the GABRIEL measurements.

Based on our previously noted insensitivity of OH concentration to changes to the effective OH+isoprene rate constant, as well as our underestimation of isoprene mixing ratio by approximately 50% in our run with a production of two artificial OH radicals (Fig. 8), we determine that a reduction in the effective OH+isoprene rate constant of 50% (relative to the lower bound of the range recommended by IUPAC) is necessary to produce good agreement between model and measurements. We show the model-measurement comparison of OH and isoprene for this simulation (still with a production of two artificial OH radicals in Eq. 2) in Fig. 10. This is equivalent to an intensity of segregation between isoprene and OH of -0.5. We note that this method of determining the intensity of segregation should be considered a "top-down" approach, in which we effectively treat $<I_{s,A+B}>$ as the single unknown in Eq. (4). The effect of this reduction in the isoprene + OH rate constant is an approximate doubling of the simulated isoprene mixing ratio

over the Guyanas when compared with the run using MIM2 with two artificial OH radicals. The simulated isoprene is now in much better agreement with the GABRIEL measurements. The effect on OH of this change is fairly small, although simulated OH from this run is slightly closer to the GABRIEL measurements than in the previous run. We show the model-measurement comparison for other species measured during the campaign in Fig. 8 of the Electronic Supplement http://www.atmos-chem-phys.net/8/4529/2008/acp-8-4529-2008-supplement.pdf to this paper. The change in the isoprene+OH rate constant reduces the modelled mixing ratios of organic peroxides and MACR+MVK (bringing these modelled mixing ratios closer to the mixing ratios observed during the GABRIEL campaign). Simulated mixing ratios of CH_3CHO and HCHO remain largely unchanged in this simulation compared with the previous simulation. We still underestimate the CH_3CHO measurements and overestimate the HCHO measurements.

Krol et al. (2000) found that the intensity of segregation between reactive hydrocarbons and OH is increased when the heterogeneity of the surface flux is taken into account, and they report a maximum effect on the average bulk reaction rates between reactive hydrocarbons and OH of 30%. This corresponds with an intensity of segregation of -0.3, which is not as great as the -0.5 which we must assume if our model is to agree with both the OH and the isoprene measured during GABRIEL. In order to avoid numerical instabilities in their model, Krol et al. (2000) used a surface flux of reactive hydrocarbon which was distributed according to a relatively smooth Gaussian emission function. The isoprene flux at the forest canopy can be expected to be more heterogeneously distributed still, and therefore lead to a larger intensity of segregation between isoprene and OH, and therefore a larger reduction in the effective rate constant for reaction between OH and isoprene than the 30% suggested by Krol et al. (2000) as a maximum effect. It is also reasonable to expect that the isoprene flux at the forest canopy coincides with fluxes of other, more reactive NMHC, and that these NMHC may deplete OH in isoprene-rich dry convective plumes, which may amplify the intensity of segregation between isoprene and OH, thus further lowering the effective rate constant for reaction between OH and isoprene.

LES studies (Avissar and Schmidt, 1998) have found that the influence of heterogeneity in the surface heat flux on boundary layer dynamics largely decreases if the winds are stronger than approximately $2.5\,ms^{-1}$. We have examined the routine observations taken at the observing station "SJMP", which is located at Zanderij International Airport, the base used by the learjet during the GABRIEL campaign. Filtering these data for observations taken during the campaign between the hours of 12:00 UTC and 20:00 UTC (the times of day during which GABRIEL flights were made), we find (based on 59 observations) that the average wind speed was $3\,ms^{-1}$, with a standard deviation of $1.5\,ms^{-1}$. Calm conditions were reported 8.5% of the time. The influence of

wind speed on the effect of heterogeneities in the surface flux of reactive trace gasses remains an interesting topic for future investigation.

4 Global implications

In order to examine the global implications of our changes to the isoprene oxidation mechanism, the OH recycling efficiency, and the effective rate constants in the isoprene-OH system, we have performed four year-long simulations: a simulation with the MIMvK mechanism (MIMvK); a simulation with the MIM2 mechanism (MIM2); a simulation with MIM2 and a production of 2.5 artificial OH radicals from Eq. (2) (MIM2+); and a simulation with MIM2 including a production of 2.0 artificial OH radicals from Eq. (2), and with an effective rate constant for reaction between OH and isoprene of 50% lower than the lower bound recommended by IUPAC (MIM2+Slow). Of course, the 50% intensity of segregation which we have determined here is necessary in order to correctly simulate both isoprene and OH is only applicable to the Guyanas, but we examine the effects of applying it to the whole globe in our last sensitivity simulation.

