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OH reactivity in
a Tropical rainforest
during OP3

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OH reactivity in a South East Asian Tropical rainforest during the Oxidant and Particle Photochemical Processes (OP3) project

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Abstract

OH reactivity, the reciprocal of its lifetime from reaction with its sinks, was measured for 12 days in April 2008 within a tropical rainforest on Borneo as part of the OP3 project. The maximum observed value was $83.8 \pm 26.0 \text{ s}^{-1}$ with the campaign averaged noon-time maximum being $29.1 \pm 8.5 \text{ s}^{-1}$. The maximum OH reactivity calculated using the campaign averaged noon-time concentrations of observed sinks was $\sim 18 \text{ s}^{-1}$, significantly less than the observations, consistent with other studies in similar environments. OH reactivity was dominated by reaction with isoprene. Numerical simulations of isoprene oxidation using the Master Chemical Mechanism (v3.2) in a highly simplified physical and chemical environment show that the steady state OH reactivity is a linear function of the OH reactivity due to isoprene alone, with a maximum multiplier being equal to the number of isoprene OH attackable bonds (10). Thus the emission of isoprene constitutes a significantly larger emission of reactivity than is offered by the primary reaction with isoprene alone, with significant scope for the secondary oxidation products of isoprene to constitute the missing reactivity. A physically and chemically more sophisticated simulation (including physical loss, photolysis, and other oxidants) showed that the calculated OH reactivity is reduced by the removal of the OH attackable bonds by other oxidants and photolysis, and by physical loss (mixing and deposition). The calculated OH reactivity is increased by peroxide cycling, and by the OH concentration itself. Notable in these calculations is that the lifetime of OH reactivity is significantly longer than the lifetime of isoprene and critically depends on the chemical and physical lifetime of intermediate species. When constrained to the observed campaign averaged diurnal concentrations of primary volatile organic compounds (VOCs), O_3 , nitrogen oxides (NO_x) and other parameters, the model underestimated the observed mean OH reactivity by 30%. However, it was found that: (1) the short lifetimes of isoprene and OH lead to a large variability in their concentrations and so significant variation in the calculated OH reactivity, (2) uncertainties in the OH chemistry in these high isoprene environments can lead to an underestimate of the OH reactivity, and (3)

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the physical loss of species that react with OH plays a significant role in the calculated OH reactivity, (4) a missing primary source of reactive carbon would have to be emitted at a rate equivalent to 50 % that of isoprene to account for the missing OH sink. A clear argument for a significant missing flux of primary emitted VOC compounds to account for the unmeasured reactivity is not found and the development of techniques for the measurement of secondary multifunctional carbon compounds is needed to close the OH reactivity budget.

1 Introduction

The hydroxyl radical (OH) is the dominant oxidant in the troposphere. It is highly reactive leading to low concentrations (globally averaged $\sim 1 \times 10^6$ molecule cm^{-3} , Lelieveld et al., 2004) and short lifetimes (~ 1 s, Heard and Pilling, 2003). Reaction with OH is the dominant removal mechanism for methane and it plays a central role in the production of ozone (O_3) and secondary organic aerosol (SOA). OH thus plays an important role in understanding climate and air quality. Observations of OH concentrations have been available for almost three decades and the ability of models to simulate these concentrations has been considered a metric of our understanding of tropospheric chemistry (Logan et al., 1981; Heard and Pilling, 2003; Stone et al., 2012). However, given the close chemical coupling between its production and loss terms, there is a potential that a model may successfully reproduce the observed OH concentrations but for the wrong reasons. The ability to explicitly measure the rates of production or loss of OH offer a strong constraint on our understanding of tropospheric chemistry.

Measurements of the chemical loss rate of OH (OH reactivity) in the atmosphere have been performed since 2001 (Kovacs and Brune, 2001). However, the ability of models to simulate these OH reactivity observations varies greatly. As a general trend, it has been found that our understanding is best in high NO_x environments, where the reaction of OH and NO_2 is the main constituent of the total OH loss (Ren et al., 2003; Di Carlo et al., 2004; Lee et al., 2009; Lou et al., 2010; Dolgorouky et al., 2012). The

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greatest discrepancies between measured and calculated OH reactivity are usually found under low NO_x conditions in the presence of elevated levels of Volatile Organic Compounds (VOC), typical of those found in forested locations (Di Carlo et al., 2004; Sinha et al., 2008, 2010).

5 This failure to account for OH sinks within remote forested regions is significant, as they constitute the overwhelming source of reactive carbon into the troposphere. Biogenic Volatile Organic Compounds (BVOCs) are emitted in large quantities ($\sim 1000\text{TgCyr}^{-1}$, Goldstein and Galbally, 2007) and play a significant role in the chemistry of the troposphere. This flux of carbon is dominated by the emission of isoprene
10 (C_5H_8), with mono-terpenes ($\text{C}_{10}\text{H}_{16}$) also playing an important role (Guenther et al., 1995, 2006). The tropics are the principal region for this emission, given their large size and high biogenic productivity. Despite their importance, the oxidation chemistry of these BVOCs is complex and currently subject to some debate (Lelieveld et al., 2008; Paulot et al., 2009a, b; Peeters et al., 2009). Biogenic hydrocarbons as well as
15 being OH sinks themselves generate oxidation products that also constitute sinks for OH.

There have been a small number of OH reactivity studies in remote forested environments, predominantly in extra-tropical regions. For example, measurements of OH reactivity alongside a suite of BVOCs in a deciduous forest, at the PROPHET field site,
20 inferred a missing OH sink corresponding to up to 50% of the total OH reactivity, correlating with temperature, and potentially indicating that the unmeasured species may have emissions driven by temperature such as monoterpenes. Sinha et al. (2010) made brief observations of OH reactivity alongside measurements of 30 other compounds in a boreal forest in Finland, and found missing OH sinks of between 25–75% of the total
25 measured OH reactivity. These missing OH sinks were again attributed largely to unmeasured BVOCs. The presence of significant concentrations of unmeasured BVOCs in forested environments was also a conclusion of Holzinger et al. (2005), who reported emissions of highly reactive BVOCs in a Ponderosa pine forest in California, inferred

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from the presence of large quantities of previously unreported oxidation products, measured by Proton Transfer Mass Spectrometry (PTR-MS).

Despite their importance, observations of OH reactivity from the tropical rainforest are sparse. The only previously reported observations of OH reactivity were those by Sinha et al. (2008) who report values for approximately 2 h from within the Amazon forest canopy, Suriname, in October 2005. Average observed OH reactivity was approximately 53 s^{-1} , peaking to $72 \pm 18 \text{ s}^{-1}$. The calculated OH reactivity from measured OH sinks was found to account for only $\sim 35\%$ indicating the presence of a large missing OH sink in this tropical forest environment. Unfortunately, the limited data coverage of OH reactivity observations during this study meant that any conclusions about the potential identity of this missing OH sink were difficult to make.

This failure to reconcile measurements of OH sinks with observed OH reactivity in biogenically active environments is generally attributed to unmeasured primary emitted BVOCs, implying a globally significant missing carbon source into the atmosphere with concomitant implications for climate and air-quality. However, other studies suggest that the missing reactivity is due to unmeasured oxidation products of measured primary emitted VOCs (Kovacs et al., 2003; Hofzumahaus et al., 2009; Lou et al., 2010). This role of oxidation products is supported by observations by Kim et al. (2011) of OH reactivity within branch enclosures where no significant oxidation chemistry had taken place, which found that the observed OH loss rate could be accounted for by the measured BVOCs. This suggests that the missing OH sink found in the forest boundary layer may be due to unmeasured oxidation products of the initially emitted primary BVOC rather than unmeasured primary species.

The OP3 (Oxidant and Particles Photochemical Processes) (Hewitt et al., 2010) project was a field campaign that took place in a remote tropical forest location in Malaysian Borneo during which observations of OH reactivity were made for a continuous period of approximately 2 weeks. After introducing the observations this paper considers a theoretical framework for the reactivity of a low NO_x high-VOC chemical system in relation to the flux of carbon into the system (Sect. 4). Once this conceptual

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system has been developed the OP3 OH reactivity observations are placed into this context and the sources of OH reactivity in the forest are outlined and investigated.

2 The OP3 campaign

The OP3 campaign aimed to address uncertainties in biogenic VOC processing in and around remote, low NO_x, tropical forested environments on local, regional and global scales (Hewitt et al., 2010). The ground based measurements were located at the Bukit Atur Global Atmospheric Watch (GAW) station (4°58' N, 117°49' E, elevation 426 m) in the Danum Valley Conservation Area. Observations were made during April-May 2008, from a clearing atop a hill surrounded by pristine rainforest, in the Sabah region of northern Borneo. The complex terrain surrounding the site meant that local dynamics have significant implications for interpreting chemical processes at the site. In particular it has been suggested that, although during the day the site was in a well-mixed planetary boundary layer (Hewitt et al., 2010), at night the hilltop location was above the nighttime boundary layer (Pike et al., 2010; Pugh et al., 2010).

A range of observations were made during the campaign, but critical for this study were observations of $j(\text{O}^1\text{D})$ (2π Filter radiometer), O₃ (Thermo Environmental Instruments 49C UV absorption instrument), hydrocarbons (GC-FID, Jones et al., 2011), and NO_x (Ecophysics CLD 780TR/PLC 760SR chemiluminescence instrument). Instrument inlets were all co-located with the OH instruments to ensure sampling from the same air mass (Hewitt et al., 2010). The campaign averaged diurnal concentrations of the observed species are shown in Fig. 1.

