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# Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest

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## Abstract

The lifetime of methane is controlled to a very large extent by the abundance of the OH radical. The tropics are a key region for methane removal, with oxidation in the lower tropical troposphere dominating the global methane removal budget (Bloss et al., 2005). In tropical forested environments where biogenic VOC emissions are high and  $\text{NO}_x$  concentrations are low, OH concentrations are assumed to be low due to rapid reactions with sink species such as isoprene. New, simultaneous measurements of OH concentrations and OH reactivity,  $k'_{\text{OH}}$ , in a Borneo rainforest are reported and show much higher OH than predicted, with mean peak concentrations of  $\sim 2.5 \times 10^6 \text{ molecule cm}^{-3}$  (10 min average) observed around solar noon. Whilst  $j(\text{O}^1\text{D})$  and humidity were high, low  $\text{O}_3$  concentrations limited the OH production from  $\text{O}_3$  photolysis. Measured OH reactivity was very high, peaking at a diurnal average of  $29.1 \pm 8.5 \text{ s}^{-1}$ , corresponding to an OH lifetime of only 34 ms. To maintain the observed OH concentration given the measured OH reactivity requires a rate of OH production approximately 10 times greater than calculated using all measured OH sources. A test of our current understanding of the chemistry within a tropical rainforest was made using a detailed zero-dimensional model to compare with measurements. The model over-predicted the observed  $\text{HO}_2$  concentrations and significantly under-predicted OH concentrations. Inclusion of an additional OH source formed as a recycled product of OH initiated isoprene oxidation improved the modelled OH agreement but only served to worsen the  $\text{HO}_2$  model/measurement agreement. To replicate levels of both OH and  $\text{HO}_2$ , a process that recycles  $\text{HO}_2$  to OH is required; equivalent to the OH recycling effect of 0.74 ppbv of NO. This recycling step increases OH concentrations by 88% at noon and has wide implications, leading to much higher predicted OH over tropical forests, with a concomitant reduction in the  $\text{CH}_4$  lifetime and increase in the rate of VOC degradation.

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## 1 Background

OH radicals are responsible for the removal of the majority of reactive trace gases emitted into the atmosphere (Heard and Pilling, 2003; Monks, 2005). In remote, background environments, far from anthropogenic emissions, OH is primarily produced by the photolysis of O<sub>3</sub> and the subsequent reaction of O(<sup>1</sup>D) atoms with H<sub>2</sub>O vapour:



The photolysis of other trace gases, for example HONO and H<sub>2</sub>O<sub>2</sub> can also act as direct OH sources. Reactions of O<sub>3</sub> with alkenes may contribute to OH formation in the daytime and these reactions may be a significant source of the radical at night in the absence of photolytic sources (Salisbury et al., 2001). In the presence of NO, HO<sub>2</sub> can also be recycled back to OH. In contrast to these relatively few well defined OH sources, in all but the cleanest of background environments there are a multitude of OH sinks, and, due to the large variety of these, it becomes virtually impossible to measure each explicitly. In tropical rainforests, the emissions of highly reactive biogenic VOCs are large. Global modelling studies estimate that such biogenic emissions may significantly *reduce* the oxidising capacity in tropical forests (Lelieveld et al., 2002, 2004), and, in turn, extend the lifetime of CH<sub>4</sub> in these areas considerably. In contrast to model predictions, recent field studies in forested regions have found that appreciable concentrations of OH are maintained even in the presence of high biogenic emissions (Carslaw et al., 2001; Tan et al., 2001; Thornton et al., 2002; Lelieveld et al., 2008; Butler et al., 2008; Kubistin et al., 2010; Martinez et al., 2010) indicating that OH sources are not properly captured by models under tropical conditions.

Thornton et al. (2002) first suggested that uncertainties in the product of the branching ratio and/or rate constant for organic peroxide formation from HO<sub>2</sub> + RO<sub>2</sub> reactions could be a cause for large modelled/measured OH discrepancies. Lelieveld et

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al. (2008) extended this idea, proposing that the source of unpredicted OH over Amazonia may derive from the reaction of HO<sub>2</sub> with organic peroxy radicals (formed via isoprene oxidation) directly forming OH. In support of this, several studies have highlighted that the modelled/measured discrepancy increases as a function of isoprene (Ren et al., 2008; Kubistin et al., 2010). Modelling studies suggest that between 2 to 3.2 OH radicals need to be recycled from these reactions to reproduce the OH mixing ratios measured over Amazonia (Butler et al., 2008; Kubistin et al., 2010). However, kinetic studies of reactions of HO<sub>2</sub> with a number of peroxy radicals do not support such high OH yields (Hasson et al., 2004; Dillon and Crowley, 2008).