For our MIMvK simulation, we calculate a global methane lifetime of 7.3 yr. Our calculated methane lifetime is 0.1 yr shorter than the lower uncertainty bound of the methane lifetime quoted in the IPCC-AR4 (8.7 ± 1.3 yr, Denman et al., 2007). Compared with a 26-model intercomparison (Stevenson et al., 2006), our methane lifetime is 1.1 standard deviations below the model ensemble mean methane lifetime of 8.7 yr. For our MIM2+Slow run, we calculate a methane lifetime of 7.0 yr. The effect of all of our changes to the isoprene oxidation mechanism on the global methane lifetime is a reduction of 0.3 yr, or 4%. This represents 23% of the standard deviation among the 26 models from the study of Stevenson et al. (2006).

We compare the results of each of our four year-long simulations with measurements of isoprene, OH, and NO from three field campaigns (AEROBIC97, PROPHET98, and PMTACS-NY) in Table 1. It should be noted that during these campaigns NO mixing ratios are typically up to an order of magnitude higher than during GABRIEL, even under the selected lowest-NO conditions. We clearly do a poor job in our simulation of the AEROBIC97 campaign, significantly underestimating isoprene mixing ratios while overestimating NO and OH. Harrison et al. (2001) mention that the dominant plant species in the region had not been previously thought to emit isoprene. This probably explains why our modelled isoprene emissions are so low. For PROPHET98 and PMTACS-NY, we correctly simulate low-NO_x environments. Our simulated isoprene for the PROPHET98 campaign is an order of magnitude too low. Apel et al. (2002) show a peak isoprene flux over this site of about $4\,mg(C)\,m^{-2}\,h^{-1}$. Our model calculates a flux twenty times smaller than this, explaining our underestimation of the

Table 1. Measured OH concentrations ($\times 10^6$ molecules cm^{-3}) and mixing ratios of isoprene (nmol mol^{-1}) and NO (pmol mol^{-1}) at local noon from three field measurement campaigns compared with various runs of our model.

AEROBIC97					
	Measured	MIMvK	MIM2	MIM2+	MIM2+ Slow
Isoprene[a]	1	0.01	0.01	0.01	0.08
OH[b]	4	16	15	16	15
NO[b]	<100	130	130	120	120

PROPHET98					
	Measured	MIMvK	MIM2	MIM2+	MIM2+ Slow
Isoprene[c]	2	0.3	0.3	0.1	0.4
OH[d]	4	5	5	7	7
NO[d]	<100	57	55	41	44

PMTACS-NY					
	Measured	MIMvK	MIM2	MIM2+	MIM2+ Slow
Isoprene[e]	<1	0.7	0.6	0.2	0.9
OH[e]	3	5	5	8	8
NO[e]	≈100	70	77	76	60

[a] Harrison et al. (2001).
[b] Carslaw et al. (2001).
[c] Apel et al. (2002).
[d] Tan et al. (2001).
[e] Ren et al. (2006).

measured isoprene mixing ratios. Without artificial OH recycling, our modelled OH over the PROPHET98 site is quite close to the observations. When we add this artificial recycling, our OH becomes a factor of two too high. Perhaps if we were to get the isoprene flux about right, we might get closer to the observed OH. For PMTACS-NY, we correctly simulate low mixing ratios of isoprene, although this is with OH concentrations higher than observed. If our OH were to be closer to the measurements, we would probably have too much isoprene. We are not aware of any measurements, either direct or indirect, of the isoprene flux during the PMTACS-NY campaign, but it appears, based on the above discussion, that our modelled flux may have been higher than the actual flux during this campaign. A possible reason for our overestimation of OH at this site is that our model lacks biogenic NMHC other than isoprene, which according to Ren et al. (2006) formed a very large fraction of the total OH reactivity measured during the PMTACS-NY campaign.

We show the effect of all of our changes to the MIM2 isoprene oxidation mechanism (OH recycling and reduction of the effective rate constant for OH+isoprene) on the chemistry of the boundary layer in Fig. 11, where we compare the MIM2+Slow model run with the MIM2 model run.

Differences between MIM2 and MIMvK are described in Taraborrelli et al. (2008). For all of the panels comparing isoprene in the mixed layer (right hand side of Fig. 11), we have restricted the comparison to grid cells which have a boundary layer integrated column density of at least 1×10^{14} molecules cm^{-2}, which is approximately two orders of magnitude lower than the global peak value.

