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**Simulating
atmospheric
composition over a
tropical rainforest**

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Simulating atmospheric composition over a South-East Asian tropical rainforest: Performance of a chemistry box model

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Atmospheric composition and chemistry above tropical rainforests is currently not well established, particularly for south-east Asia. In order to examine our understanding of chemical processes in this region, the performance of a box model of atmospheric boundary layer chemistry is tested against measurements made at the top of the rainforest canopy near Danum Valley, Malaysian Borneo. Multi-variate optimisation against ambient concentration measurements was used to estimate average canopy-scale emissions for isoprene, total monoterpenes and nitric oxide. The excellent agreement between estimated values and measured fluxes of isoprene and total monoterpenes provides confidence in the overall modelling strategy, and suggests that this method may be applied where measured fluxes are not available. The largest contributors to the optimisation cost function at the point of best-fit are OH (41%), NO (18%) and total monoterpenes (16%). Several factors affect the modelled VOC chemistry. In particular concentrations of methacrolein (MACR) and methyl-vinyl ketone (MVK) are substantially overestimated, and the hydroxyl radical [OH] concentration is substantially underestimated; as has been seen before in tropical rainforest studies. It is shown that inclusion of dry deposition of MACR and MVK and wet deposition of species with high Henry's Law values substantially improves the fit of these oxidised species, whilst also substantially decreasing the OH sink. Increasing [OH] production arbitrarily, through a simple OH recycling mechanism, adversely affects the model fit for volatile organic compounds (VOCs). Given the constraints on isoprene flux provided by measurements, a substantial decrease in the rate of reaction of VOCs with OH is the only remaining option to explain the measurement/model discrepancy for OH. A reduction in the isoprene + OH rate constant of 50–70% is able to produce both isoprene and OH concentrations within error of those measured. Whilst we cannot rule out an important role for missing chemistry, particularly in areas of higher isoprene flux, this study demonstrates that the inadequacies apparent in box and global model studies of tropical VOC chemistry may be more strongly influenced by representation of detailed

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physical and micrometeorological effects than errors in the chemical scheme.

1 Introduction

Global emission of non-methane biogenic volatile organic compounds (BVOCs) are estimated to total 1150 Tg C yr⁻¹ (Guenther et al., 1995) and exceed those of their anthropogenic counterparts by a factor of 10 (WMO, 1995). Furthermore BVOCs typically have much shorter atmospheric lifetimes than anthropogenic VOCs and hence are believed to play a dominant role in the chemistry of the planetary boundary layer (PBL) and lower troposphere (Fuentes et al., 2000). A modelling study by Poisson et al. (2000) found that BVOCs could affect the composition of the entire troposphere due to the formation of longer-lived intermediates (e.g. CO), with strong increases in O₃ and depletion in boundary layer OH concentrations being observed. Convection of BVOC oxidation products is a major source of HO_x in the upper atmosphere (Poisson et al., 2000; Tan et al., 2001), whilst relatively long-lived oxides of nitrogen such as PAN can influence remote tropospheric NO_x, and hence ozone, chemistry. Much work has been carried out on defining the reactions of these species (Jenkin et al., 2007; Saunders et al., 2003; Pinho et al., 2005), however, due to the number of compounds and complexity of the reaction schemes involved, their precise roles in controlling chemical budgets and processes in the atmosphere are poorly understood.

Over half the world's forests are found in the tropics, and, due to the prevailing high temperatures and solar fluxes, they are believed to account for almost half of all BVOC emissions to the atmosphere (Guenther et al., 1995). In recent years knowledge of tropical BVOC emissions and chemistry has been greatly increased by several measurement studies (e.g., Kuhn et al., 2004, 2007; Karl et al., 2007) and modelling studies (e.g., Lelieveld et al., 2008; Butler et al., 2008; Ganzeveld et al., 2008; Kubistin et al., 2008). In particular, flaws have been suggested in the current understanding of the reaction of isoprene and OH under low [NO_x] conditions, resulting in questions about current understanding of global oxidant budgets.

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Rapid land-use change makes it imperative to understand the chemistry of tropical forests, both for a holistic understanding of natural processes, and to predict the effect of such land-use changes on local/regional photochemistry and climate change. Therefore it is important to test current photochemical models, currently optimised for the polluted mid-latitudes, in this relatively pristine environment. Reproducing measurements at box-model level is an important step towards generating accurate predictions from global and regional models.

This study tests the performance of the CiTTyCAT box model of atmospheric chemistry against measurements made at Bukit Atur, Sabah, Malaysian Borneo, as part of the Oxidant and particle photochemical processes above a South-East Asian tropical rain forest (OP3-Danum-08) field campaign (Hewitt et al., 2009). Particular attention is paid to the replication of the concentrations of BVOCs and their oxidants under the low NO_x conditions observed. First, the measurement site (§2) and model parametrisation (§3) are outlined. Then the model is used to generate estimates of biogenic emissions from the site (§4) and the resultant model output is compared to observations and improvements suggested (§5). This is followed by an investigation of the relationship between isoprene and OH (§6).

2 Measurement site description

The OP3-Danum-08 field campaign was carried out in three phases: (i) ground-based measurements only, during April/May 2008, (ii) a reduced set of flux and concentration measurements at a nearby oil palm estate during May/June, and (iii) both ground and aircraft measurements, during June/July 2008. We focus here on measurements made during the first campaign, OP3-1. Ground-based measurements of atmospheric composition were primarily made at the Bukit Atur Global Atmospheric Watch station (4° 58' 59" N, 117° 50' 39" E) (Hewitt et al., 2009). These measurements included concentrations of NO, NO₂, NO_y, O₃, OH, HO₂ (3rd campaign only), HO₂ + RO₂, PAN, organic nitrates, isoprene, total and speciated monoterpenes and oxygenated organic

compounds (formaldehyde and glyoxal). Fluxes of isoprene, total monoterpenes, O₃, latent and sensible heat were also measured. Physical parameters measured included relative humidity, wind, mixing height and J(O¹D). A detailed description of the site and measurements is given in Hewitt et al. (2009). Most measurements were made at a height of 5 m above the ground, with the exception of PAN (30 m) and VOCs (5 m and 75 m). Fluxes were measured at 75 m using eddy covariance (Langford et al., 2009). The present study uses VOC concentrations at 75 m, as the extra distance from their surface source should provide a better approximation to the mean mixed boundary layer concentrations.