OH reactivity and OH concentration measurements were made by the University of Leeds FAGE instrument (Whalley et al., 2010; Ingham et al., 2009). The Leeds OH reactivity instrument (full description given in Ingham et al., 2009) is composed of a moveable injector inside a polytetrafluoroethylene (PTFE) flow tube. OH is made inside the movable injector via the photolysis of water vapour at 185 nm using a mercury lamp. This flow of artificially generated OH is injected into a turbulent flow (Reynolds number

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> 3950) of ambient air, which is drawn down the PTFE flow tube. The OH concentration generated within the flow tube is kept sufficiently low ($[\text{OH}] \approx 10^8 \text{ molecule cm}^{-3}$) that pseudo-first-order conditions are maintained, meaning the absolute OH concentration does not need to be known. The Fluorescence Assay by Gas Expansion (FAGE) technique (Heard and Pilling, 2003; Stone et al., 2012) is used to detect the OH via laser-induced fluorescence at low pressure. The OH residence time within the ambient airflow can be calculated from the measured flow velocity and known injector position relative to the sampling point for OH detection. Moving the injector in relation to the sampling pinhole of the detection cell is performed to vary the residence time. As the residence time is increased, the signal (S) due to OH decreases as the radicals react with species present in the ambient air sample and are lost to the flow tube walls. The loss of OH within the flow tube can thus be considered in terms of a chemical loss (k'_{OH}) due to the composition of the gas phase components flowing through the system and a physical loss of OH to the flow tube walls (k'_{phys}). The OH exponential decay is described by Eq. (1):

$$[\text{OH}]_t = [\text{OH}]_0 \exp(-k_{\text{OH}} t) \quad (1)$$

where $k_{\text{OH}} = k'_{\text{OH}} + k'_{\text{phys}}$. Thus:

$$\ln \frac{[\text{OH}]_t}{[\text{OH}]_0} = \ln \left(\frac{S_t}{S_0} \right) = -(k'_{\text{OH}} + k'_{\text{phys}}) t \quad (2)$$

where $[\text{OH}]_0$ and $[\text{OH}]_t$ are the initial OH concentration and that at time t , respectively, and S_0 and S_t are the observed laser-induced fluorescence (LIF) signals at these two times, respectively.

Previous calibrations of the detection of OH within the OH reactivity instrument have demonstrated a linear relationship between OH concentration and signal (Whalley et al., 2010). Thus a plot of $\ln(\text{OH signal})$ (with any background subtracted) versus residence time, t , yields a straight line with slope equal to $-(k'_{\text{OH}} + k'_{\text{phys}})$. k'_{phys} is then determined experimentally by flowing zero-air (Air products 99.999 %) down the flow tube and measuring the rate of OH decay (for this study the observed $k'_{\text{phys}} = 6.1 \pm 0.7 \text{ s}^{-1}$).

Figure 2 shows a typical OH decay measured in the field during the OP3 campaign. Decays were measured over a period of approximately 100 s, with 10 s spent at each injector position. A linear least-squares fit, taking into account errors in the X and Y coordinates, namely the 1σ variability on the log of the OH signal during each 10 s measurement at a particular injector position and the uncertainty on the reaction time, was performed to extract the observed k'_{OH} . The uncertainty on the calculated reactivity is the combination in quadrature of the error on the gradient obtained from the linear fit and the 1σ uncertainty on the measured value of k'_{phys} (Ingham et al., 2009).

A reduction in the OH reactivity from the true value due to the conversion of HO_2 (which is generated together with OH inside the injector) to OH by its reaction with NO has been identified (Kovacs et al., 2003; Ingham et al., 2009). However, during the OP3 campaign, the average NO concentration during the period of OH reactivity observations was 42 pptv. At these concentrations the rate of OH production from $\text{HO}_2 + \text{NO}$ is insignificant and does not perturb the OH decay (Ingham et al., 2009).

3 Observations of OH reactivity

OH reactivity observations were made on 12 days between 14 and 28 April 2008 (Fig. 3), from a height of approximately 5 m in a forest clearing. Figure 3 shows the 1071 OH reactivity observations made, with the error bars indicating the uncertainty on each individual observation (see Sect. 2). The maximum observed OH reactivity was $83.6 \pm 26.0 \text{ s}^{-1}$ (the variation here represents the uncertainty on this one observation rather than a typical uncertainty). The average diurnal variation is shown in Fig. 4 with OH reactivity peaking at an average of $29.1 \pm 8.5 \text{ s}^{-1}$ (the variation here represents the standard deviation in the observations in each 30 min time bin) in the early afternoon, and dropping to a minimum of approximately $7 \pm 3 \text{ s}^{-1}$ just before dawn. Figure 4 also shows the calculated OH reactivity from the observations of OH sinks shown in Fig. 1 (NO_2 , CO, isoprene, α -pinene, β -pinene, camphene, Δ -3-Carene, γ -terpinene, limonene, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, *n*-pentane,

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ethene, propene, acetylene, methane) (blue), and the calculated OH reactivity from reaction with just isoprene (green).

The OH reactivity calculated using the supporting measurements underestimates the average observations by as much as 70%, in keeping with previous studies of OH reactivity in forested regions (Di Carlo et al., 2004 (PROPHET), Sinha et al., 2008 (GABRIEL), 2010 (BFORM)). The OH reactivity calculated from just the measured isoprene shows an almost identical trend to the full calculation, as isoprene accounts for up to 80% of the calculated reactivity.

Figure 5 is the observed OH reactivity data plotted against the reactivity calculated for isoprene alone (i.e. the OH + isoprene rate constant multiplied by the observed isoprene concentration at each point), showing some correlation ($r^2 = 0.5$). The best fit gradient of this plot (2.0 ± 0.2) gives the number of OH radicals lost per isoprene molecule, and is higher than the gradient calculated from the observed compounds which react with OH (1.10 ± 0.01). The small increase in the gradient calculated from the observations above unity reflects the correlation in the diurnal profiles of the BVOCs (Fig. 1), and demonstrates the dominance of isoprene.

The difference in these gradients can be interpreted in two non-exclusive ways. The first is that the observed gradient is higher than the simulated as there are unmeasured isoprene degradation products which act to increase the reactivity associated with the isoprene concentration. Or, the gradient is higher as there are unmeasured primary emitted compounds with emissions that correlate with isoprene's emissions. The ability of isoprene derived oxidation products to increase the gradient is investigated in the next section.

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4 Conceptual framework

4.1 Base simulation

To investigate the role of the isoprene oxidation products to increase the gradient in Fig. 5 we use the Dynamically Simple Model of Atmospheric Chemical Complexity (DS-
5 MACC) (Emmerson and Evans, 2009; Stone et al., 2010) running the Master Chemical Mechanism (MCM) v3.2 (Saunders et al., 2003; Jenkin et al., 2003). We initially perform some highly stylised experiments, and introduce increasingly more realistic factors.

The initial simulations use the OP3 average observed concentrations of isoprene (2.5 ppbv) (Jones et al., 2011), OH (2×10^6 molecule cm^{-3} , Whalley et al., 2011, for
10 one simulation and 2×10^5 molecule cm^{-3} for another to investigate the impact of OH concentration) that are kept constant with no photolysis of compounds and a constant zero concentration of HO₂, O₃, and NO_x. The concentration of all other compounds are allowed to vary according to the chemistry scheme, with the only source of carbon being the constraining isoprene concentration, and the model is run to a chemical
15 equilibrium where the flux of carbon into the model from the oxidation of isoprene by OH is balanced by the flux of carbon out of the system as CO₂. The top panel in Fig. 6 shows the time evolution of the simulated OH reactivity ($= \sum k_{X+\text{OH}}[X]$) for the two different OH concentrations. The lower panel in Fig. 6 shows the simulated total OH reactivity divided by the simulated system reactivity due to isoprene alone (i.e.
20 in this simulation the only reactive loss for isoprene is reaction with OH therefore the reactivity due to isoprene = $k_{\text{OH}+\text{isop}}[\text{isop}]$), which is a measure of the number of OH radicals lost per isoprene molecule oxidized and is equivalent to the gradient in Fig. 5. This parameter is a useful tool for investigating the OH reactivity due to the oxidation products of isoprene and is defined as “ α ” (Eq. 3).

$$\alpha = \frac{\text{OH reactivity}}{\text{Isoprene reactivity}} = \frac{\sum k_{X+\text{OH}}[X]}{1/\text{isoprene lifetime}} \quad (3)$$

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The α value can be considered the isoprene flux multiplier for reactivity, i.e. how much extra reactivity over the initial oxidation step an emission of isoprene represents. In these initial simulations we assume that an isoprene emission flux is being balanced by its loss by the OH radical alone, and so for simplicity we can consider the isoprene flux to be equivalent to the flux from the reaction of OH with isoprene.

For both simulations α tends to the value of 10, which is attributable to the total number of OH attackable bonds in the isoprene molecule (8 C–H bonds, 2 C=C bonds). Thus in this case the isoprene flux multiplier for reactivity is 10. From a reactivity perspective, the emission of an isoprene molecule into this simple system can be considered as an emission of 10 bonds that ultimately need to react with an OH radical before the molecule can become CO₂ and H₂O vapour. The OH concentration used in either case does not impact the final value of α , only the time it takes for the system to get to steady state. At higher OH concentrations the equilibrium value of α is reached more quickly.

The time taken to reach equilibrium in both the simulations shown in Fig. 6 is significant (days), however, the α value of 10 is much larger than the observed number of OH radicals lost per isoprene of 2 (best-fit line, Fig. 5). This suggests that, at least from this simplistic analysis, the question should not be why the gradient observed in Fig. 5 is as high as 2 but why it is as low as 2.