From Fig. 11, we see that the Amazon region, including the Guyanas, is unique in the world, in that the combined effect of extra OH recycling and a reduced effective OH+isoprene rate constant is a year-round decrease in our modelled isoprene mixing ratios in the mixed layer of between about 10 and 50% over several contiguous model grid cells. This effect is also seen in tropical southern Africa and north eastern Australia, but is restricted to the summer and autumn months. Such large effects on our modelled isoprene mixing ratios also usually coincide with increases in our modelled OH radical concentrations of around 100%, or a doubling of the OH concentration, which is necessary in order to overcome the 50% reduction in the OH + isoprene effective rate constant. Over other regions of the globe, and at other times of the year, the extra OH recycling we introduce has the effect of increasing OH in the mixed layer by more
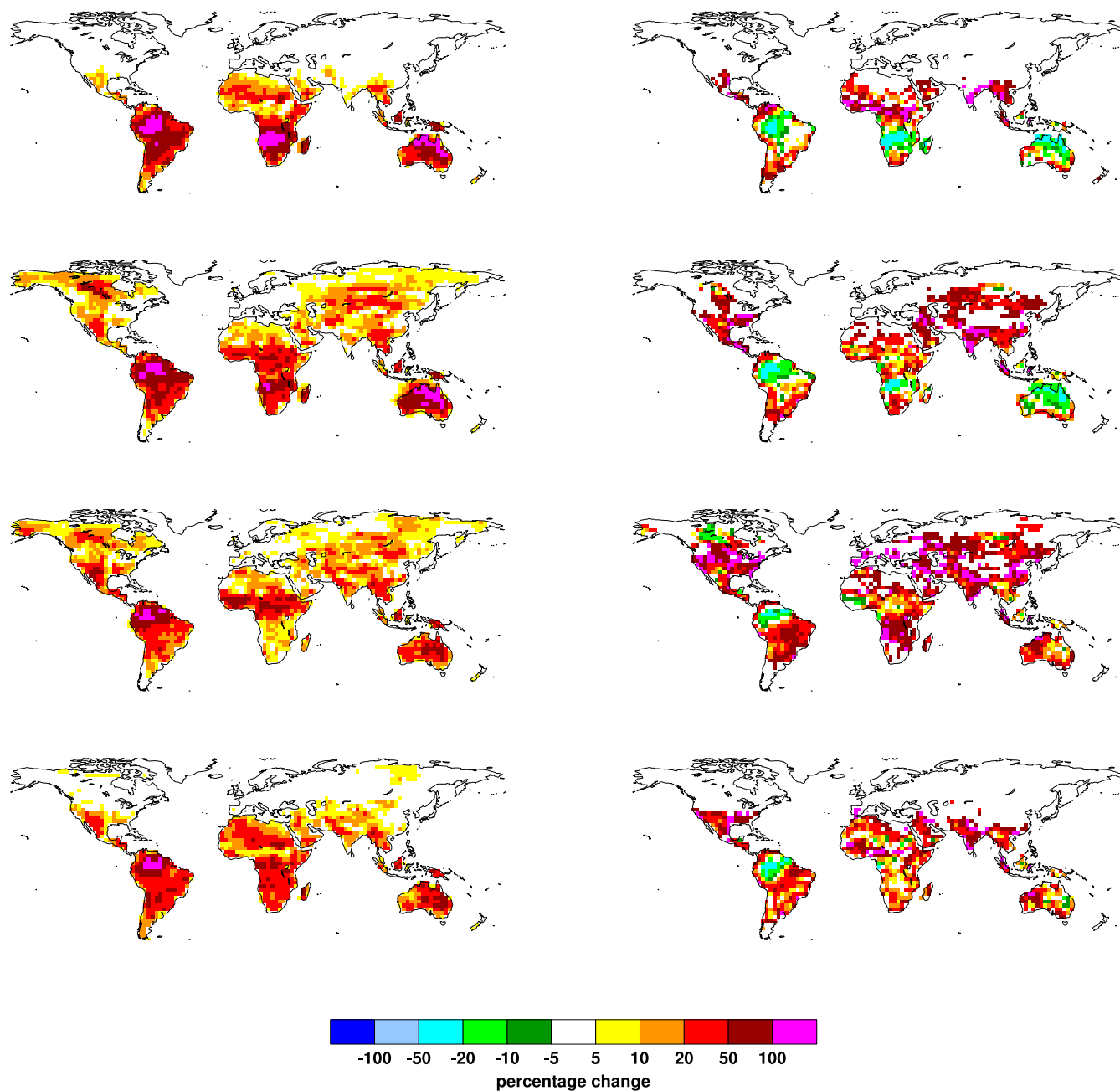
Fig. 11. Percentage change in mixed layer-integrated density of OH (left) and isoprene (right) in the MIM2+Slow run compared with the MIM2 run. From top to bottom we show: the seasonal averages for December, January and February; March, April, May; June, July, August; and September, October, November.

modest amounts, leading to net increases in our modelled isoprene mixing ratios. We also notice some large increases in modelled isoprene mixing ratios in NO_x-rich regions (e.g. north eastern USA, India) where OH production due to artificial recycling is negligible, but our reduced effective rate constant is still in effect.