A number of novel mechanisms that provide a significant yield of OH following the OH initiated oxidation of isoprene have recently been reported, determined by theoretical *ab initio* calculations (Peeters et al., 2009; Da Silva et al., 2010; Nguyen et al., 2010) or by laboratory studies (Paulot et al., 2009). The mechanism of Peeters et al. (2009) postulates that one OH radical may be re-generated per isoprene molecule oxidised, and has the greatest potential to sustain the oxidising capacity in rainforests. Calculations suggest that if this source were to be included in the MECCA modelling scheme used in the GABRIEL project, the OH model under-prediction could be rectified (Peeters et al., 2009; Archibald et al., 2010; Stavrakou et al., 2010). However, during the PRIDE-PDR campaign, Hofzumahaus et al. (2009) excluded any such additional HO<sub>x</sub> initiation pathways, as their inclusion in model calculations caused an over-estimation in the previously well replicated HO<sub>2</sub> concentrations. Instead, Hofzumahaus et al. (2009) proposed that the additional OH source could derive from the recycling of RO<sub>2</sub> radicals to HO<sub>2</sub> and subsequently of HO<sub>2</sub> radicals to OH via reaction with unidentified species. A similar observation was also made by Tan et al. (2001) during the PROPHET 98 campaign, in which the measured OH concentrations were, on average, a factor of 2.7 times greater than modelled concentrations, whilst the HO<sub>2</sub> modelled and measured concentrations were in reasonable agreement, suggesting a missing process converting HO<sub>2</sub> to OH rather than a missing direct OH source.



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approximately 5 m. The surrounding tree tops were at a height of  $\sim 10$  m and the container was located  $\sim 10$  m from the forest edge. The measurement inlets for OH and OH reactivity were in full sunlight from approximately 06:00 a.m.–06:00 p.m. local time. The sum of  $\text{HO}_2 + \text{RO}_2$  were detected at a height of  $\sim 5$  m using the PERoxy Radical Chemical Amplification (PERCA) technique (Fleming et al., 2006), from the roof of a second shipping container displaced  $\sim 20$  m from the OH measurement container. The measurement of the sum of  $\text{HO}_2 + \text{RO}_2$  has been used to assess the potential importance of an OH source from reaction of  $\text{RO}_2$  radicals with  $\text{HO}_2$  radicals. A rate coefficient,  $k_{\text{HO}_2+\text{RO}_2} = 2.05 \times 10^{-13} e^{(1300/T)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is the Master Chemical Mechanism (MCM) recommendation for reaction of isoprene derived peroxy radicals with  $\text{HO}_2$ , is used in these calculations.

A number of measurements used in the Photostationary Steady State (PSS) analyses (Sect. 3) were limited or missing during the April intensive, in some cases data taken during the second measurement period have been utilised to provide an estimate of typical values of these species in this environment. For example, such an approach has been employed for  $\text{HO}_2$  concentration measurements, which were not made during the first measurement period owing to the unavailability of nitric oxide gas to convert  $\text{HO}_2$  to OH for subsequent detection. The average diurnal profile of  $\text{HO}_2$  measured during OP3-III was used in the PSS.  $j(\text{O}^1\text{D})$  was measured from the roof of the OH measurement container using a filter radiometer (Bohn et al., 2008) throughout both intensives. Similar peak photolysis rates were observed during both measurement periods although increased cloud cover during the second campaign led to more frequent brief reductions in  $j(\text{O}^1\text{D})$ . The photolysis rates of other species such as  $j(\text{peroxides})$  have been calculated using the Tropospheric Ultraviolet and Visible (TUV) radiation model (Madronich and Flocke, 1998). The correlation between TUV calculated  $j(\text{peroxides})$  with TUV calculated  $j(\text{O}^1\text{D})$  was determined allowing these photolysis rates to be scaled to the measured  $j(\text{O}^1\text{D})$  values to account for passing clouds. The presence of clouds is likely to affect the photolysis rates of these chemical species by different amounts adding an additional uncertainty into the calculations

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performed. No peroxide measurements were made during either intensive period. A constant concentration has been assumed for  $\text{H}_2\text{O}_2$  and organic peroxides (in the PSS analyses we have assumed that the total organic peroxides are all  $\text{CH}_3\text{OOH}$ ) of 2.41 ppbv and 0.96 ppbv, respectively, which represent measured concentrations of these species that were made in the boundary layer over Amazonia during the GABRIEL campaign (Lelieveld et al., 2008). The OH yield of 0.26 from  $\text{O}_3$ -isoprene reactions was taken from recent recommendations (Malkin et al., 2010).

HONO was not measured during OP3-I; low concentrations of HONO (peak concentration was  $\sim 15$  pptv, Pugh et al., 2010a) were detected during OP3-III, however. At these mixing ratios, the photolysis of HONO has a negligible impact as an OH source and, as such, is not included in the results presented in this paper.

## 2.1 OH and $\text{HO}_2$ measurements

OH was measured using the fluorescence assay by gas expansion (FAGE) technique, and details of the experimental arrangement can be found in Whalley et al. (2010). Air was drawn into a large cylindrical, stainless steel cell via a 1 mm diameter nozzle set upon a 5 cm tall turret. The cell was maintained at 0.9 Torr. The OH radicals were electronically excited at  $\sim 308$  nm using a tuneable, pulsed laser. The fluorescence at the same wavelength was detected perpendicular to the laser axis using a channel photo-multiplier (CPM) and gated photon counting. The sensitivity of the cell towards OH was calibrated using VUV photolysis of  $\text{H}_2\text{O}$  vapour in a flow of zero air, coupled to  $\text{O}_2$  actinometry, to generate a known quantity of OH radicals. Data were collected every 10 seconds and then averaged up to the 10 min radical concentrations presented here. The average limit of detection (LOD) of the system during the campaign was  $\sim 1.95 \times 10^5$  molecule  $\text{cm}^{-3}$  (10 min data collection period), with an associated uncertainty due to the accuracy of the calibration of  $\sim 15\%$  ( $1\sigma$ ).  $\text{HO}_2$  may also be detected using the FAGE technique by first titrating  $\text{HO}_2$  to OH by the addition of small quantities ( $\sim 30$  sccm) of NO (99.5%, BOC) above the excitation region and this method was employed to detect  $\text{HO}_2$  during the second intensive. The  $\text{HO}_2$  measurements made

in OP3-III and used in the subsequent analysis are taken during periods when local  $\text{NO}_x$  concentrations were not elevated from natural background levels.