In order to investigate the fate of the reactivity generated during the oxidation of isoprene, and how it controls OH reactivity and the value of alpha, increasingly realistic conditions are now used in the stylised box model.

4.2 Reactions of peroxides

In the simulations in Fig. 6 the HO₂ concentration was maintained at zero. A constant HO₂ concentration of 2.5×10^8 molecule cm⁻³ (10 pptv) is now introduced into the simulation together with an OH concentration of 2×10^6 molecule cm⁻³ (see Fig. 7). Again the HO₂ concentration used is the average noon-time concentration observed during

the OP3 campaign (Whalley et al., 2011). In this case the final calculated steady state reactivity is higher than in the equivalent simulation without HO₂, with a steady-state value of $\alpha = 11.4$. This increase in reactivity is due to the production of peroxides, which can re-cycle their parent peroxy radical upon reaction with OH. Thus an OH is destroyed without effectively destroying one of the originally emitted isoprene bonds so increasing the overall reactivity.



Thus this peroxide re-cycling mechanism creates a catalytic route to OH destruction; and the reactivity of the system can be increased beyond the reactivity available from the bonds in the isoprene molecule alone.

4.3 Photolysis and other oxidants

The evolution of the system's OH reactivity is also found to be impacted by the introduction of photolysis and oxidants other than OH into the modelling system. Figure 8 shows the impact of both other oxidants and photolysis on the system. For the photolysis we use a constant photolysis rate calculated at the appropriate rates for a solar zenith angle of 45°, and an O₃ column of 260 Dobson units. This reduces the reactivity in the system and α by around 20%. This reduction is due to the breaking of certain emitted isoprene bonds by photolysis rather than through reaction with OH, in particular those of formaldehyde (a significant product of isoprene oxidation, Finlayson-Pitts and Pitts, 1986).

Oxidants other than OH have a similar but smaller impact on reactivity (Fig. 8). For example O₃ at constant concentrations of 10 and 100 ppbv reduces the reactivity by 0.34% and 2.44% respectively. In order to make a consistent comparison, the model simulation shown above has had the reaction of O₃ with isoprene switched off so that the impact is on the secondary products alone. Otherwise the reaction produced enhanced concentrations of secondary products as it increased the flux of isoprene. NO₃

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(not shown) has a similar impact to O₃ but at the concentrations calculated for the OP3 site the changes are insignificant.

From these investigations of this physically simplified chemical system we conclude that to a 1st order the steady state reactivity is related to the rate of oxidation of isoprene by OH multiplied by the number of OH attackable bonds (10). 2nd order effects then include the increase in reactivity due to peroxide recycling, and a decrease in reactivity due to photolysis and other oxidants. Section 4.4 investigates how physical loss of compounds impacts these conclusions.

4.4 Physical loss

For a simple box, the physical loss of chemical species, whether from dilution into a lower background or the deposition of species to the surface or the canopy, or the formation of aerosol, can be considered to be a 1st order loss process. For simplicity we give all unconstrained compounds the same physical loss lifetime. Figure 9 shows the impact of physical lifetimes of 12, 24, 48 or 72 h (the range is based on studies of deposition of oxygenated VOCs to forest canopies, Hall et al., 1999; Karl et al., 2004). This significantly reduces the reactivity of the system as isoprene degradation compounds are physically removed before they can impact the OH reactivity, either directly or through the production of further oxidation products. As the physical loss rate increases the oxidation products are increasingly rapidly removed from the system and the alpha of the system tends to 1, which is the value of the reactivity for isoprene alone. The timescale to reach steady state is significantly reduced by the introduction of this physical loss. The time to generate 75 % of the steady state oxidation product reactivity (i.e. 50 % of the steady state reactivity not including the reactivity due to reaction with isoprene itself) is over 20 days without physical loss but this becomes 12 h with a 72 h lifetime and less than 8 h for the 12 h lifetime case.

These reductions in reactivity are much larger than was seen from the introduction of other oxidants or photolysis (Fig. 8), due to the removal of molecules that have

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multiple potential OH reaction sites. Thus, physical loss represents a potent mechanism to remove reactivity from the model.

4.5 Impact of the OH concentration

The analysis described in Sect. 4.1 (no physical loss) showed no relationship between the OH concentration and the steady state value of reactivity (Fig. 6), as changing the OH concentration does not change the number of bonds that need to be oxidized. However, with the inclusion of the physical loss process the system does become sensitive to the OH concentration. A competition is set up between the rate at which the oxidation products are produced and the rate at which they are removed from the system by physical loss. Figure 10 shows the effect of OH concentration on the calculated steady state reactivity and the value of α achieved. In these more realistic of simulations we include photolysis, peroxide formation, O_3 and NO_x , and a lifetime with respect to physical loss of model-calculated species of 24 h (i.e. a first order loss rate constant of $1.15 \times 10^{-5} \text{ s}^{-1}$ applied to all species). As the OH concentration is increased so does the reactivity and the α value. Isoprene degradation products are thus produced at a faster rate compared to their physical loss and so their concentrations increase leading to reactivity increasing at a faster rate.

4.6 Summary

This very simple modelling has provided a framework to understand OH reactivity. At a zeroth order, reactivity can be considered as a quantity related to the number of OH attackable bonds in a molecule and the flux of that molecule. 1st order chemical processes can act to increase (peroxide cycling) or decrease the reactivity (photolysis and other oxidants) but these processes seem to have relatively small impacts ($\leq 20\%$). However, physical processes can significantly reduce reactivity by removing bonds permanently from the system. Within a system with physical loss, increases

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in the OH concentrations tend to increase reactivity as it increases the rate at which oxidation products are produced.

After constructing this framework for considering OH reactivity the following sections attempt to explain the OH reactivity observations described in Sect. 3.

5 Observationally constrained model simulations

To investigate the mechanisms controlling OH reactivity during OP3 (Sect. 3), the OH reactivity observations were simulated using the box model described in Sect. 4.1. This model was constrained by the observed diurnal cycle in isoprene, mono-terpenes, NO₂, O₃, CO and the other observed hydrocarbons shown in Fig. 1, and utilised the MCM v3.2 oxidation schemes for all of the constraining species. The OH concentration was similarly constrained to the average observed diurnal reported in Whalley et al. (2011). The model is run forward in time using the campaign averaged diurnally varying concentrations of the observed compounds and with diurnally varying photolysis rates, calculated using TUV (Madronich, 1998) scaled to the observed $j(\text{O}^1\text{D})$, until a steady state is reached (i.e. the concentration of all compounds in day i is the same (within 1 %) of the compounds in day $i - 1$). As the rate of the physical loss of unmeasured species, via processes such as mixing, transport, deposition and SOA formation, is poorly constrained, a single first order loss rate has been used for all unconstrained species in the chemistry scheme giving these compounds a physical lifetime of 24 h. This is equivalent of a mixing out of the canopy into the boundary layer to a zero background concentration, or a deposition to a surface (the ground, the canopy or aerosol).

Figure 11 shows the calculated OH reactivity concentrations compared with the observations. The calculated OH reactivity at nighttime is calculated to within the uncertainty of the observed OH reactivity. However, the calculated daytime OH reactivity significantly underestimates the observations. This again is consistent with the previous studies (Kovacs et al., 2003; Di Carlo et al., 2004; Sinha et al., 2008, 2010; Hofzumahaus et al., 2009; Lou et al., 2010).

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However, the model is capable of producing OH reactivity that is much closer to observed when it is constrained to the diurnal concentration profiles of OH and isoprene each increased by one standard deviation of their observations (dashed red lines in Fig. 11 show calculated OH reactivity using ± 1 standard deviation of OH and isoprene concentration). Given the short lifetime of isoprene (approximately 1.3 h at local noon) and the significantly longer lifetime of the reactivity produced (longer than the physical lifetime of 1 day) it is not unreasonable to expect some mismatch (magnitude and timing) between the concentrations of isoprene and observed OH reactivity. As the OP3 observations were made on a ridge in a clearing in the forest, it seems likely that the source of the isoprene oxidation products that make up a significant fraction of the observed OH reactivity may not be the products of isoprene being sampled at the site, but from the oxidation of isoprene introduced within the forest canopy some distance from the site. The concentration of observed isoprene on the ridge is likely to be lower than the isoprene experienced earlier by the air mass within the canopy, which is the isoprene defining the observed reactivity.

6 Processes determining OH reactivity in the rainforest

The idealised simulations described in Sect. 4 identified various processes that impact the magnitude of the OH reactivity due to the oxidation products of the primary emitted VOCs. Using the observationally constrained model described in Sect. 5, the sensitivity of the calculated OH reactivity to these processes is now investigated in a set of more realistic simulations.

6.1 Sensitivity to OH concentration

Previous modelling studies of forested environments with high biogenic VOC emissions have significantly underestimated the observed OH concentrations (Tan et al., 2001; Kubistin et al., 2010; Hofzumahaus et al., 2009; Whalley et al., 2011; Stone

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et al., 2011). A simulation with unconstrained OH for OP3 exhibits a similar result (not shown but consistent with Whalley et al., 2011). The calculated daily maximum OH concentration peaks at approximately 5×10^5 molecule cm^{-3} compared with the observed 2×10^6 molecule cm^{-3} and the calculated daily mean OH concentration was 2×10^5 molecule cm^{-3} compared to the observed 8×10^5 molecule cm^{-3} . Figure 12 shows the impact of the lower modelled OH on the calculated reactivity. The OH reactivity drops by 20%, roughly consistent with the change in going from 8×10^5 molecule cm^{-3} to 2×10^5 molecule cm^{-3} as was shown in Fig. 10.