3 Model description and parametrisation

The CiTTYCAT atmospheric chemistry model (Wild et al., 1996; Evans et al., 2000; Emmerson et al., 2004; Donovan et al., 2005) was run in stationary-box mode at ground level over the Bukit Atur GAW site. Unless otherwise stated, all model species are allowed to evolve freely and are not constrained to observations. Hence, the model provides a bridge between 0D constrained box studies (e.g., Emmerson et al., 2007, and other papers this issue) and global models (e.g., Cook et al., 2007, and other papers this issue). Model runs were carried out for 8-day periods to achieve a nearly steady diurnal cycle, with all model-data comparisons being made using output from the last day. The model was initialised using average measured midnight concentrations, however the results are insensitive to the initial conditions. Isoprene chemistry follows the MIM2 scheme (Taraborrelli et al., 2009) and monoterpene chemistry is split equally between the α -pinene (Jenkin, 1996) and d-limonene (Stockwell et al., 1997) schemes, representing the approximately equal split between more- and less-reactive monoterpenes seen in GC-FID measurements at Bukit Atur. The average diurnal temperature variation measured at Bukit Atur is used. Photon fluxes are calculated using the on-line photolysis scheme (Wild et al., 1996). As no direct measurements of cloud cover were made, model cloud cover is adjusted such that the generated diurnal vari-

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ation of the photolysis frequency of ozone to form excited oxygen atoms, $J(\text{O}^1\text{D})$, fits the average measured at the site.

Surface emissions of BVOCs, NO, CO and CH_4 were emitted into the box at each timestep and are assumed to be mixed instantaneously throughout the box. CH_4 and CO are emitted following Ohara et al. (2007), whilst BVOC and NO emissions are described in §4. The box height is defined during the day by the height of the well-mixed PBL, which LIDAR (light detection and ranging) measurements indicate to be 800 m between 10:00–18:00 LT (Pearson et al., 2009). Upon collapse of the boundary layer at 18:00 LT, the box is split into two separate layers, the lower one representing the inversion-capped surface layer, and the upper one representing the residual layer. These layers are integrated separately with no mixing between them. When turbulent mixing is re-initiated between 08:00–10:00 LT the following morning (Pearson et al., 2009), the residual layer concentrations are gradually mixed into the lower box as the mixing height rises, until the lower box has engulfed the residual layer. In the absence of reliable measurements, the nighttime PBL height is set at 200 m following sensitivity studies of the measurement fit. No other mixing is permitted.

Dry deposition is included for O_3 , NO_x , N_2O_5 , HNO_3 , HO_2NO_2 , H_2O_2 , HCHO, CH_3CHO , CH_3OOH , $\text{CH}_3\text{CO}_3\text{H}$, PANs and isoprene nitrates using the values listed in Evans et al. (2000). The deposition velocity for isoprene nitrates is assumed to be as for HNO_3 following Horowitz et al. (2007). Wet deposition is considered in §5.2.

4 Emissions optimisation

Hewitt et al. (2009) report an average midday NO_x concentration of 200 ppt. In such a remote NO_x -limited scenario, accurate emissions of NO are vital to effective modelling. However above-canopy measurements of NO fluxes at Bukit Atur are not available. Therefore it is necessary to make an estimate of the emission from the available ambient concentration data. This estimation process was also used to estimate isoprene and total monoterpene fluxes, as a cross-check. A tri-variate sensitivity

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study of 336 runs was carried out, varying 24-h average NO emissions from 0.005 to 0.011 mg N m⁻² h⁻¹ and monoterpene and isoprene emissions from 0.06 to 0.24 and 0.14 to 0.37 mg m⁻² h⁻¹ respectively. The selection of these ranges was informed by previous coarser resolution runs, covering a wider range of values. The isoprene emission followed a diurnal cycle defined by its characteristic light dependence (Guenther et al., 2006). Monoterpene emission was set to follow a the same diurnal cycle as isoprene, following the findings of Kuhn et al. (2004) and the OP3 measurements, which also suggested very little monoterpene emission during the night. A cost function was then run over the model output to locate the optimum emission fluxes that replicate the concentrations observed in the field. The cost function uses OP3-1 campaign-median values for each hour of a 24-h cycle for OH, NO, NO₂, O₃, isoprene, monoterpenes and HO₂+RO₂, in the form,

$$C_{\text{total}} = \sum_{t=10}^{t=18} \sum_{i=1}^n \left(w(i) \frac{|x_i(t) - \hat{x}_i(t)|}{\hat{x}_i(t)} \right) \quad (1)$$

where C_{total} is the total cost, a dimensionless metric where small numbers indicate a better fit, t is the hour of the day, n is the number of species used in the fitting, \hat{x}_i is the campaign median concentration of a species for each hour of the day and x_i is the modelled concentration of that species, w is a weighting function for that species (typically $w = 1$). Only 10:00–18:00 LT concentrations were used, as LIDAR measurements give confidence that the flux tower is fully enveloped by the PBL during that period, and hence the well-mixed assumption of the model is valid. Median values are selected to represent the “typical” day, and eliminate the influence of extreme events. To reflect the fact that the OH and HO₂ + RO₂ measurements may carry more uncertainty, the function was also run with $w = 0.5$ for these species. The result returned was virtually identical, indicating a robust fit with respect to the observations.

The best-fit cost function result of $C_{\text{total}} = 1.57$ was found at a 24-h-average monoterpene emission of 0.15 mg m⁻² h⁻¹, isoprene emission of 0.23 mg m⁻² h⁻¹ and NO emission of 0.009 mg N m⁻² h⁻¹. It can be seen from Fig. 1 that the region of values below

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$C_{\text{total}} < 1.65$ (coloured dark blue) is quite broad. The best fit is located at the furthest-right point of this dark blue area (black dot in Fig. 1), however this quite broad general minima indicates that monoterpene emissions can be traded on an approximately 1:1 basis for isoprene emissions for only a small penalty in fit. This is not altogether surprising given the broadly comparable atmospheric chemistry and lifetimes of these species, at least as far as the model is concerned. It was not possible to use observations of methacrolein (MACR) or methyl-vinyl ketone (MVK), which are oxidation products unique to isoprene, to distinguish between isoprene and monoterpene chemistry, as the strong model overestimation of MACR and MVK (see §5), suggests these products are not being treated correctly in the model.