## 2.2 OH reactivity

OH reactivity ( $k'_{\text{OH}}$ ) was measured using an apparatus which has been described in detail by Ingham et al. (2009). Ambient air was drawn into a 2 m long, 10 cm internal diameter PVC flow tube at a rate of 300 L/min, generating a turbulent flow. OH was generated by 185 nm photolysis of  $\text{H}_2\text{O}$  vapour in a  $\text{N}_2$  flow and introduced into the flow tube via a sliding injector, and was detected downstream in the flowtube using a second FAGE cell. Increasing the distance (and, therefore, time,  $t$  as the flow-velocity was known) between the point of injection and the FAGE sampling point enables the decay of OH to be recorded, which was found to be exponential and is described by:

$$[\text{OH}]_t = [\text{OH}]_0 e^{-(k'_{\text{OH}} + k'_{\text{physical}})t} \quad (\text{R3})$$

where  $k'_{\text{physical}} = 6.1 \pm 0.65 \text{ s}^{-1}$  is the physical OH loss rate.  $k'_{\text{physical}}$  was determined post-campaign by replacing the ambient air flow with an extremely clean flow of gas and recording the subsequent decay (Edwards et al., 2010).

## 2.3 Box model incorporating the Master Chemical Mechanism

The Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) zero-dimensional box model (Stone et al., 2010) has been used to estimate  $\text{HO}_2$  concentrations for comparison with the ambient  $\text{HO}_2$  concentrations measured during OP3-III. The chemistry scheme, generated by the Master Chemical Mechanism (Carslaw et al., 2001), includes near explicit degradation schemes for the observed hydrocarbons, isoprene,  $\alpha$ -pinene,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$ ,  $i\text{C}_4\text{H}_{10}$ ,  $n\text{-C}_4\text{H}_{10}$ ,  $i\text{-C}_5\text{H}_{12}$ ,  $n\text{-C}_5\text{H}_{12}$ ,  $n\text{-C}_6\text{H}_{14}$  and  $\text{C}_2\text{H}_2$ . Rate coefficients for inorganic reactions and three body reactions were updated to recent recommendations. Simulations were integrated forwards using a Rosenbrock solver (Hairer and Wanner, 1991) with a timestep of 600 s until a diurnal

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steady state was reached, at which point the diurnal cycles of simulated species were considered to exhibit less than 0.01% variation from day to day.

5 Simulations were constrained to the observed average diurnal cycles of O<sub>3</sub>, NO, NO<sub>x</sub>, CO, H<sub>2</sub>O vapour,  $j(\text{O}^1\text{D})$ , temperature and the observed hydrocarbons listed above for all days of OP3-I, averaged into 30 minute time bins. The modelled HO<sub>2</sub> was compared to one day of HO<sub>2</sub> measurements taken during OP3-III. This day was chosen for comparison with the model as the concentrations of auxiliary measurements on this day were similar to the measurement values used as model constraints. The mean total peroxy radicals (HO<sub>2</sub> + RO<sub>2</sub>) concentrations, as detected using the PERCA method (Fleming et al., 2006), were similar during OP3-I and OP3-III supporting the assumption that the OP3-I HO<sub>2</sub> concentrations were likely similar to the HO<sub>2</sub> concentrations recorded during OP3-III. NO<sub>2</sub> and total NO<sub>x</sub> were the only constrained species permitted to vary during each 24 h period in the model with their concentrations constrained in such a way as to constrain the NO<sub>2</sub> to its observed value at the end of each 24 h period in the model whilst maintaining the modelled partitioning between NO<sub>x</sub> species. NO was constrained to its observed concentration at the beginning of the model run and then permitted to vary with the constraints placed on NO<sub>2</sub> and total NO<sub>x</sub>. This approach has been employed previously by Ren et al. (2008) and Stone et al. (2010). The methane concentration in the model was set to 1770 ppbv and the hydrogen concentration was set to 550 ppbv (Novelli et al., 1999; Ehhalt and Rohrer, 2009).

25 Photolysis rates, except for  $j(\text{O}^1\text{D})$ , which was measured, were calculated using the tropospheric ultraviolet and visible (TUV) radiation model at solar zenith angles (SZA) between 0 and 90° in 5° steps. Spline fits were applied to the calculated photolysis rates as a function of SZA, and the appropriate photolysis rates selected for the SZA. Calculated photolysis rates were subsequently scaled to the mean ratio of TUV calculated and observed  $j(\text{O}^1\text{D})$ . A surface albedo of 0.1 (Govaerts et al., 2008) was used for all model runs. In order to prevent the build-up of long-lived unconstrained species such as H<sub>2</sub>O<sub>2</sub> and other peroxides in the model, a deposition lifetime was applied to all

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calculated species, to represent physical loss of species either through deposition or mixing. As there are no observations of these species to allow a true deposition rate to be estimated, a rate coefficient for the deposition process of  $1 \times 10^{-5} \text{ s}^{-1}$  was chosen for all runs presented here, corresponding to a deposition lifetime of 24 h; the modelled HO<sub>2</sub> concentration increases by 14% if the deposition lifetime increases to 48 h. A full sensitivity study to this model parameter for this study may be found in Edwards et al. (2011) and is further described by Stone et al. (2010).