Thus, simulations of reactivity which use calculated rather than observed OH concentrations are likely to underestimate the reactivity produced from unmeasured isoprene oxidation products, as the modelled OH concentration is known to significantly underestimate the measured value. However, this impact is small compared to the magnitude of the missing reactivity.

6.2 Sensitivity to other oxidants and photolysis

In Sect. 4.3 oxidants other than OH, and photolysis were shown to be able to reduce the OH reactivity calculated by the model. However, simulations run under OP3 conditions show that the calculated reactivity has little or no sensitivity to these parameters (< 10%). This reflects the physical loss timescale imposed on the model (lifetime with respect to physical loss of 24 h) that removes reactivity significantly faster than other oxidants or photolysis are able to.

6.3 Physical loss

It was shown in Sect. 4 that the physical loss represented a significant sink for OH reactivity. Figure 13 shows the impact of changing the physical loss lifetime from 1 h to 108 h. Within this range, the model calculates a wide range of OH reactivity, and is within the uncertainty range of the observed values.

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The value of this physical loss parameter is difficult to determine experimentally, and our treatment of this process, via a uniform loss rate for all compounds, is simplistic. However, it does point towards the large sensitivity of modelled OH reactivity towards this parameter. More complex representations of canopy mixing (such as that used by Wolfe and Thornton, 2011) may be one approach to better constrain this parameter. Uptake to aerosols and the deposition of species to the forest soils and canopy through wet and dry processes is complex and poorly understood. It is thought that wet deposition is a major loss route for these oxygenated VOCs (OVOCs), due to their high solubility (Hall et al., 1999; Reeves and Penkett, 2003; Matsunaga et al., 2007). However, the solubility of many hydroperoxides and other oxygenated organics is extremely uncertain and known to cover a wide range, with the measured Henry's law constants for methyl hydroperoxide and peroxyacetic acid being 2–3 orders of magnitude lower than that for H₂O₂ (Lind and Kok, 1986). Observations of OVOC deposition velocities are sparse, with only a handful reported for forested regions (Hall and Claiborn, 1997; Valverde-Canossa et al., 2006; Hall et al., 1999; Karl et al., 2004; Kuhn et al., 2002). An observation of the deposition velocity of the sum of methyl vinyl ketone (MVK) and methacrolein (MACR) in a tropical rainforest by Karl et al. (2004), found velocities of $0.45 \pm 0.15 \text{ cm s}^{-1}$. Using an average observed boundary layer height during OP3 of 800 m (Hewitt et al., 2010) this is equivalent to a lifetime of approximately 2 days.

The removal of species out of the forest canopy into the boundary layer via mixing will also play a key role in this physical removal term. Complex topography results in complex local meteorology at the Bukit Atur site, with several studies identifying very different meteorological conditions between the day and the night (as discussed in Sect. 2) (Pearson et al., 2010; Pike et al., 2010; Pugh et al., 2010). Given the local meteorology, it seems unlikely that the mixing lifetime of compounds in the canopy remained constant throughout the day, and instead would have displayed significant diurnal variability.

Although deposition and mixing have the same impact on the modelled OH reactivity, on a global scale their impact is very different. On a global scale mixing conserves

reactivity, it is just moved from one location to another, whereas deposition removes reactivity. Considering reactivity as a tracer in itself poses some interesting questions for a global perspective. What is the global budget for the OH reactivity of isoprene or other hydrocarbons? The 500 Tg C yr⁻¹ of isoprene emitted each year is equivalent to ~ 1.5 Tmol Isoprene yr⁻¹ or 15 Tmol OH attackable bonds per year. What fraction of those bonds are removed by reaction with OH, O₃, NO₃, or deposited? Globally how much reactivity is created by peroxide cycling? Do models appropriately conserve reactivity through their chemical mechanism? Considering such questions on a global or regional basis may provide insights into the mechanisms controlling global OH concentrations.

7 Missing OH reactivity owing to primary emitted species

Given the variability in the isoprene concentration and the mis-match between the lifetime of isoprene and that of the OH reactivity generated by the subsequent isoprene oxidation steps, uncertainties in the physical loss rates and in the photolysis environment, it is not clear that the underestimate of reactivity (as shown in Fig. 11) really reflects a missing process. However, the existence of a missing primary emitted compound cannot be ruled out. At noon the model calculates a reactivity of ~ 15 s⁻¹, missing ~ 7 s⁻¹ compared to the observations. This is equivalent to ~ 3 ppbv of isoprene ignoring its degradation products or ~ 1.5 ppbv if degradation products are included (using the observed 2 OH radicals lost per isoprene from Fig. 5). This value of 1.5 ppbv is equivalent to half the measured isoprene concentration. If this missing emission were occurring globally it would provide a significant global source of reactive carbon to the atmosphere. If the missing primary sink was a monoterpene or larger terpenoid then the required concentration would be less reflecting the larger number of carbon bonds per molecule.

Identifying missing reactive carbon in the atmosphere can be informed to some extent by considering the “gaps” in capability left by existing instrumentation. The OP3 project used three instruments to determine reactive gas phase carbon: a GC-FID,

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5 a GC-MS and a PTR-MS (Jones et al., 2011; Langford et al., 2010). This is typical
of many large-scale process studies. Taking each in turn helps identify what species
types may evade detection and comprise an undetected carbon sink. GC-FID in this
experiment covered a carbon range of approximately C2 to C12 using two different GC
10 columns. Whilst identification of higher hydrocarbons (meaning C and H containing)
is difficult with just FID, the presence of such species would be seen in the form of
unknown peaks. The FID acts simply by burning carbon so any compound that could
pass through the column would create a response. A similar situation would arise with
GC-MS, in this instance if operated in full scan mode. Sample collection on adsorbent
15 traps adds a further degree of constraint and selectivity but in general terms is
amenable to all gas phase CH species and many CHO compounds. Some species un-
dergo chemical transformation upon sampling but the carbon is typically conserved, so
a missing sink would be detected but would perhaps be misidentified. The combination
of both methods provides a strong indication that a missing sink is unlikely to be a sim-
ple hydrocarbon. Both techniques also resolve some more polar species, as does the
PTR-MS method. GC techniques are generally good at resolving ketones and aldehydes
20 but become increasingly unreliable as functionality and polarity increases. Acids
and peroxides for example would probably escape detection by chromatographic meth-
ods unless derivatisation was used. PTR-MS provides a further useful constraint. In
full scan it essentially detects all organic compounds with a suitable proton affinity.
This spans basic hydrocarbons and most oxygenated species. Similar to FID a miss-
ing species would be seen as an unusual signal even if the exact identification of the
species could not be made. The simple inlets to PTR-MS make semi volatile species
reasonable to sample. For complex mixtures of isobaric species such as sesquiter-
penes the simple common ion generated by PTR should help detection – but these
25 species are not seen in any abundance. For a more comprehensive review of VOC
measurement techniques and their capabilities and limitations see Koppmann (2007).

Overall therefore there is only a relatively small subset of gas phase compound
classes that would evade detection when this combination of instruments is used in

full scan modes. Multifunctional species are one possibility, as are difficult to ionise compound classes such as organic peroxides, or difficult to handle species such as acids. Whilst a process of elimination does not necessary get close to finding the exact species needed to close budgets it does suggest where attention could reasonably be focused in future instrument development

8 Make-up of unmeasured carbon species

The observations made during this project do not enable the budget for OH reactivity to be closed, nor does the box modelling provide a definitive explanation for the source of the missing reactivity. However, the modelling can be used to identify those compounds that should be measured in future studies to enable a better constraint on this problem. Figure 14 illustrates the fractional contribution of different compounds (and compound types) to the noon-time OH reactivity calculated by the model (solid red line in Fig. 11). Isoprene accounts for ~ 37% of the reactivity, with the remaining observed constraining species (CH_4 , CO , H_2 , NO_x , O_3 and observed BVOCs including terpenes) accounting for 16%. Unmeasured degradation products account for almost 50% of the calculated reactivity. This fraction consists of over 900 different oxygenated compounds, with the largest fraction (over 30% of the total calculated reactivity) coming from multi-functional oxygenates such as methyl-glyoxal and epoxides formed during isoprene oxidation, as well as numerous aldehydes and ketones.

Although current technology allows for some of these to be measured (for example MVK, MACR, HCHO and some peroxides) the majority of the multi-functional model generated intermediates are not readily amenable to current experimental techniques. However, if the reactivity budget is to be closed, these more complex organic compounds need to be measured.

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Observations of OH reactivity were made for a period of 12 days during April 2008 in a tropical rainforest in Borneo. The maximum observed OH reactivity was $83.6 \pm 26.0 \text{ s}^{-1}$ with the campaign averaged noon time maximum being $29.1 \pm 8.5 \text{ s}^{-1}$. OH reactivity calculated using the observed sinks peaks at approximately 18 s^{-1} , significantly less than the observations and consistent with previous studies in similar environments. This calculated reactivity is dominated by isoprene (37 % at noon), with the diurnal trend in observed reactivity following that of the isoprene concentration.

A series of idealised model simulations have provided a framework in which to investigate OH reactivity, where to a first order the flux of reactivity into the system was equivalent to the flux of isoprene multiplied by a factor to represent the number of OH attackable bonds per molecule (10). These idealised simulations show that the lifetime of reactivity into the system is significantly longer than the lifetime of the initial oxidation step and depends on the lifetime of intermediate species. The OH reactivity of a system thus depends not only on the rate of emission of primary sink species, but also on the competition between OH and other processes that remove the reactivity produced throughout the entire oxidation chain. Physical loss is identified as the dominant processes that changed the reactivity calculated with the OH concentration, other oxidants and peroxide cycling playing a smaller role.