The best-fit isoprene and monoterpene emissions show excellent agreement with the measured eddy-covariance fluxes, following the median measurement very closely throughout the day (Fig. 2). It should be noted that these isoprene emissions are much less than the $1.7 \text{ mg m}^{-2} \text{ h}^{-1}$ predicted for the region by Müller et al. (2008) for the year 2001. The 24-h average measured isoprene (monoterpene) emission for the “typical” day was 0.28 (0.19) $\text{mg m}^{-2} \text{ h}^{-1}$. The model-data agreement suggests that the model is oxidising a realistic amount of VOC and gives confidence in the estimated NO emission. It also suggests that this method may be useful in estimating emissions in other scenarios where flux measurements are not available. As the model generated fluxes can only account for what remains or is reacted in the boundary layer, it is possible that much of the 18% difference between model estimated and measured emissions may be explained by venting to the free troposphere. If venting out of the top of the boundary layer is occurring, then comparisons against the eddy-covariance fluxes, which measure the total flux from the surface, only necessitate that the model generated net flux into the PBL be less.

The model-estimated NO emission compares well with the yearly average above-canopy flux estimate of $0.005 \text{ mg N m}^{-2} \text{ h}^{-1}$ given for the area in April by the Yienger and Levy (1995) database. Monthly values in this database range from 0.002 in February to $0.012 \text{ mg N m}^{-2} \text{ h}^{-1}$ in July. Given the minimal variability of the seasonal climate

cycle in Borneo (Chappell et al., 2001; Hewitt et al., 2009) these minima and maxima nicely bracket the estimated emission. Anthropogenic contributions to the local NO_x budget are small in comparison to soil NO_x in this very remote location.

However, the model-estimated NO emission is 15 times smaller than the soil flux of 0.13 mg N m⁻² h⁻¹ (J. Dorsey, personal communication) measured via the chamber method (van Dijk and Duyzer, 1999) at a nearby under-canopy site (4° 58' 50" N, 117° 51' 19" E). As the PBL can be considered well-mixed during the day, then the model estimate may be considered to be representative of the above-canopy NO flux over a fairly large locality. The difference between the model estimate and under-canopy measurements is 93%, compared to the 75% canopy reduction estimated by Yienger and Levy (1995) for tropical rainforest. However, three factors may go some way to explaining this difference. Firstly the chamber method generates a flux representative of the area under the chamber. Differences between the seven chambers used illustrate the heterogeneity of the natural soils, and this factor alone might explain the difference. Second, the measurements of NO_x which the model is constrained against, were made 5 m above grass in a rainforest clearing. It is possible that the soil in the clearing will have a different characteristic NO emission to the surrounding rainforest (possibly lower due to less decaying plant matter). The proximity of a different NO source could have some effect on measured concentrations at that point and hence the emission estimate. However, given the proximity of the tree canopy to the edge of the clearing (<10 m), it appears unlikely that a pronounced effect would be seen in a well-mixed boundary layer, such as is observed in the daytime. Finally, it is possible that a significant amount of NO_x is lost from the boundary layer by entrainment into the free troposphere.

5 Comparison of best-fit model concentrations with measurements

A comparison of the output generated by running the model with the emissions defined in §4, against the in-situ measurements made at Bukit Atur during OP3-1, is shown

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in Fig. 2. As mentioned in §4, due to the nighttime meteorology, the comparison is most valid between 10:00–18:00 LT, hence concentrations from the surface box are only shown between these times. Concentrations modelled in the nighttime residual layer (dashed blue line) are also shown for context, although direct comparison should not be made between modelled residual layer concentrations and 5 m level measurements. No concentrations are shown between 08:00–10:00 LT as the concentrations observed at this point will depend strongly on the height of the observer in the boundary layer. Table 1 lists the individual contributions, C_i , to the total cost, C_{total} , between 10:00–18:00 LT. It also lists the mean-bias error (MBE) as a percentage of the average 10:00–18:00 concentration. This statistic gives the average percentage by which the model under- or over-predicts the measurements. It is calculated using Eq. (1), but without taking the absolute value of the numerator.

Good agreement in particular is seen for O_3 , and NO_2 with MBEs of +4% and +10% respectively. This robust fit to O_3 and NO_x was also observed by Pike et al. (2009). The relatively poor fit of NO compared to the other two variables is probably due to the proximity of the soil NO source to the measurements. NO_y concentrations are overestimated in the model and this may well be attributable to the measurements being made close to the ground where many nitrogen containing species are deposited (e.g. PAN) and new emissions will have had little time to form these products. Wet deposition may also play a role for NO_y , although species such as nitric acid, for which this would apply, show very low concentrations in the model (<100ppt). The behaviour of O_3 , NO and NO_2 during the night will be the focus of a subsequent paper (Pugh et al., 2009).

Modelled OH concentrations are around 2–3 times less than those measured with an MBE of –64%. Analysis of modelled OH loss mechanisms concludes that 70% of OH loss at midday is attributable to isoprene or its direct oxidation products, with a further 11% due to monoterpenes and their oxidation products. Given the constraints on fluxes provided by measurements and the close fit gained for peroxy radicals during the day, it appears something may be amiss within the isoprene oxidation scheme, as

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hypothesised by Lelieveld et al. (2008). This possibility will be explored in more detail in §6. Morning monoterpene concentrations are somewhat underestimated by the model. The reasons for this are not entirely clear, but may be due to uncertainty in the speciation of monoterpenes at the canopy level, meaning the split between monoterpene schemes used here may not be ideal. Routing monoterpene concentrations entirely though the α -pinene or d-limonene schemes results in changes of +14% and –15% respectively.

Modelled peroxy radical ($\text{HO}_2 + \text{RO}_2$) concentrations display a reasonable fit to the measurements during the day, particularly considering the uncertainty of this measurement, with an MBE of +18%. This indicates that the ratio of production and destruction rates of peroxy radicals is simulated well and suggests that the modelled [OH] underestimation is not due to insufficient cycling of peroxy radicals to OH, via reaction with NO or NO-like species. During the night, modelled residual layer concentrations of $\text{HO}_2 + \text{RO}_2$ are 2–3 times larger than measured at 5 m, suggesting that something is depleting peroxy radical concentrations near the surface during the night. It is likely that this is linked to the relatively high nighttime [NO] at 5 m, which would react with HO_2 and RO_2 , leading to the formation of the relatively high nocturnal [OH] observed at 5 m (see e.g., Geyer and Stutz, 2004).

5.1 Dry deposition of MACR and MVK

Whilst daytime modelled isoprene and monoterpene concentrations are quite close to the measurements, there is a substantial overestimation, by 5–10 times, of modelled MACR and MVK concentrations, compared to the measurements. This is much larger than the measurement uncertainty of a factor of two. As these products are principally formed through the reaction of OH + isoprene, this lends further credence to the idea that something may be wrong with the way isoprene oxidation is represented. Indeed Peeters et al. (2009) suggest that current yield for the reaction of isoprene peroxy radicals with NO may produce 50% too much MACR and MVK in these low $[\text{NO}_x]$ conditions. However, this alone cannot account for the overestimation seen. Such

large overestimations are not apparent in other oxidation products, such as $\text{HO}_2 + \text{RO}_2$ or PAN (Fig. 2).