### 3 Results and discussion

The average diurnal profile, constructed from 25 days of OH measurements during the first OP3 campaign (OP3-I), and shown in Fig. 1, is used in all subsequent analyses. The  $1\sigma$  standard deviation of this averaged profile is mainly due to the variability of the data from day-to-day caused by variability in chemical composition, but also contains a contribution from instrumental precision. The corresponding average diurnal profiles of NO, O<sub>3</sub>,  $j(\text{O}^1\text{D})$ , isoprene and OH reactivity,  $k'_{\text{OH}}$ , all of which influence the OH profile, are also shown in Fig. 1 for the OP3-I campaign. The mean daytime isoprene concentration of  $\sim 1.9$  ppbv (averaged between 06:00 a.m.–06:00 p.m.) measured during OP3-I is comparable to isoprene measurements made in the boundary layer over the Suriname rainforest during the GABRIEL project (mean daytime isoprene  $\sim 2$  ppbv observed (Lelieveld et al., 2008)). NO concentrations are also similar ( $\sim 0.02$  ppbv) to those measured during the GABRIEL project (Lelieveld et al., 2008) at all times other than at sunrise when a reproducible spike in NO peaking at  $\sim 0.2$  ppbv was observed during the OP3 project (Fig. 1); please refer to Pike et al. (2010) for further details on the OP3-I NO profile. Both O<sub>3</sub> concentration and O<sub>3</sub> photolysis rates were higher over the Suriname forest (O<sub>3</sub>  $\sim 18.5$  ppbv, mean daytime concentration and  $j(\text{O}^1\text{D}) \sim 6.3 \times 10^{-5} \text{ s}^{-1}$  at solar noon, Martinez et al., 2010) than in the Borneo forest (Fig. 1) indicating that the rate of primary production of OH from the photolysis of O<sub>3</sub> and subsequent reaction with H<sub>2</sub>O vapour was higher during the GABRIEL project than

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OP3. This higher primary rate of production likely results in the higher daytime mean OH concentrations observed during the GABRIEL project ( $\sim 5.6 \times 10^6$  molecule  $\text{cm}^{-3}$ ) than during OP3 ( $\sim 1.2 \times 10^6$  molecule  $\text{cm}^{-3}$ ) (Fig. 1). One of the most notable results from the OP3 project is that significant OH concentrations are maintained despite a high OH reactivity, defined by  $k'_{\text{OH}} = \sum k'_{\text{OH}+\text{Y}}[\text{Y}]$ , where Y represents an OH sink, suggesting that there are significant OH sources present.

The short lifetime of OH (daytime mean of  $\sim 59$  ms, Fig. 1) indicates that OH exists in a photostationary steady state, where OH production is balanced by OH loss. Simultaneous measurements of OH concentration and  $k'_{\text{OH}}$  enable “measurement” of the total rate of OH production,  $\Sigma_{\text{OH}_{\text{sources}}}$  using:

$$\Sigma_{\text{OH}_{\text{sources}}} = [\text{OH}] \times k'_{\text{OH}} \quad (\text{R4})$$

In many environments the major source of OH is from the reaction of  $\text{O}(^1\text{D})$  with water vapour, the rate of which is given by:

$$\rho(\text{OH}) = 2 \times j(\text{O}^1\text{D}) \times [\text{O}_3] \times [\text{H}_2\text{O}] \times f \quad (\text{R5})$$

where  $f$  is the fraction of  $\text{O}(^1\text{D})$  that reacts with  $\text{H}_2\text{O}$  vapour to form OH, rather than being quenched to  $\text{O}(^3\text{P})$ . Although  $j(\text{O}^1\text{D})$  and  $\text{H}_2\text{O}$  concentrations were large, as expected in the tropics (peak  $j(\text{O}^1\text{D}) \sim 3 \times 10^{-5} \text{ s}^{-1}$  on average and  $[\text{H}_2\text{O}] \sim 2.5\%$  v/v),  $\rho(\text{OH})$  was limited by the low  $\text{O}_3$  concentrations observed (peak  $[\text{O}_3] \sim 11$  ppbv). If it is assumed that  $\rho(\text{OH})$  represents the *only* source of OH, i.e.  $\Sigma_{\text{OH}_{\text{sources}}} = \rho(\text{OH})$  (Scenario 1, Table 1), then the OH concentration, calculated by rearrangement of Reaction (R4):

$$[\text{OH}]_{\text{calc}} = \frac{\Sigma_{\text{OH}_{\text{sources}}}}{k'_{\text{OH}}} \quad (\text{R6})$$

would be expected to be very low given to the high value of  $k'_{\text{OH}}$ . Figure 2 shows a comparison of the average diurnal measured OH concentration ( $[\text{OH}]_{\text{meas}}$ ) and