A constrained box model substantially underestimates the observations of OH reactivity. There is substantial variability in the observations of isoprene and OH and increasing the concentrations of these compounds within the model by one standard deviation of their variability greatly improves agreement between calculated and observed OH reactivity. Given the mismatch between the lifetime of isoprene and that of OH reactivity (by roughly an order of magnitude) it is not obvious that the observations themselves provide the appropriate information for the modelling study. The model is particularly sensitive to the physical loss (deposition or mixing) parameterization used, which highlights the need for improved constraints on these key processes. We find

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that our modelling provides substantial uncertainties in the calculated reactivity, which makes the need for a missing primary emitted compound less pressing compared with previous studies. If a missing compound were invoked to explain all the difference between the modelled and measured OH reactivity it would need to provide a carbon input equivalent to a 50 % increase in the isoprene concentration.

The supporting measurements of OH sinks made during the field campaign do not close the reactivity budget, with the model suggesting that at least 50 % of carbon-containing compounds which react with OH were not measured. Modelling indicates that this missing carbon appears to consist of a large number of complex multifunctional organic compounds and it is a challenge to the observational community to better constrain this part of the budget.

From a global perspective considering the budget of “emitted” reactivity (sources and sinks) may offer insights into the fate of organic carbon and ensure that this important property is modelled appropriately by regional, global and earth system models.

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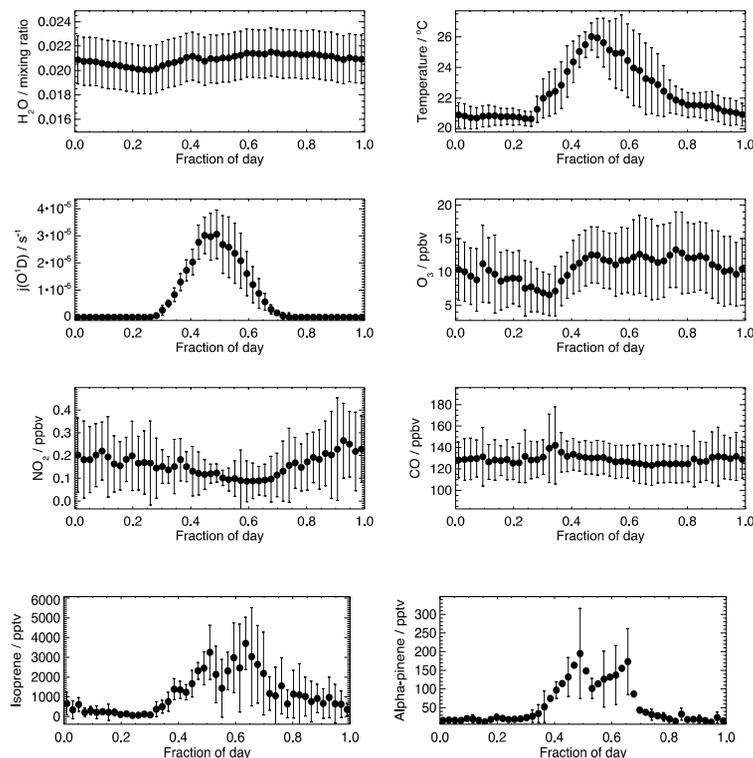


Fig. 1. Average diurnal cycles (local time) of measured species used to constrain the model, averaged into 30 min time bins, with error bars indicating the 1σ variability on the observations. All average values are means, except for NO_2 where the median has been used due to large spikes in the data. For hydrocarbons where the sampling period was less than every 30 min, the data were interpolated between their measurement points.

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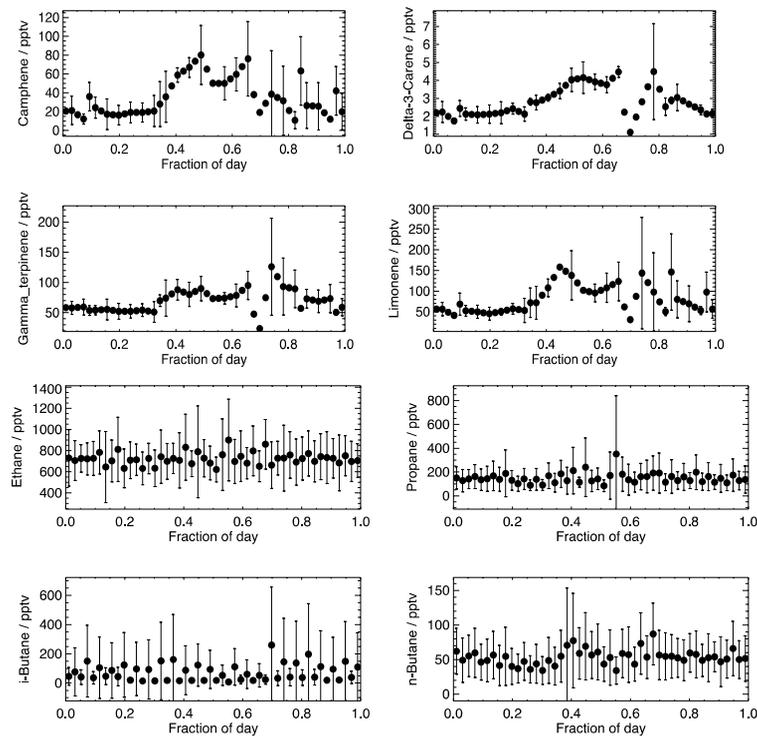


Fig. 1. Continued.

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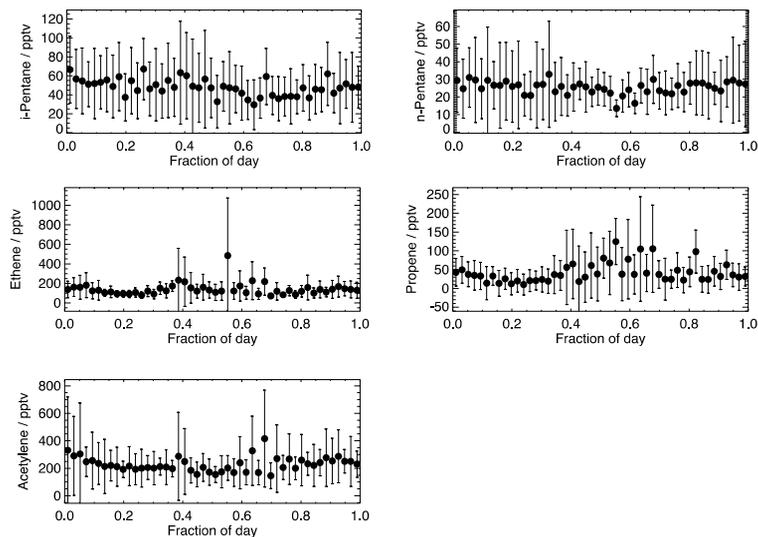


Fig. 1. Continued.

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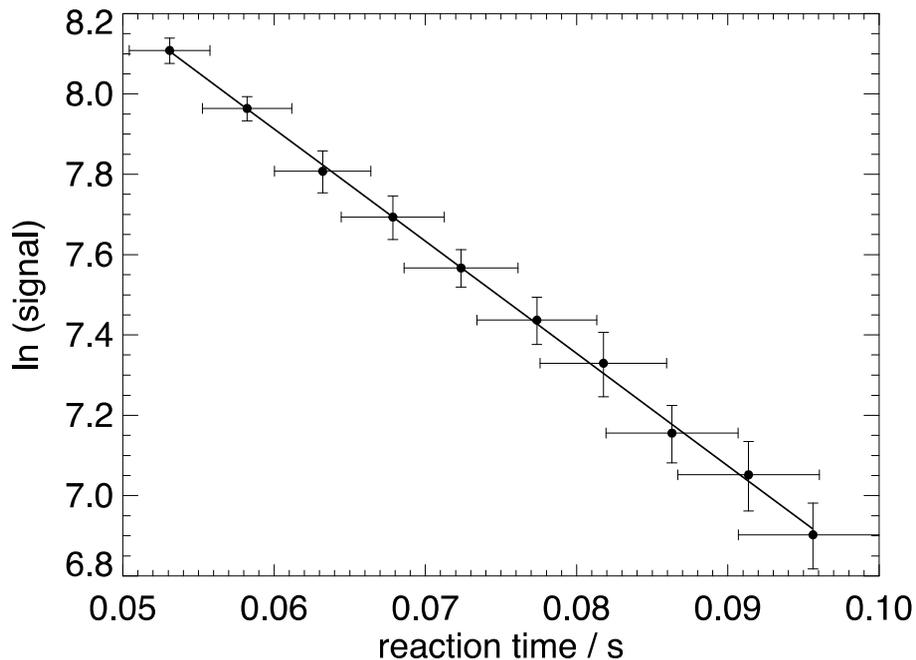


Fig. 2. Decay of OH measured between 12:25–12:27 Malaysia Time Zone (UTC + 08.00 h) on 21 April 2008 during the OP3 campaign, showing the line of best fit used to calculate the OH reactivity. The linear least squares fit to this decay yields an OH reactivity of $22.8 \pm 2.9 \text{ s}^{-1}$, after the subtraction of k'_{phys} . Error bars represent the 1σ variability on the OH signal during each 10 s measurement and the total calculated 1σ uncertainty on the residence time.