Another possibility is that MACR and/or MVK undergoes significant dry deposition. The existence of a substantial dry deposition flux of MACR/MVK has been suggested before by Karl et al. (2004), following measurements made in Costa Rica. Using eddy-covariance measurements and taking account for the effects of chemistry and dew, they measure an average deposition velocity ($V_d(\text{MACR} + \text{MVK})$) of 0.1 cm s^{-1} . However, they also calculate a possible deposition velocity over the Amazon of $2\text{--}4 \text{ cm s}^{-1}$ utilising data published by Andreae and Merlet (2001). Zhang et al. (2002) estimate daytime deposition velocities over evergreen deciduous forest of 0.341 and 0.499 cm s^{-1} for MACR and MVK respectively, using a dry deposition model calibrated using measurements of O_3 and SO_2 . However they note that very little data is available to evaluate these values. Ganzeveld et al. (2008) overestimate MACR + MVK by 2–3 times compared to concentrations measured over Suriname during the GABRIEL campaign. This is despite including deposition velocities of up to 1.0 cm s^{-1} during the day and 0.1 cm s^{-1} at night. This range of values illustrates that MACR and MVK deposition rates are currently poorly characterised, yet they may be large enough to significantly impact upon concentrations.

To test the importance of MACR/MVK deposition for the Danum Valley scenario, model runs were carried out with $V_d(\text{MACR} + \text{MVK}) = 0.1 \text{ cm s}^{-1}$ and $V_d(\text{MACR} + \text{MVK}) = 2.0 \text{ cm s}^{-1}$. A 0.1 cm s^{-1} deposition velocity only decreases MACR+MVK concentrations by 15% to just under 2 ppb. However, a 2.0 cm s^{-1} deposition velocity can explain much of the difference between the model and measurements, causing a 65% reduction in peak concentrations to 0.8 ppb, about twice the magnitude measured. MACR/MVK flux measurements show no clear net flux. However, it is quite possible that any dry deposition flux is masked in the measurements due to the spatial variation of MACR and MVK chemical sources and sinks within the PBL.

Dry deposition of MACR and MVK at 2.0 cm s^{-1} decreases the OH sink, increasing modelled peak $[\text{OH}]$ by 60% to $10^6 \text{ molecules cm}^{-3}$. This increase in $[\text{OH}]$ in turn

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increases modelled isoprene and monoterpene loss rates, hence decreasing their concentrations substantially below measurements. Re-computing a new best-fit then increases isoprene and monoterpene emissions, in order to maintain a fit to observed isoprene and monoterpene concentrations, consequently reducing [OH] back to similar levels to those in Fig. 2. This illustrates the importance of correctly characterising MACR/MVK deposition velocities to simulating PBL chemistry, and raises the possibility that deposition of other important intermediate species might lead to significant errors in model studies.

5.2 Wet deposition

The model runs above also show a large build-up of organic peroxides (ROOH) to >3 ppb over the 8 day period, These are produced as part of isoprene oxidation, typically by the reaction of organic peroxy radicals (RO_2) with hydrogen peroxide (HO_2). Some of these higher peroxides have reaction rates with OH similar to that of isoprene with OH ($\sim 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and hence may contribute substantially to the OH sink. However organic peroxides typically have high Henry's Law coefficients $> 1 \times 10^6 \text{ M atm}^{-1}$, and hence are very susceptible to wet deposition processes.

In this study wet deposition has been simulated using the S-WET2 scheme described in Real et al. (2008). This scheme has been extended to cover all appropriate species in the extended organic schemes used here. Henry's Law constants have been taken from Sander (2009) where available. For those species lacking a measured value for Henry's Law, the most structurally similar compound with available measurements has been utilised. The pH of rainwater in this remote scenario is assumed to be 5.6. Notable species aside from ROOH which undergo wet deposition in the scheme are HCHO, HO_2 , H_2O_2 , HNO_3 , HO_2NO_2 , CHOCHO and CH_3CHO . The rain rates supplied to the model are the diurnal averages of those measured at Danum Valley Field Centre ($4^\circ 57' 42'' \text{ N } 117^\circ 48' 12'' \text{ E}$) during the course of OP3-1. This profile gives no rain during the morning, but a strong peak of $\sim 3 \text{ mm h}^{-1}$ at 15:00 LT, with levels circa 0.5 mm h^{-1} persisting throughout the afternoon and evening. All rainfall is assumed to

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be convective.

Applying this wet deposition parametrisation to the model run shown in Fig. 2 leads to an 88% reduction in modelled midday [ROOH] to ~ 0.4 ppb. This is in broad agreement with aircraft measurements made during OP3-3 of ~ 0.2 ppb. Furthermore the tendency of ROOH to accumulate in the box is greatly reduced. Peak HCHO concentrations are reduced from ~ 2.5 ppb to ~ 1 ppb, with almost no HCHO persisting in the afternoon. Clearly wet deposition is a very important loss process for several BVOC oxidation products in this environment.

The photolysis of HCHO is an important source of HO_2 , so a reduction in HCHO concentrations will play a role in the 21% reduction in modelled peroxy radical concentrations, yielding a negative impact on OH production. However, overall, the change in the OH sink dominates, leading to an increase in peak [OH] of 15% and a consequent decrease in peak isoprene concentration of 6%. This demonstrates that consideration of wet deposition is also an important factor in correctly modelling the oxidising capacity of the tropical boundary layer.

6 Isoprene and OH

The cause of [OH] underestimation over tropical rainforest is currently unknown. It has been suggested (e.g., Karl et al., 2007) that the reaction of terpenes and ozone could produce sufficient OH to bridge the gap between models and measurements. However Ganzeveld et al. (2008) concluded that this pathway alone could not explain the model deficiencies. Modifying the model such that each reaction of a terpene with O_3 produces one OH molecule, can only generate [OH] within the bounds of measurements at terpene emission rates much greater than those of isoprene. This test was carried out utilising the rate constant of beta-caryophyllene, which, compared to most monoterpenes, has a very fast reaction with O_3 and a relatively slow reaction with OH. Lelieveld et al. (2008) noted that errors in the photochemical rate constants could be responsible, particularly those for the dissociation of higher peroxides. However Kubistin et al. (2008) found no evidence for this.