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$[\text{OH}]_{\text{calc}}$ ;  $[\text{OH}]_{\text{calc}}$  under-predicts  $[\text{OH}]_{\text{meas}}$  by a factor of  $\sim 20$  at noon. As  $k'_{\text{OH}}$  is measured (representing all OH sinks), the comparison shows that significant additional OH sources must be present in addition to production of OH from the reaction  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$  Eq. (R5). Figure 2 also shows  $[\text{OH}]_{\text{calc}}$  when all *known* OH sources are incorporated in Eq. (R6) ( $\text{C}_5\text{H}_8$  = isoprene) (Scenario 2, Table 1) (see Sect. 2 for further details on

$$\Sigma_{\text{OH}_{\text{sources}}} = \rho(\text{OH}) + k_{\text{NO}+\text{HO}_2}[\text{HO}_2][\text{NO}] + k_{\text{O}_3+\text{HO}_2}[\text{O}_3][\text{HO}_2] + 0.26k_{\text{O}_3+\text{C}_5\text{H}_8}[\text{O}_3][\text{C}_5\text{H}_8] + 2.j(\text{H}_2\text{O}_2)[\text{H}_2\text{O}_2] + j(\text{CH}_3\text{OOH})[\text{ROOH}] \quad (\text{R7})$$

$[\text{OH}]_{\text{calc}}$  increases, predominantly due to inclusion of an OH source from  $\text{HO}_2 + \text{NO}$  (78% of the increase is due to inclusion of  $\text{HO}_2 + \text{NO}$ ) despite NO concentrations being very low; this OH source has the biggest impact on the PSS calculation during the early morning hours when NO peaks at  $\sim 200$  pptv.  $[\text{OH}]_{\text{calc}}$  still significantly under-predicts  $[\text{OH}]_{\text{meas}}$  (by a factor of 10 at noon) however, demonstrating that there is still a large, uncharacterised OH source.

Recent theoretical calculations (Peeters et al., 2009; Da Silva et al., 2010) and laboratory studies (Paulot et al., 2009) have shown that OH may be regenerated during the OH initiated oxidation of isoprene under low  $\text{NO}_x$  conditions, and if these are included as OH sources, (Scenario 3, Table 1)  $\Sigma_{\text{OH}_{\text{sources}}}$  becomes:

$$\Sigma_{\text{OH}_{\text{sources}}} = \rho(\text{OH}) + k_{\text{NO}+\text{HO}_2}[\text{HO}_2][\text{NO}] + k_{\text{O}_3+\text{HO}_2}[\text{O}_3][\text{HO}_2] + 0.26k_{\text{O}_3+\text{C}_5\text{H}_8}[\text{O}_3][\text{C}_5\text{H}_8] + \alpha k_{\text{OH}+\text{C}_5\text{H}_8}[\text{OH}][\text{C}_5\text{H}_8] + 2.j(\text{H}_2\text{O}_2)[\text{H}_2\text{O}_2] + j(\text{CH}_3\text{OOH})[\text{ROOH}] \quad (\text{R8})$$

where  $\alpha$  is the recycled yield of OH following the OH reaction with isoprene.  $[\text{OH}]_{\text{calc}}$  increases considerably if  $\alpha = 1$  as suggested by Peeters et al. (2009) (Fig. 2), for which there is a direct OH source (0.03) and a larger OH source (0.97) from the rapid photolysis of photo-labile co-products and subsequent photochemistry. This mechanism also suggests an appreciable yield of  $\text{HO}_2$  (0.7). Even with this new, considerable,

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OH yield of 1 from OH initiated isoprene oxidation OH concentrations are still under-predicted by ~63% at midday. To achieve  $[\text{OH}]_{\text{calc}}/[\text{OH}]_{\text{meas}} = 1$  during the afternoon and evening, approximately 2.7 OH radicals would need to be produced per isoprene molecule oxidised ( $\alpha = 2.7$ , Scenario 4, Table 1), potentially indicating that the OH yield from isoprene may actually be greater than 1 (Stravrakou et al. (2010) propose that the rapid photolysis of the co-products formed during isoprene oxidation may actually yield 3 OH radicals). It should be noted, however, that OH concentrations are still under-predicted during the morning even with a yield of 2.7 from isoprene oxidation, as the isoprene concentrations are lower at this time, suggesting that the diurnal profile of the missing OH source does not entirely follow the isoprene concentration profile. It is possible that similar mechanisms may also occur during the oxidative degradation of other biogenic species, for example mono-terpenes. A small subset of mono-terpenes were measured during the project; the concentrations of these species are insufficient to reconcile the missing OH source however. High concentrations of unmeasured mono-terpenes would have had to be present in addition to those measured if these species are to account for the remaining missing OH source. In support of an unmeasured VOC (or VOC group), Edwards et al. (2011) have demonstrated that the OH reactivity measured during the campaign can only be reconciled if an unmeasured species were present and contributed to the total OH reactivity.

The effect of including different OH sources on the calculated  $\text{HO}_2$  concentration has been investigated using a full modelling approach (see Sect. 2.3), the results of which are shown in Fig. 3. A base run (brown line) corresponding to all OH sources that are included in Reaction (R7), excluding any recycled OH from isoprene, overestimates the  $\text{HO}_2$  observations taken during OP3-III. OH concentrations are significantly under-predicted by this model. Inclusion of the Peeter's mechanism (Peeters et al., 2009), which generates ~1 OH radical and ~0.7  $\text{HO}_2$  radicals per isoprene molecule oxidised leads to a considerable increase in the modelled  $\text{HO}_2$  concentration (~20% at noon) both as a consequence of an additional primary  $\text{HO}_2$  source and an increase from VOC and CO oxidation by OH. This mechanism causes the model to further over-predict the