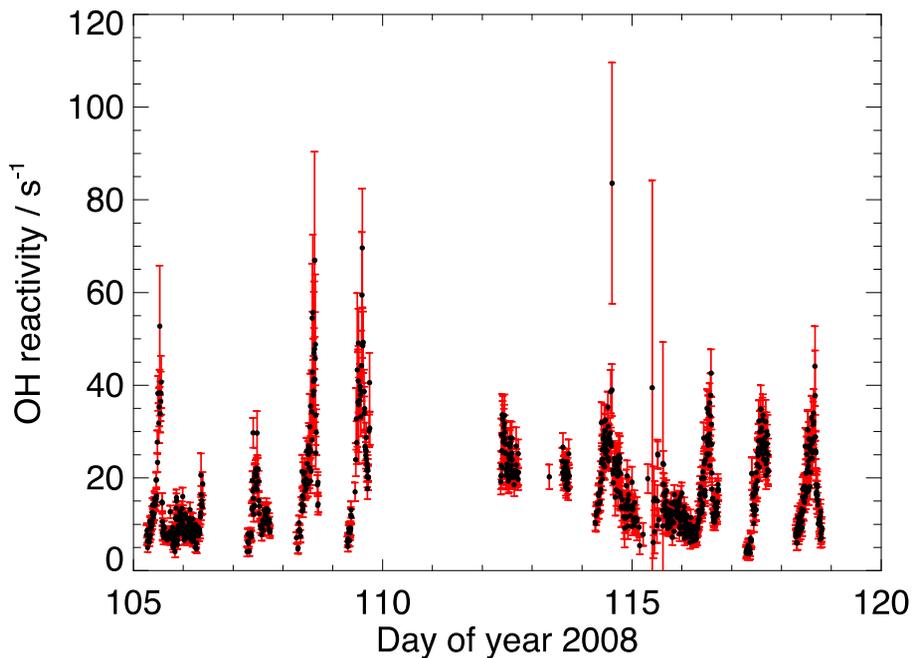


Fig. 3. OH reactivity observation time series for the OP3 campaign, with error bars indicating the 1σ uncertainty of the measurements described in Sect. 3.

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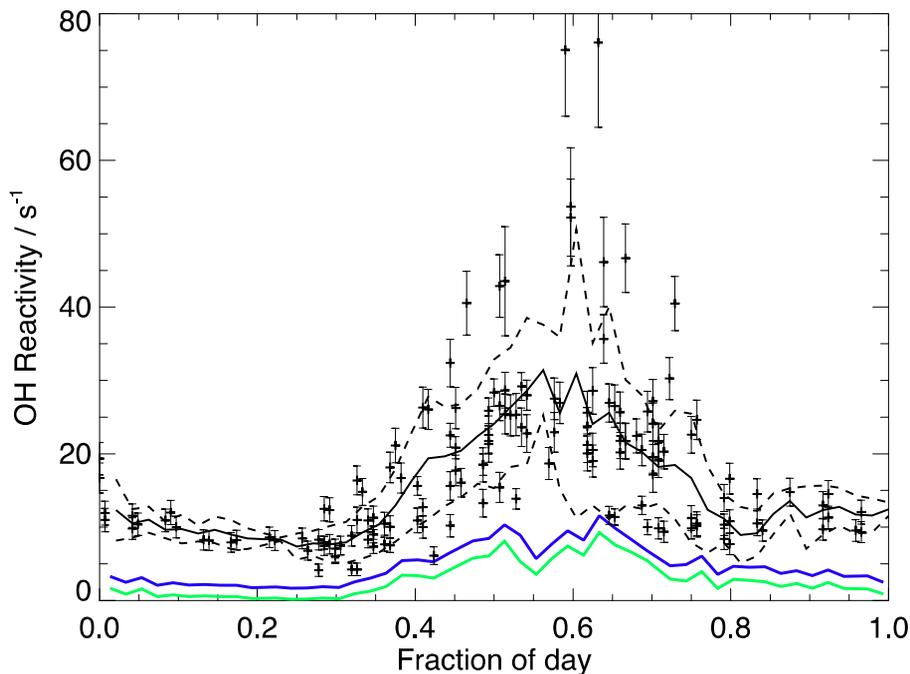


Fig. 4. OH reactivity observations (black markers), filtered for when supporting observations of major OH sinks were available, plotted against fraction of local day, with error bars indicating ± 1 sigma uncertainty on each observation. The solid black line is the mean diurnal, averaged into 30 min time bins, with the dashed lines indicating ± 1 standard deviation. The blue line shows the calculated OH reactivity from the supporting observations of OH sinks shown in Fig. 6. The green line is the calculated OH reactivity from reaction with only the observed isoprene.

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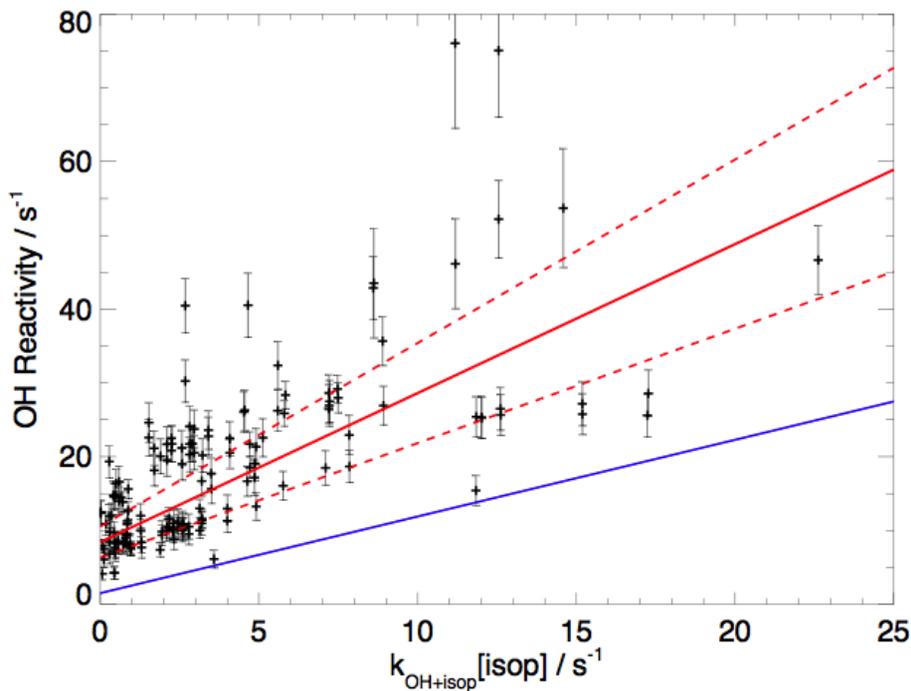


Fig. 5. OH reactivity observations (black points with error bars indicating measurement uncertainties) plotted as a function of the calculated OH reactivity from isoprene alone for each measurement point. The solid red line is the linear least squares fit to the data, yielding a slope of 2.0 ± 0.2 , with the dashed red lines showing the 1 sigma uncertainty on the fit. The blue line is the fit to the calculated OH reactivities based only on the measured OH sinks (blue line in Fig. 3), with a slope of 1.1 ± 0.01 .

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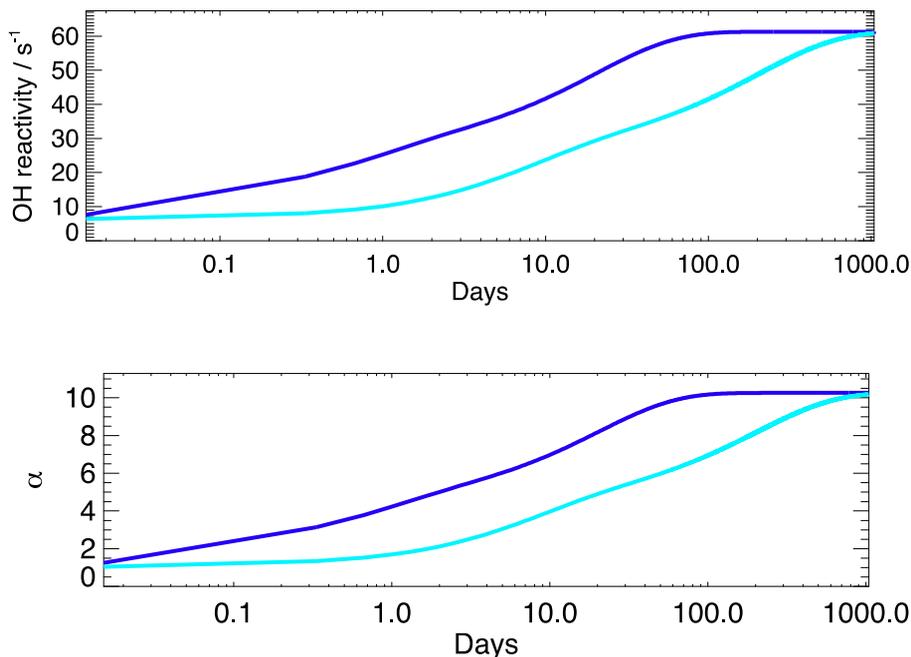


Fig. 6. Time evolution of OH reactivity (upper plot) and α (OH reactivity divided by the reactivity due to isoprene alone) (lower plot) in a model simulation with fixed mixing ratios/concentrations of 2.5 ppbv of isoprene, $[\text{OH}] = 2 \times 10^6 \text{ molecule cm}^{-3}$ (dark blue) and $2 \times 10^5 \text{ molecule cm}^{-3}$ (pale blue), $[\text{NO}_x] = [\text{HO}_2] = 0$, and no photolysis.