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6.1 OH recycling

Several recent studies (Lelieveld et al., 2008; Butler et al., 2008; Kubistin et al., 2008) have noted the apparent correlation between OH and isoprene concentrations, and hypothesised that, under low-NO_x conditions, there is an as-yet-unknown pathway in the isoprene oxidation process that is responsible for recycling OH. Their suggestion is supported to some extent by the experimental work of Hasson et al. (2004), Jenkin et al. (2007) and Dillon and Crowley (2008), who found that OH could be produced by the reaction of HO₂ with organic peroxy radicals containing a carbonyl group. Following this, Lelieveld et al. (2008) proposed an OH recycling mechanism of,



where ISOPROO are peroxy radicals formed from the reaction of isoprene with OH, ISOPROOH is the resulting peroxide, and n is the number of OH produced. Lelieveld et al. (2008) found values of $n = 24$ gave the best fit to their measurements.

The proposed chemistry behind this recycling hypothesis was tested by modifying the model chemistry scheme following the results of Dillon and Crowley (2008). All reactions of HO₂ with carbonyl containing peroxy radicals in the isoprene and monoterpene schemes were altered to include a further reaction channel producing OH. The branching coefficient assigned to the new channel depended on the position of the carbonyl group on the peroxy radical. If the carbonyl group was on the same carbon as the peroxy group a branching coefficient of 0.5 was applied, following the result for CH₃CO₃ in Dillon and Crowley (2008). For all other positions of the carbonyl group relative to the peroxy group, a coefficient of 0.15 was applied, following CH₃C(O)CH₂O₂ in Dillon and Crowley (2008). Non-carbonyl containing peroxy radicals are assumed not to display this reaction channel. Only a 4% increase in the peak [OH] is realised, resulting in a similarly small decrease in isoprene and monoterpene concentrations. Hence it may be concluded that recycling of OH via the reaction of carbonyl containing peroxy radicals is only able to produce a very small fraction of the missing OH.

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In order to test the hypothesis that unknown OH recycling within the isoprene oxidation scheme could improve the model fit, a tetra-variate sensitivity study was carried out, varying OH recycling, isoprene, monoterpene and NO emissions. Rather than assume a method for OH recycling, the generic reaction,



was used. The cost function unambiguously returned a minimum at $m = 0.0$, showing that “artificial” OH recycling did not improve the model fit to the measurements.

To try and understand this lack of improvement, a run was carried out with $m = 1.3$ as suggested by Kubistin et al. (2008) and utilising the emissions derived in §4. Figure 3 compares the results of this run with those shown in Fig. 2 and the observations. The OH fit appears much improved. But once again this is at the cost of the isoprene and monoterpene profiles, whose concentrations are heavily reduced. Increasing the isoprene and monoterpene emission can bring these profiles back into line with the best fit previously achieved. However, this requires isoprene and monoterpene emissions to exceed the measured values. Furthermore, this reduces the OH concentration almost back to the levels of no recycling, whilst the $\text{HO}_2 + \text{RO}_2$ levels become unacceptably high. A similar test is also carried out by constraining the model to measured [OH]. This reduces peak isoprene concentrations to 0.6ppb.

A recent theoretical paper by Peeters et al. (2009) postulates an alternative mechanism which may result in significant OH recycling via the reactions of the ISOPROO channel. We have not implemented the details of the Peeters et al. (2009) scheme but, as regards the OP3-1 scenario, we expect it will behave similarly to the simpler schemes described above. However in scenarios of intermediate [NO], in the 100 s of ppt, it appears the Lelieveld et al. (2008) scheme may prove unable to produce significant amounts of OH (Hofzumahaus et al., 2009), whereas Peeters et al. (2009) expect their mechanism to be important up to NO concentrations approaching 1 ppb.

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6.2 Mass balance analysis

OH concentrations may be calculated indirectly from the isoprene flux and concentrations after Karl et al. (2007) using,

$$F_s - F_e = (k_{\text{OH}} \times [\text{OH}] + k_{\text{O}_3} \times [\text{O}_3]) \times C_{\text{mean}} \times z_{\text{mix}} \quad (2)$$

where F_s is the surface flux of isoprene and F_e is the entrainment flux of isoprene from the top of the PBL into the free troposphere, C_{mean} is the mean concentration of isoprene, z_{mix} is the height of the PBL, and k_{OH} and k_{O_3} are the rate constants for the reaction with isoprene of OH and O_3 respectively. Concentrations were only derived for the daytime due to the lack of mixing at night. The resultant [OH] is compared to measurements and the optimum model output (without OH recycling) in Fig. 4. This suggests an OH concentration in line with that provided by the model, suggesting that the main features of the modelled relationship between isoprene and OH can be represented by Eq. (2), and hence allowing a more simplified analysis of the isoprene and OH problem.

Measured values are available for the isoprene and O_3 concentrations and the isoprene flux. Due to low concentrations and slow kinetics, the isoprene + O_3 reaction is relatively unimportant. In order to increase [OH] in line with measurements we can reduce the net isoprene flux into the PBL by venting out of the top of the box. However this also results in a reduction in isoprene concentration, below the bounds of the measurements. Another possibility is the mixing height (z_{mix}). Following Eq. (2), a decrease in the mixing height would negate the need for a decrease in the isoprene concentration with a decreased flux. However, z_{mix} may be estimated quite accurately from the lidar measurements. Furthermore halving the daytime z_{mix} from 800 m to 400 m, whilst appropriately reducing the emitted fluxes, realises only a 4% [OH] increase.

The only remaining possibility is the rate of reaction. The utilised rate constants for the reactions of isoprene with OH and O_3 ($1.0 \pm 0.2 \times 10^{-10}$ and $1.27 \pm 0.25 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K respectively) are the result of numerous studies (IUPAC, 2009).

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Assuming a well mixed atmosphere, such well defined rates give very little room for manoeuvre, unless an outside process can influence the rate of reaction.

6.3 BVOC segregation

Following the work of Krol et al. (2000), Butler et al. (2008) argue that the segregation of isoprene into distinct plumes may result in a depletion in OH within those plumes. This would invalidate the well-mixed assumption of box models and lead to a lower effective rate constant. They suggest utilising a 50% reduction in rate constant, which, when combined with OH recycling, improves their isoprene and OH fits.