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measured HO<sub>2</sub> concentration (green line, Fig. 3). This model still underestimates OH and, in line with the PSS calculation (and other modelling studies, e.g. Stavrakou et al., 2010), an OH yield from isoprene oxidation greater than unity is required to improve the modelled to measured agreement for OH. Such an increase in the OH yield from this mechanism only serves to increase HO<sub>2</sub>, reducing the modelled to measured HO<sub>2</sub> agreement further. These results are consistent with the findings during the PRIDE-PRD (Hofzumahaus et al., 2009) and PROPHET-98 (Tan et al., 2001) campaigns and suggest that if OH and HO<sub>2</sub> are generated during the OH initiated oxidation of isoprene as postulated by Peeters et al. (2009) an additional mechanism that removes HO<sub>2</sub> must also occur to reconcile the measurements.

Hofzumahaus et al. (2009) found that additional recycling of RO<sub>2</sub> radicals to HO<sub>2</sub> and HO<sub>2</sub> to OH (via an unknown species X) could reconcile both OH and HO<sub>2</sub> concentrations during the PRIDE-PDR campaign, and this is incorporated in the rate of OH production via:

$$\begin{aligned} \Sigma_{\text{OH}_{\text{sources}}} = & \rho(\text{OH}) + k_{\text{NO}+\text{HO}_2}[\text{HO}_2][\text{NO}] + k_{\text{O}_3+\text{HO}_2}[\text{O}_3][\text{HO}_2] + 0.26k_{\text{O}_3+\text{C}_5\text{H}_8}[\text{O}_3][\text{C}_5\text{H}_8] \\ & + 2.j(\text{H}_2\text{O}_2)[\text{H}_2\text{O}_2] + j(\text{CH}_3\text{OOH})[\text{ROOH}] + k_{\text{X}+\text{HO}_2}[\text{X}][\text{HO}_2] \end{aligned} \quad (\text{R9})$$

To achieve  $[\text{OH}]_{\text{calc}}/[\text{OH}]_{\text{meas}} = 1$  from an additional HO<sub>2</sub> + X → OH step under OP3 conditions, but without any OH recycling from isoprene, would require ~0.74 ppbv of unspecified reactant(s) (referred to as X) converting HO<sub>2</sub> to OH with the same rate coefficient by reaction with NO (or a HO<sub>2</sub> turnover rate to OH of ~6.5 s) (Scenario 5, Table 1). We have also included this additional recycling term in box model calculations of HO<sub>2</sub> as shown in Fig. 3 (pink line). Inclusion of the sources of OH given by Eq. (7) replicates the observed HO<sub>2</sub> concentrations well.

The additional recycling of OH may derive from a HO<sub>2</sub> + RO<sub>2</sub> reaction as suggested by Lelieveld et al. (2008). However, even if it is assumed that every RO<sub>2</sub> radical measured reacts with HO<sub>2</sub>, a yield of ten OH radicals on average is required to replicate OH observations. Such a high OH radical yield from RO<sub>2</sub>+HO<sub>2</sub> reactions is not supported by the recent kinetic studies (Hasson et al., 2004; Dillon and Crowley, 2008). Only RO<sub>2</sub>

radicals which contain a carbonyl functionality adjacent to the peroxy group have been found to regenerate significant OH upon reaction with HO<sub>2</sub> radicals, however, even the yield of OH from these reactions is only ~0.5 (Dillon and Crowley, 2008) demonstrating that other major OH recycling mechanisms must exist in addition to reconcile the OH concentrations observed.

It is possible that models may be missing both an OH source mechanism (for example OH regeneration during isoprene oxidation, Peeters et al., 2009) and a separate HO<sub>2</sub> loss mechanism. The fast HO<sub>2</sub> turnover rate of just a ~6.5 s suggests that the unknown HO<sub>2</sub> reactant must either be present at reasonable concentrations (e.g. with a reaction rate coefficient equal to  $\sim 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  then ~3 ppbv of reactant would be required) or react extremely rapidly with HO<sub>2</sub> (e.g. if ~65 pptv of reactant was present then a reaction rate coefficient of  $\sim 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  would be necessary). Although results from recent theoretical (Peeters et al., 2009; Da Silva et al., 2010; Nguyen et al., 2010) and laboratory studies (Dillon and Crowley, 2008) can help to suggest mechanisms that may help to reduce the modelled-measured discrepancy that is observed under high isoprene, low NO<sub>x</sub> conditions, it seems clear that additional novel OH source mechanisms and HO<sub>2</sub> sink mechanisms are needed to fully reconcile these recent radical measurements. Further laboratory measurements are also needed to confirm the identity and yield of first generation products from the reaction of OH with isoprene and other BVOCs, as well as the degradation mechanisms of these products, for example by photolysis, which could generate further molecules of OH or HO<sub>2</sub>.