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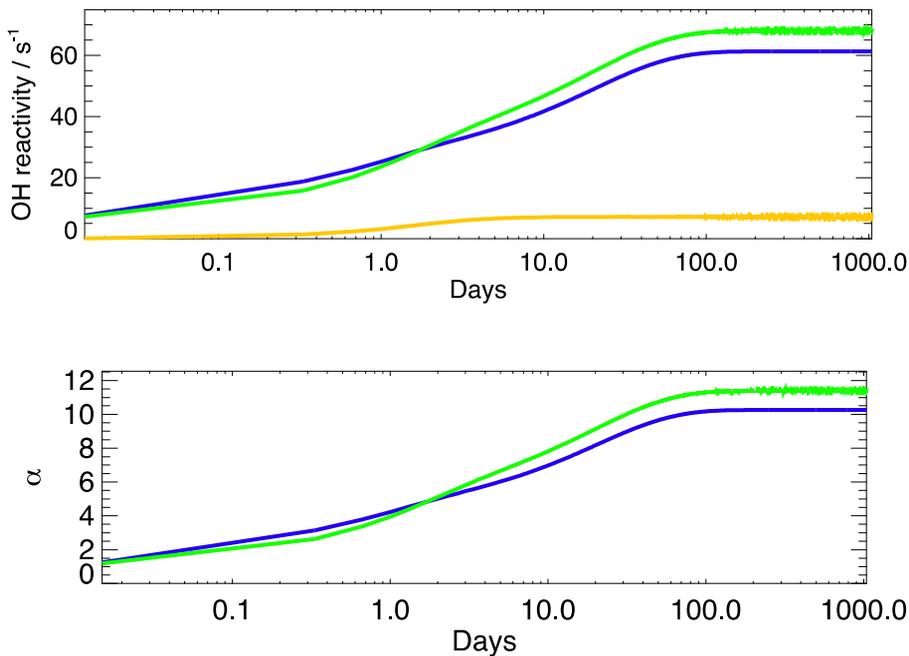


Fig. 7. Evolution of total OH reactivity and α in the base simulation with constant zero HO_2 concentration (dark blue) and a simulation with a HO_2 concentration of $2.5 \times 10^8 \text{ molecule cm}^{-3}$ (green). This increase in both reactivity and α is due to the formation of peroxides that can catalytically destroy OH as described in the text. The reactivity due to the peroxides alone is shown in the yellow trace.

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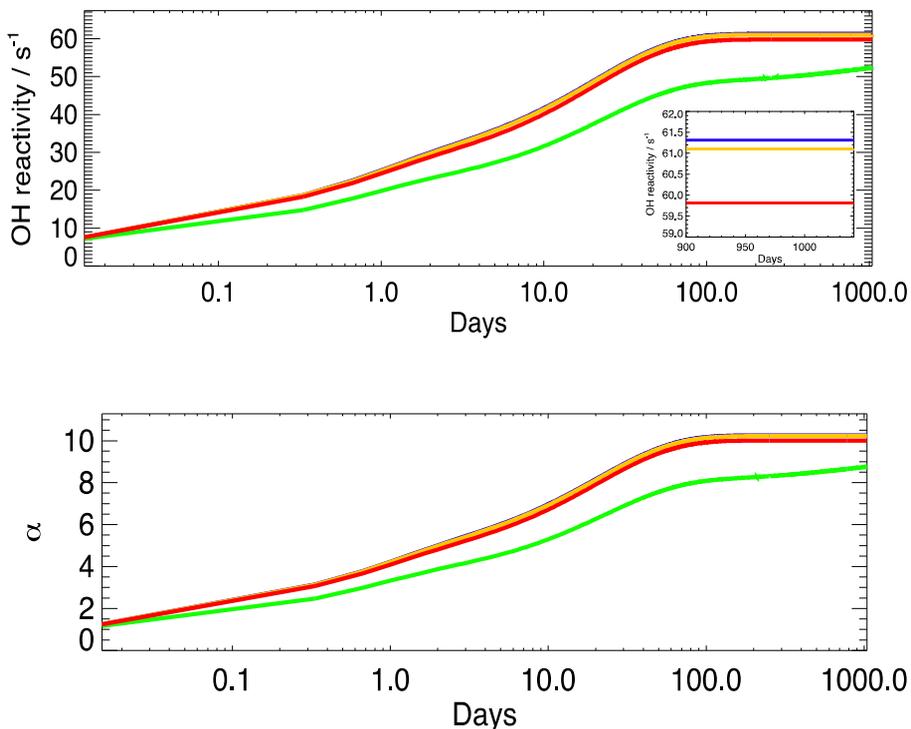


Fig. 8. Evolution of total OH reactivity and α in the base simulation (dark blue, hidden beneath red and yellow) compared with a simulation using photolysis rates calculated for a solar zenith angle of 45° (green), resulting in a value of $j(\text{O}^1\text{D})$ of approximately $2.5 \times 10^{-5} \text{ s}^{-1}$. The effect of other oxidants on the calculated OH reactivity and α are shown using simulations that include O_3 mixing ratios of 10 ppbv (yellow) and 100 ppbv (red). The inset plot shows the spread of the calculated reactivities with different O_3 mixing ratios at steady state.

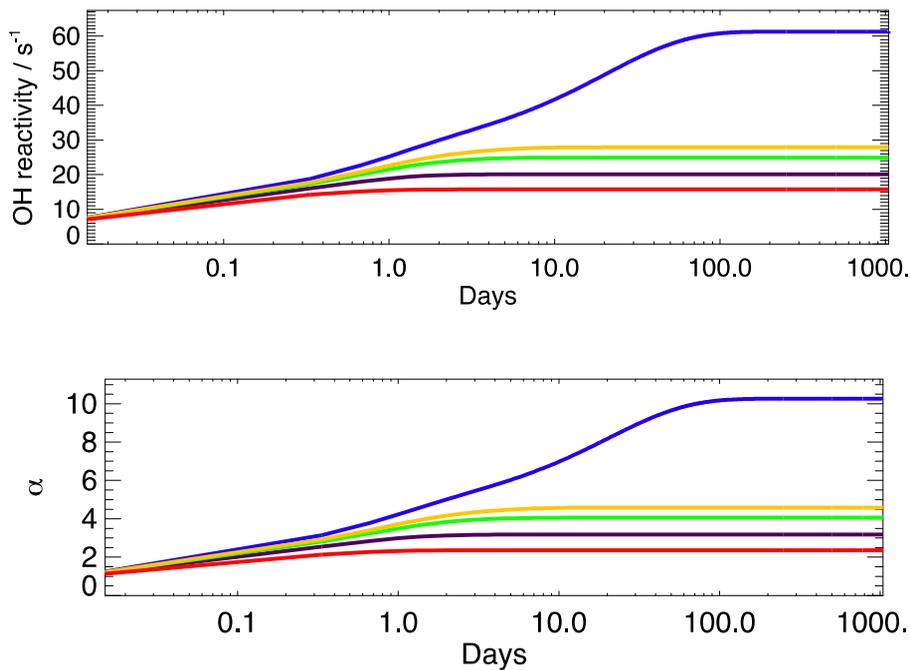


Fig. 9. Evolution of total OH reactivity and α in the base simulation (dark blue) compared with simulations containing a rate of loss of all non-constrained species to physical processes equivalent to a lifetime of 12 h (red), 24 h (purple), 48 h (green) and 72 h (yellow).

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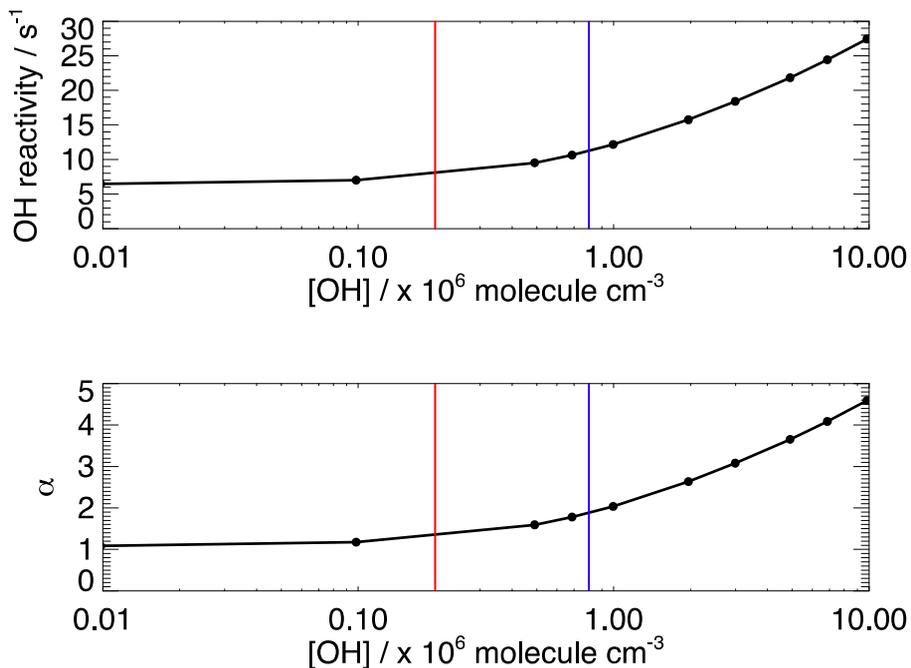


Fig. 10. Dependence of calculated steady state OH reactivity (top panel) and α (lower panel) on OH concentration when the physical removal rate within the model is equivalent to a 24 h lifetime. The vertical lines represent daily mean OH concentration during OP3 ($8 \times 10^5 \text{ molecule cm}^{-3}$, Whalley et al., 2011) (blue), and daily mean OH concentration calculated by the MCM V3.2 chemistry scheme ($2 \times 10^5 \text{ molecule cm}^{-3}$) (red line). The MCM model calculations and the impact of the OH concentrations are discussed further in Sect. 6.