The importance of segregation can be assessed using the Damkhlner number (Da) following Krol et al. (2000),

$$Da = \frac{\tau_{\text{mix}}}{\tau_{\text{chem}}} \quad (3)$$

where τ_{chem} is the chemical lifetime and τ_{mix} is the mixing timescale. If then segregation effects are likely to be most prominent. Using average midday [OH] during the first OP3 campaign, yields an isoprene lifetime (τ_{chem}) of ~ 80 min. τ_{mix} can be approximated by the convective velocity timescale,

$$t_* = \frac{z_i}{w_*} \quad (4)$$

where,

$$w_* = \frac{g \times z_i}{T_v} F_H \quad (5)$$

where z_i is the height of the boundary layer, T_v is the virtual temperature and F_H is the kinematic heat flux. Using average values yields $w_* = 1.4 \text{ m s}^{-1}$ at midday, giving $t_* = 9$ min. In this case $Da = 0.1$, suggesting segregation does not play a significant role at Bukit Atur. In comparison, Butler et al. (2008) suggest an isoprene lifetime of

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<30 min over the Guyanas, which is comparable to the convective mixing timescale in their scenario of 8–16 min. However unlike the Guyana measurements, which were made with an aircraft, the OH measurements here were made at 5 m above ground, very close to the BVOC source. If emissions of BVOCs from the canopy occur intermittently (e.g., Gao and Li, 1993; Turner et al., 1994), rather than continuously, then this could result in segregation near the emission source. In order to definitively prove the segregation hypothesis, high-frequency, co-located measurements of VOCs and OH are required. These are not available from the OP3 or other campaigns.

In order to ascertain the best model fit obtainable by reducing the rate constant, a tetra-variate sensitivity study was carried out with rate constant reduction factors varied between 0.1 and 1.0. As any physical process affecting the OH + isoprene rate would also likely affect the OH + monoterpene rate, reduction factors are also applied to these reactions. Emissions for isoprene, monoterpenes and NO were varied as in the previous sensitivity runs. Applying the cost function defined in Eq. (1) to this run generated a minima of $C_{\text{total}} = 1.05$ at a 24 h average monoterpene emission of $0.15 \text{ mg m}^{-2} \text{ h}^{-1}$, an isoprene emission of $0.16 \text{ mg m}^{-2} \text{ h}^{-1}$ and NO emission of $0.009 \text{ mg N m}^{-2} \text{ h}^{-1}$. The rate constant reduction was 70%.

Model output using these settings is shown in red in Fig. 5. The green line shows a model run with the same emission rates, but without the change in effective rate constant, so as to show the effect of the rate constant reduction more clearly. OH concentrations are approximately doubled, to within variability of those measured, whilst isoprene concentrations are maintained at a reasonable level. A substantial decrease in modelled isoprene emission is required to generate this fit. This may be justified in terms of venting out of the boundary layer, as the previous justification for not lowering isoprene emission, its concentration falling too low, is no longer relevant. However no data regarding isoprene flux out of the boundary layer is available to validate this theory.

O_3 and NO_x concentrations are largely unaffected by this model scenario. The reduced quantity of oxidised VOC is evident in the modelled MACR/MVK concentrations

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which are reduced by 50%, and in the HO₂ + RO₂ and PAN concentrations, both of which are closer to the measurements. Some care however, must be taken in using the modelled MACR/MVK concentrations as support for the rate constant reduction, as it is possible that any physical process which impacts upon the rate of the OH + isoprene reaction may also affect the MACR/MVK + OH reaction.

At this point it is worth considering that, whilst OH recycling alone was shown not to be able to reconcile OH and isoprene concentrations in §6.1, in conjunction with a reduced rate of reaction, it might be able to consume some of the missing isoprene flux, that would otherwise have to be vented out of the boundary layer. If the standard reaction rate between isoprene/monoterpenes and OH is indeed too high, the extra isoprene loss this causes would have masked the need for some OH recycling in §6.1. This will be addressed further in §6.4.

6.4 Further discussion

In the scenario presented herein, isoprene concentrations are relatively low compared to other studies over a tropical rainforest. For example, Karl et al. (2007) report an average noon isoprene flux of 7.8 mg m⁻² h⁻¹, around seven times larger than that during OP3-1, leading to a peak measured isoprene concentration of ~7 ppb. Modelled isoprene concentration for OP3-1 is approaching steady state after 8 days and is very close to the observations. However, entering the Karl et al. (2007) flux into the CiTTY-CAT model causes concentrations of isoprene to accumulate to highly unrealistic levels of over 100 ppb, clearly indicating an underestimation of the isoprene sinks. This can be explained by considering the relative contributions to OH production. Making the assumptions that every reaction of isoprene and OH regenerates one OH radical and other OH production is dominated by,



it is possible to estimate the potential contribution of OH recycling to the overall OH production using,

$$\frac{d\text{OH}_{\text{prod}}}{dt} = 2(k_1[\text{O}^1\text{D}][\text{H}_2\text{O}] + k_2[\text{HO}_2][\text{NO}] + k_3[\text{iso}][\text{OH}]) \quad (6)$$

where k_1 , k_2 and k_3 are the rate constant for the respective reactions. Entering average midday measured concentrations (except for O^1D) and HO_2 where modelled concentrations are used in the absence of measurements), shows that 4.1×10^6 molecules $\text{OH cm}^{-3} \text{ s}^{-1}$ are contributed by Reactions (R3) and (R4), whilst 7.4×10^6 molecules $\text{OH cm}^{-3} \text{ s}^{-1}$ are contributed by isoprene + OH. Hence OH recycling via isoprene would contribute 64% of OH_{prod} . However, with an isoprene concentration of 7 ppb, and all other concentrations remaining equal, OH recycling via isoprene would contribute 32.2×10^6 molecules $\text{OH cm}^{-3} \text{ s}^{-1}$ or 89% of OH_{prod} .

Hence OH recycling has the potential to dominate OH_{prod} in high isoprene environments, such as observed by Karl et al. (2007), where neglecting to consider it would be to potentially ignore the principal source of OH production. However, considering that a reduced effective rate constant for isoprene + OH may reduce the contribution by OH recycling by over half, its effect in the OP3-1 scenario may be greatly reduced. Nevertheless, it is clear from the results presented above, that whilst there may be a role for OH recycling in moderating modelled isoprene to reasonable levels in the most isoprene-rich tropical environments, it is not able to fully explain the modelled underestimation of $[\text{OH}]$ in all cases.