## 4 Conclusions

Simultaneous field measurements of OH concentration, OH reactivity, and sources/sinks of OH in the Borneo rainforest at Bukit Atur directly show a large underestimate in OH sources in tropical forests and indicate significant uncertainties in the chemistry of low NO<sub>x</sub>/high biogenic VOC environments. This work demonstrates that

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the oxidising capacity in tropical rainforests, manifested as moderate to high OH concentrations, can be sustained, despite high biogenic emissions and low ozone. Under low  $\text{NO}_x$  conditions, an OH formation route is needed which can be reconciled with both observed OH and  $\text{HO}_2$ . This work indicates that an additional OH source from isoprene oxidation cannot reconcile both the OH and  $\text{HO}_2$  observations at this location unless an additional  $\text{HO}_2$  sink mechanism is also included. An additional recycling mechanism that converts  $\text{HO}_2$  to OH can account for the combined  $\text{HO}_x$  observations (without an additional OH source from isoprene oxidation). The combination of observations made allow us to quantify this as being equivalent to the chemical interconversion as would occur in the presence of 0.74 ppb NO (or an  $\text{HO}_2$  turnover rate of  $\sim 6.5$  s). The impact of including the additional recycling step as a source of OH is an 88% increase in [OH] at noon, significantly increasing the oxidising capacity of the tropical rainforest, and reducing the lifetime of  $\text{CH}_4$  in these environments.

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**Table 1.** Description of the scenarios used in the text and figures and the impact of the different OH source terms in the PSS approximation Eq. (4). The colours of the lines in the symbol column correspond to the  $[\text{OH}]_{\text{calc}}$  diurnal profile shown in Fig. 2 calculated using the different Scenarios (1–5).  $[\text{OH}]_{\text{calc}}:[\text{OH}]_{\text{meas}}$  ratio represents the mean ratio over 24 h for all scenarios apart from Scenario 4.  $f$  is the fraction of  $\text{O}(^1\text{D})$  that reacts with  $\text{H}_2\text{O}$  vapour to form OH, rather than being quenched to  $\text{O}(^3\text{P})$ .

Scenario	$\Sigma_{\text{OH}_{\text{sources}}}$	Symbol (Fig. 2)	$\frac{[\text{OH}]_{\text{calc}}}{[\text{OH}]_{\text{meas}}}$
(1)	$2j(\text{O}^1\text{D})[\text{O}_3][\text{H}_2\text{O}]f$	yellow line	0.05
(2)	$(1) + k_{\text{NO}+\text{HO}_2}[\text{HO}_2][\text{NO}] + k_{\text{O}_3+\text{HO}_2}[\text{O}_3][\text{HO}_2] + 0.26k_{\text{O}_3+\text{C}_5\text{H}_8}[\text{O}_3][\text{C}_5\text{H}_8] + 2 \cdot j(\text{H}_2\text{O}_2)[\text{H}_2\text{O}_2] + j(\text{CH}_3\text{OOH})[\text{ROOH}]$	brown line	0.15
(3)	$(2) + k_{\text{C}_5\text{H}_8+\text{OH}}[\text{C}_5\text{H}_8][\text{OH}]$	green line	0.37
(4)	$(2) + 2.7 \times k_{\text{C}_5\text{H}_8+\text{OH}}[\text{C}_5\text{H}_8][\text{OH}]$	blue line	1.0*
(5)	$(2) + k_{\text{X}+\text{HO}_2}[\text{X}][\text{HO}_2]$ ( $[\text{X}] = 0.74$ ppbv)	pink line	1.0

\*  $[\text{OH}]_{\text{calc}}:[\text{OH}]_{\text{meas}} = 1$  during afternoon and evening hours only (noon – midnight)

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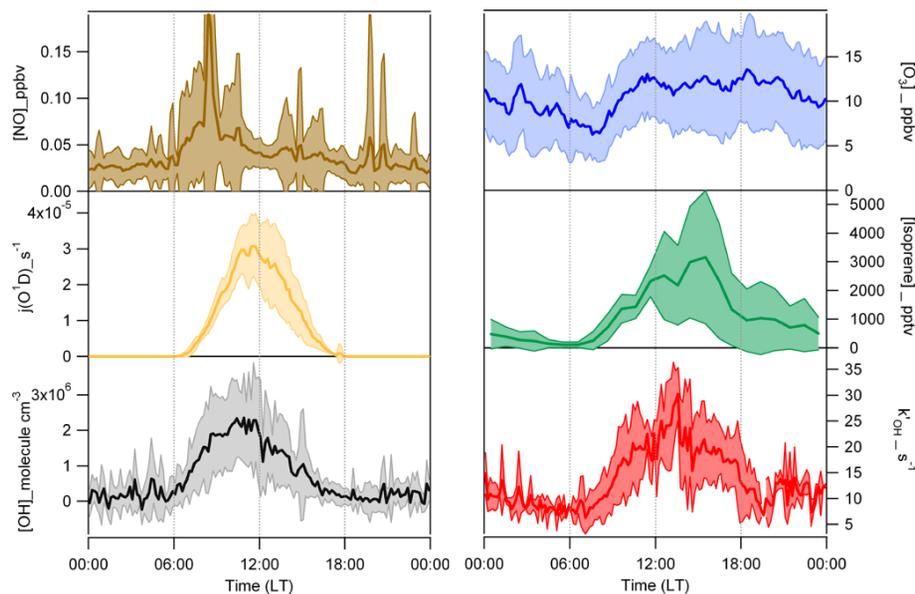
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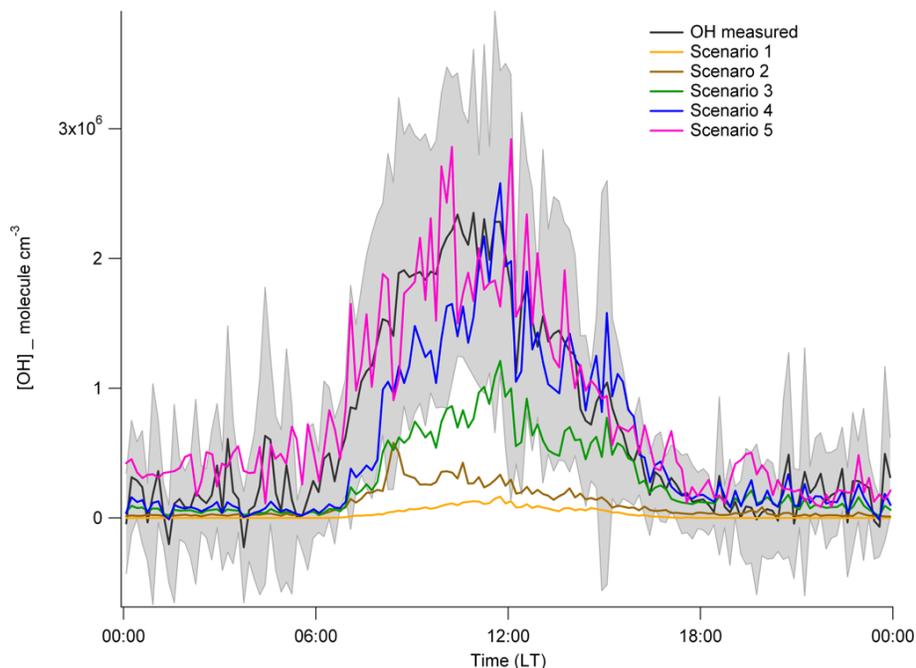