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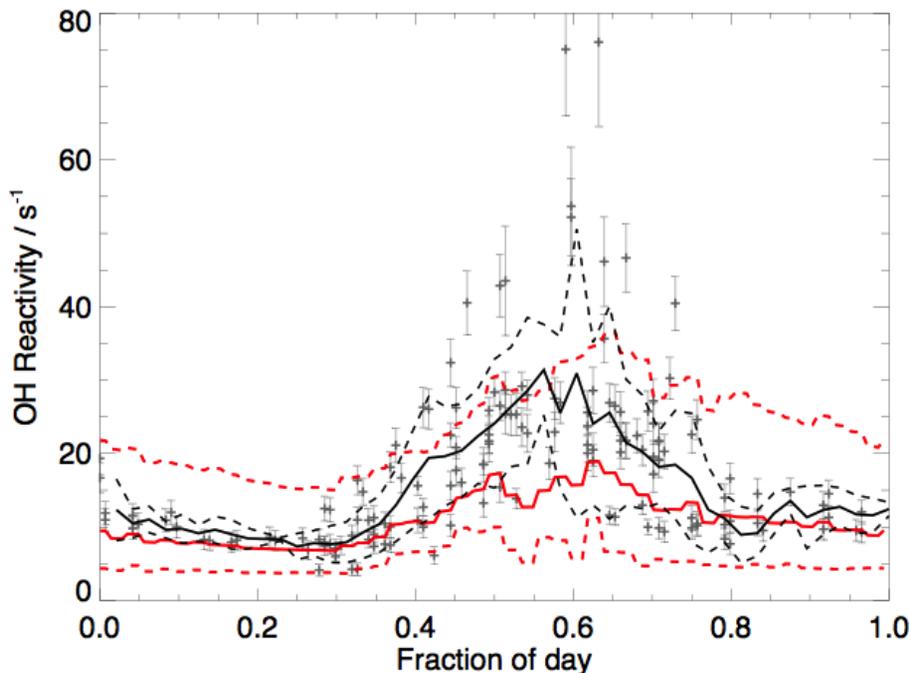


Fig. 11. OH reactivity observations (black markers) plotted as a diurnal, with error bars indicating ± 1 sigma uncertainty on each observation. The solid black line is the mean diurnal profile, averaged into 30 min time bins, with the dashed black lines indicating ± 1 standard deviation within that 30 min bin. The solid red line shows the modelled OH reactivity using the mean diurnal concentrations of the measured isoprene, OH and monoterpenes, the other measured species shown in Fig. 6 constrained to their mean value, and also using the steady state concentrations of the oxidation products of these constraining species, calculated by the MCM v3.2 chemistry scheme. The dashed red lines are the modelled OH reactivities constraining to ± 1 standard deviation of the observed OH and isoprene concentrations, with all other constraining species kept at the same concentrations as the solid red line simulation.

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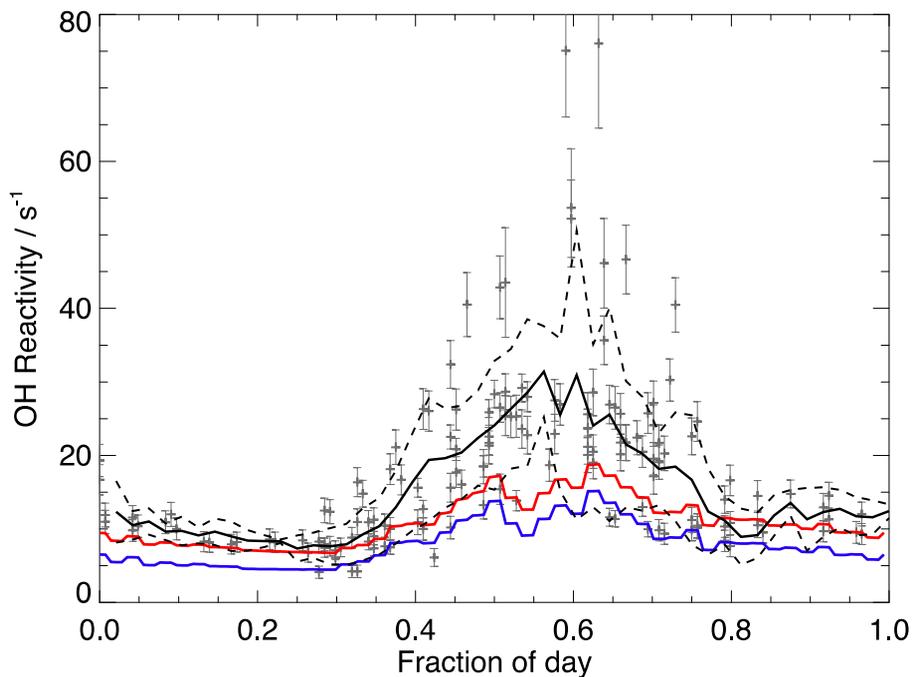


Fig. 12. OH reactivity observations (black points) plotted as an average diurnal, with error bars indicating ± 1 sigma uncertainty on each observation. The solid black line is the mean diurnal profile, averaged into 30 min time bins, with the dashed black lines indicating ± 1 standard deviation within that 30 min bin. The solid red line shows the modelled OH reactivity from the base model simulation (described in Sect. 5) with OH concentrations constrained to their mean observed value. The blue line shows the calculated OH reactivity in a model simulation where the OH concentration has been calculated by the MCM v3.2 chemistry scheme.

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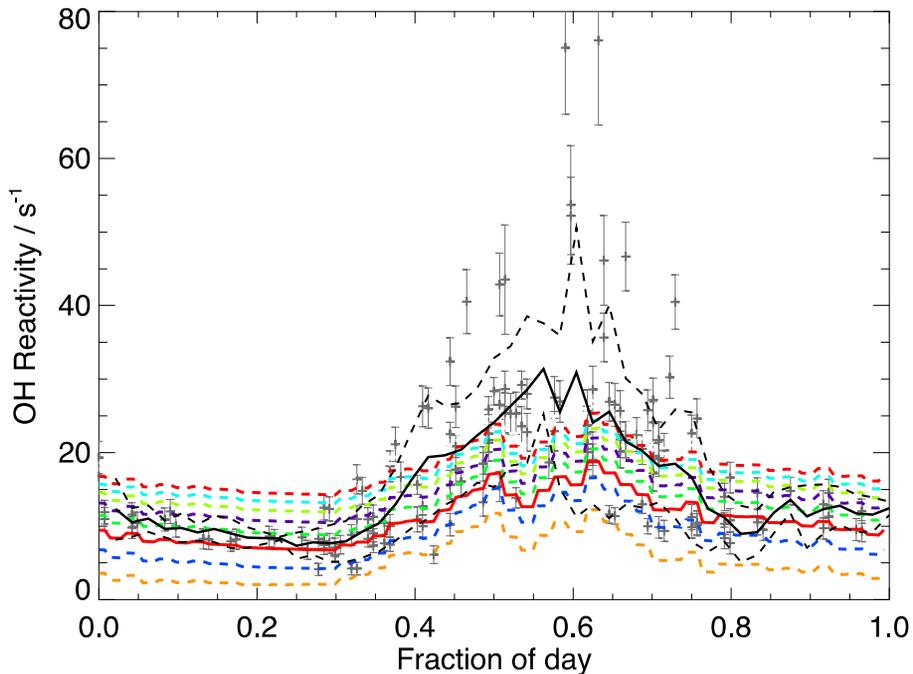


Fig. 13. Diurnal variation of the observed OH reactivity (black points) and a set of model simulations with different first order loss rates to represent the loss of model generated species to physical processes. The lifetime of species with respect to this first order loss are, in order of ascending calculated OH reactivity (i.e. lowest calculated reactivity to highest), 1, 12, 24, 36, 48, 60, 72, 84, 96 and 108 h.

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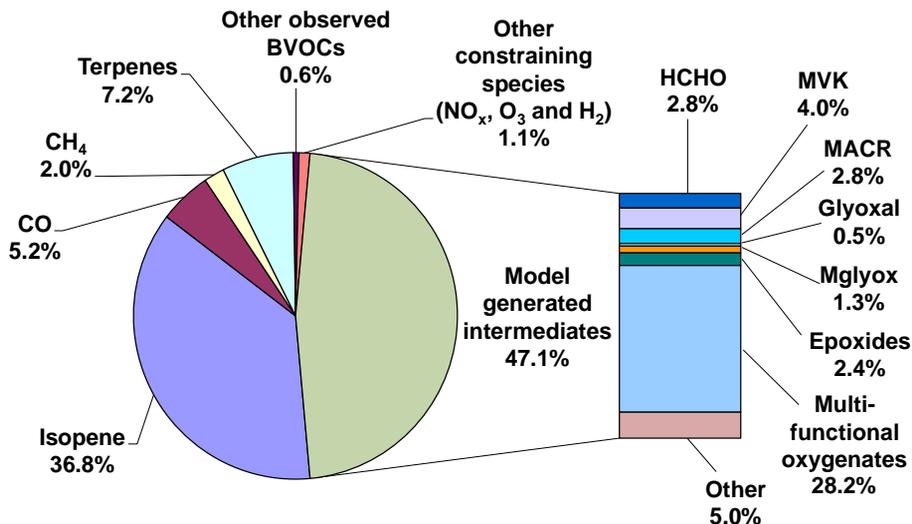


Fig. 14. Percentage contributions towards the noon time calculated OH reactivity using a 24 h lifetime with respect to physical loss of model generated species (solid red line in Fig. 11). The largest single contribution to the calculated OH reactivity comes from isoprene, however the model calculated intermediates contribute a larger fraction toward the observed OH sink than isoprene and the observed terpenes combined.

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