5 Conclusions

We have presented a comparison between measurements made during the GABRIEL field campaign, conducted over the Guyanas in October 2005, and model runs performed with the ECHAM5/MESSy AC-GCM. As is the case for other models, our model in its standard configuration significantly underestimates the concentration of OH radicals over the Amazon. This is also true for our model despite its overestimation of OH primary production. The addition of a fully revised isoprene oxidation mechanism does not significantly improve our simulation of OH. In order to approach the lower uncertainty bound on the GABRIEL OH measurements, we must introduce an artificial source of OH into our model in regions where isoprene is oxidised by OH under low NO_x conditions. The magnitude of our artificial OH source represents an increase in the OH recycling efficiency of the isoprene oxidation chain from 10% (under the MIM2 mechanism) to 40% (with the artificial OH). This may be a conservative estimate of the required additional OH recycling, given the overestimation of OH primary production in our model. Lelieveld et al. (2008) show results from a run with an imposed recycling efficiency of 50%, which produces even better agreement with the OH measured during GABRIEL (though a further degradation in the agreement with isoprene).

This study has not gone into detail speculating about the possible origins of the missing OH required by our model in order to match the GABRIEL OH measurements. We have instead focused on determining the approximate magnitude of the required extra source of OH, and exploring some of the implications of this required OH source for atmospheric chemistry. Future studies will make use of new chemical mechanisms under development and compare simulations performed using these mechanisms with the GABRIEL measurements in an attempt to determine which processes might be producing the extra OH to which we simply refer in this study as "artificial OH". In our study, the artificial OH is simply added into an existing mechanism. The other product yields are therefore not consistent with there being an extra source of OH. Organic peroxides, for example, might be reduced in future model runs involving recycling of OH through reactions of organic peroxy radicals or increased photolysis of the organic peroxides themselves. This may also explain why we have too much organic peroxide in the mixed layer, along with too much HCHO.

Based on our model runs, it appears highly unlikely that such high OH concentrations can exist in the mixed layer alongside the isoprene mixing ratios measured during GABRIEL. This apparent paradox is solved by reducing the effective rate constant for the reaction of isoprene with OH by about 50%. The physical basis for this is the separation of the two reactants, OH and isoprene, within the mixed layer due to inefficient mixing. The GABRIEL measurements do not provide enough temporal and spatial resolution to confirm that this intensity of separation between isoprene and OH in fact existed during the GABRIEL campaign, although our argument is strengthened by the high variability in the isoprene mixing ratio observed during the campaign. We recommend further measurement in similar regions using techniques able to resolve the necessary scales.

Compared with the isoprene oxidation scheme in the MIMvK chemical mechanism, the new MIM2 mechanism produces a better agreement between the observed and modelled mixing ratios of the sum of methacrolein and methyl vinyl ketone (MACR+MVK), especially when the mechanism is adjusted to match the observed OH and isoprene by introducing artificial OH recycling and reducing the effective OH+isoprene rate constant. Both mechanisms, however, consistently underestimate the observed CH_3CHO mixing ratios (which has implications for PAN production) and overestimate the observed HCHO (which could have implications for efforts to determine isoprene emissions using space-based observations of HCHO). Measurements of total organic peroxide mixing ratios over the Guyanas are also poorly simulated by our model. Improvements to our chemical mechanism do improve the model-measurement agreement at low altitudes, but we remain unable to simulate the high mixing ratios of organic peroxides observed in the free troposphere during the GABRIEL campaign.

Our year-long model runs show that our addition of OH recycling and our reduction of the effective OH+isoprene rate constant produce a consistent year-round decrease in modelled isoprene mixing ratios over the Amazon. Overestimation of isoprene mixing ratios in this region at all times of the year has been a problem with many global atmospheric chemistry models. Our results here allow us to use isoprene fluxes in our model which are based on a large number of observations of isoprene fluxes at scales ranging from leaf to ecosystem, without overestimating the available observations of isoprene mixing ratio. We also see such a reduction in modelled isoprene mixing ratios over tropical southern Africa, and north eastern Australia during the summer and autumn months. We are not aware of any measurements of isoprene in these regions with which to compare our model output. Our combination of OH recycling and segregation of reactants also leads to our model predicting higher isoprene mixing ratios in some regions. In order to better understand this complex isoprene-OH oxidation system, we recommend many more field campaigns in which isoprene fluxes and mixing ratios are measured alongside OH and

other supporting measurements, as well as laboratory work to better determine reaction rates and product yields of all species involved in the isoprene oxidation chain.

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