**Fig. 1.** Average diurnal profile of key species during OP3-I generated from 10 min data taken over 25 days (from the 6 April 2008 – 2 May 2008) for OH,  $k'_{OH}$ ,  $j(O^1D)$ , NO and  $O_3$ , and over 25 days from hourly data for isoprene. The shaded areas show the  $1\sigma$  day-to-day variability of the data used to generate the mean diurnal profiles.

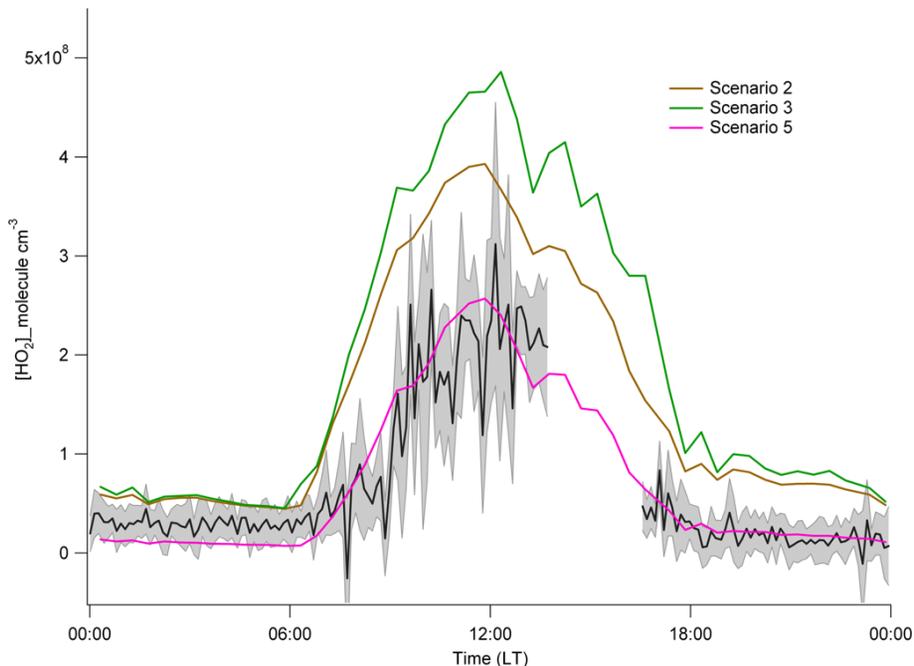
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**Fig. 2.** A comparison of the measured mean diurnal  $[\text{OH}]$  profile ( $[\text{OH}]_{\text{meas}}$ ) (black line) with  $[\text{OH}]_{\text{calc}}$  calculated using the PSS approximation (Eq. 4) constrained to measured OH reactivity ( $K_{\text{OH}}$ ) for the loss term and with various OH source terms included – see text and Table 1 for further details on the different scenarios. The grey shading represents the  $1\sigma$  standard deviation of the averaged OH profile, caused primarily by variability of the data from day-to-day due to changing atmospheric conditions, but also contains a contribution from instrumental precision.



**Fig. 3.** A comparison of the measured diurnal HO<sub>2</sub> concentration profile from one day during OP3-III (black line) (grey shading highlights the 1σ variation in 10 second HO<sub>2</sub> signal that has been averaged to generate each 10 min data point) with modelled HO<sub>2</sub> from the MCM constrained to measurements made during OP3-I. The brown line represents the modelled HO<sub>2</sub> with OH sources defined by Scenario 2 (Table 1). The green line represents the modelled HO<sub>2</sub> with an additional OH and HO<sub>2</sub> source from including the Peeters mechanism included (Scenario 3, Table 1). The pink line includes the standard OH source chemistry with an additional HO<sub>2</sub> to OH cycling step (equivalent to adding an additional 0.74 ppbv of NO) in the model (Scenario 5, Table 1).

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