Given that several factors presented herein have been able to affect the VOC + OH chemistry, a final sensitivity study of 8000 runs is carried out, varying the effective rate of isoprene + OH, $V_{d(\text{MACR} + \text{MVK})}$, OH recycling via R2 and emissions of isoprene, monoterpenes and NO. Wet deposition is also enabled. A best fit is returned at $C_{\text{total}} = 0.96$, with an effective rate due to mixing processes 50% of the IUPAC value, $V_{d(\text{MACR} + \text{MVK})} = 1.5 \text{ cm s}^{-1}$ and $m = 0.25$. Emissions of isoprene and monoterpenes were 0.28 and 0.18 $\text{mg m}^{-2} \text{ h}^{-1}$ respectively, and those for NO, 0.010 $\text{mg N m}^{-2} \text{ h}^{-1}$. A

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comparison of the modelled output with measurements is made in Fig. 6. The most startling result is the 73% reduction in the contribution of OH to C_{total} ($C_{\text{OH}} = 0.17$), giving an MBE of -14% , well within measurement uncertainty, whilst maintaining isoprene and monoterpene fits. Notably secondary species such as $\text{HO}_2 + \text{RO}_2$, PAN and NO_y also show improved fits to the measurements, further demonstrating the importance of the physical processes considered to accurate simulations of the chemistry.

These results offer an improved explanation in many respects. The measured emissions of isoprene and monoterpenes are fully accounted for, whilst the rate constant reduction of 50% is more physically likely, and identical to that suggested by Butler et al. (2008). The OH recycling fit of $m = 0.25$ was small, but the gradient in the cost function surface indicated that this was a clear minima, demonstrating the magnitude of recycling required in this scenario is much less than has been suggested in other studies.

7 Summary and conclusions

This is the first modelling study of the chemistry occurring in the tropical rainforest PBL to utilise such a wide suite of ground-based measurements, particularly VOC fluxes, to inform the modelling. The ability of the CiTTyCAT model to represent the broad features of atmospheric composition above a tropical rainforest has been demonstrated. In particular the model appears to perform robustly with respect to NO_x and O_3 chemistry. The potential to generate net fluxes of compounds into the PBL, utilising ambient concentration measurements has also been shown, and the technique may be applied to estimate fluxes where measurements are not available, or PBL venting where they are. However modelling chemistry above the south-east Asian rainforest is shown to suffer the same problems with reconciling BVOC and OH concentrations highlighted in other tropical modelling studies.

It has been shown that both dry and wet deposition of intermediate VOC oxidation products can have a very significant influence on both their concentrations and the ox-

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idation capacity of the boundary layer. It is critical that further investigation into deposition processes over tropical forests is carried out, in order to reduce the uncertainties in these regions. The importance of considering micrometeorological mixing processes when modelling compounds of intermediate atmospheric lifetime such as isoprene has also been highlighted.

In the light of the work presented here, it appears that inadequacies apparent in box and global model studies of tropical VOC chemistry may be more strongly influenced by representation of detailed physical and micrometeorological effects than by errors in the chemical scheme. Further measurement work is required to fully understand the nature of these processes, so that they may be accounted for effectively in future studies.

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Table 1. Individual contributions, C_i , to the total cost, C_{total} , and % mean-bias error (MBE), between 10:00–18:00 LT for the best fit scenario.

Species	C_i	% of C_{total}	% MBE
NO	0.29	18	–26
NO ₂	0.07	4	+10
O ₃	0.05	3	+4
OH	0.64	41	–64
HO ₂ +RO ₂	0.19	12	+18
Isoprene	0.08	5	0
Total monoterpenes	0.25	16	–25
Total	1.57	100	

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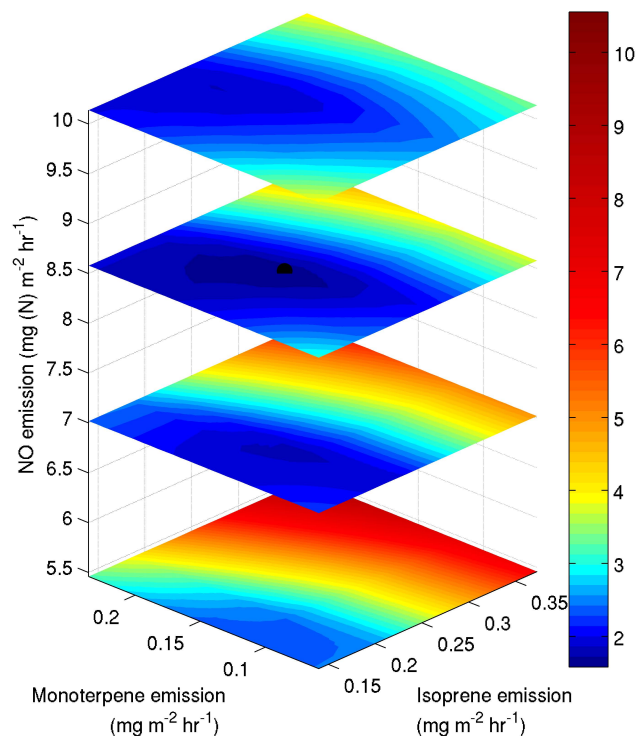


Fig. 1. Cost function surface generated to find the optimum emissions of isoprene, monoterpenes and NO to fit measurements of OH, NO, NO₂, O₃, isoprene, monoterpenes and HO₂ + RO₂. Lower values indicate a better fit, with the minima marked by a black dot.

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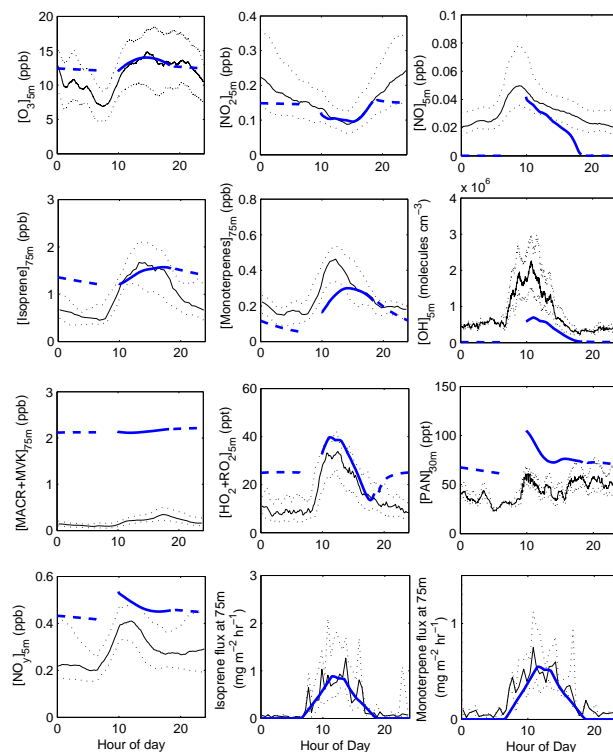


Fig. 2. Comparison of model best fits (blue line) against the OP3-1 average measurement at Bukit Atur (black line). Upper and lower quartiles for the measurements are marked by grey dots. Measurement height is shown in subscript. The solid blue line represents the well-mixed daytime box, whilst the dashed line shows the nighttime residual layer concentrations. The discontinuity between 08:00 and 10:00 LT is due to the mixing between the two layers during this period.

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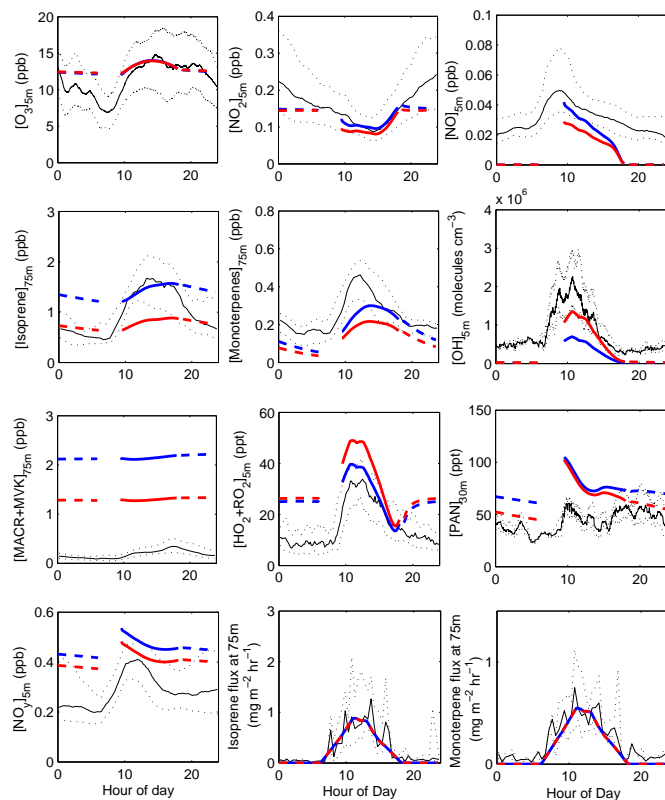


Fig. 3. Comparison of model output with (red line) and without (blue line) OH recycling of $m = 1.3$ against the OP3-1 average measurement at Bukit Atur (black line). Upper and lower quartiles for the measurements are marked by grey dots. Emissions are the same for both scenarios.

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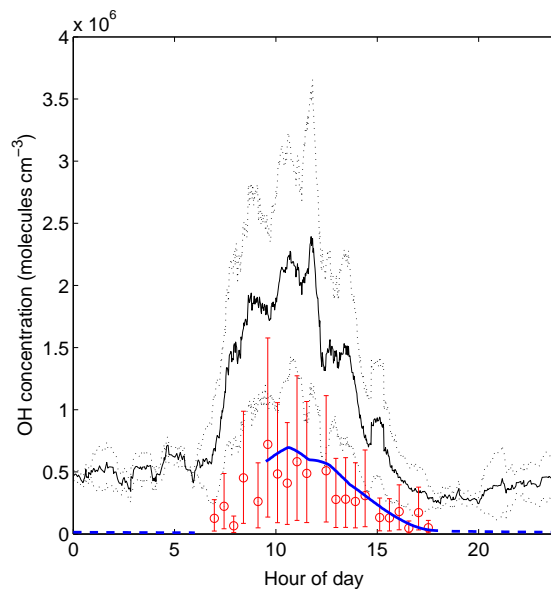


Fig. 4. Comparison of model output for OH, for a run with the best fit emissions and no OH recycling (blue line), the OP3-1 median measurements (black line, upper and lower quartiles marked by grey dots) and the OP3-1 median [OH] as computed from isoprene fluxes and concentrations following Karl et al. (2007) (red dots, propagated error shown by bars).

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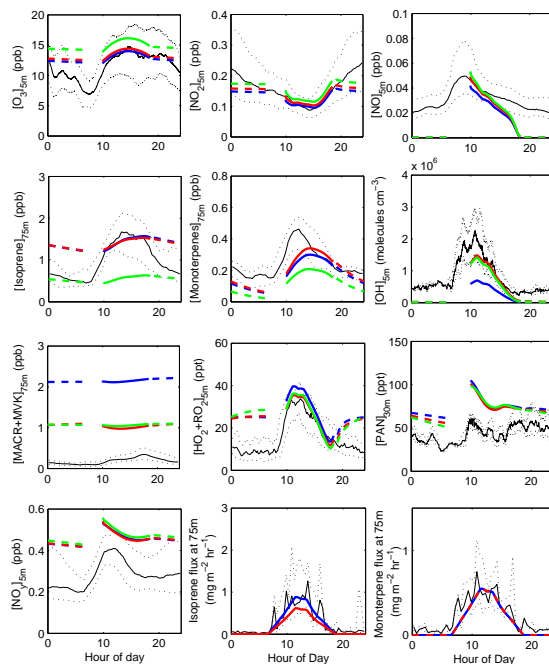


Fig. 5. Comparison of model output with the OP3-1 average measurements at Bukit Atur (black line). The blue line is the run shown in Fig. 2. The red line is a run with the isoprene + OH rate constant reduced by 70% and the emissions adjusted as per the best fit. The green line shows the effect of the emissions change alone.

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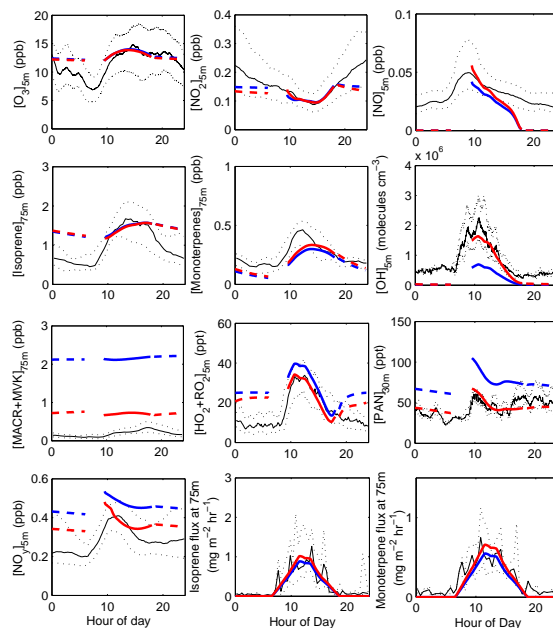


Fig. 6. Comparison of model output with the OP3-1 average measurements at Bukit Atur (black line). The blue line is the run shown in Fig. 2. The red line is a run with the isoprene + OH rate constant reduced by 50%, $V_d(\text{MACR}/\text{MVK}) = 1.5 \text{ cm s}^{-1}$, $m = 0.25$ and the emissions adjusted as per the best fit.

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