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# The influence of small-scale variations in isoprene concentrations on atmospheric chemistry over a tropical rainforest

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## Abstract

Biogenic volatile organic compounds (BVOCs) such as isoprene constitute a large proportion of the global atmospheric oxidant sink. Their reactions in the atmosphere contribute to processes such as ozone production and secondary organic aerosol formation. However, over the tropical rainforest, where 50% of the global emissions of BVOCs are believed to occur, atmospheric chemistry models have been unable to simultaneously simulate the measured daytime concentration of isoprene and that of its principal oxidant, hydroxyl (OH). One reason for this model-measurement discrepancy may be incomplete mixing of isoprene within the convective boundary layer, leading to patchiness or segregation in isoprene and OH mixing ratios and average concentrations that appear to be incompatible with each other. One way of capturing this effect in models of atmospheric chemistry is to use a reduced effective rate constant for their reaction. Recent studies comparing atmospheric chemistry global/box models with field measurements have suggested that this effective rate reduction may be as large as 50%; which is at the upper limit of that calculated using large eddy simulation models. To date there has only been one field campaign worldwide that has reported co-located measurements of isoprene and OH at the necessary temporal resolution to calculate the segregation of these compounds. However many campaigns have recorded sufficiently high resolution isoprene measurements to capture the small-scale fluctuations in its concentration. We use a box model of atmospheric chemistry, constrained by the spectrum of isoprene concentrations measured, to estimate segregation intensity of isoprene and OH from high-frequency isoprene time series. The method successfully reproduces the only directly observed segregation. The effective rate constant reduction for the reaction of isoprene and OH over a South-East Asian rainforest is calculated to be typically <15%. This estimate is not sensitive to heterogeneities in NO at this remote site, unless they are correlated with those of isoprene, or to OH-recycling schemes in the isoprene oxidation mechanism, unless the recycling happens in the first reaction step. Segregation alone is therefore unlikely to be the sole cause of

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model-measurement discrepancies for isoprene and OH above a rainforest.

## 1 Introduction

The volatile organic compound (VOC) isoprene ( $C_5H_8$ ) is believed to account for 44% of global biogenic emissions of VOCs (Guenther et al., 1995). The very high reactivity of isoprene with respect to common tropospheric oxidants makes its impact on tropospheric chemistry, particularly in the planetary boundary layer (BL), very significant. Modelling studies have suggested that areas in which high emissions of isoprene occur, for instance the tropical rainforest or mid-latitude deciduous forests, should see suppression of hydroxyl radical (OH) concentrations in the boundary layer (Wang et al., 1998; Lawrence et al., 1999; Granier et al., 2000; Poisson et al., 2000; Lelieveld et al., 2002; von Kuhlmann et al., 2004; Jöckel et al., 2006). This is of great consequence, as the OH radical is the primary sink for a large range of chemicals emitted into the atmosphere, including the greenhouse gas methane.

Over the past decade several measurement studies have noted much higher concentrations of OH in areas of high isoprene concentration than has been predicted by models of atmospheric chemistry (Tan et al., 2001; Carslaw et al., 2001; Ren et al., 2008; Lelieveld et al., 2008; Martinez et al., 2010; Hofzumahaus et al., 2009; Pugh et al., 2010). It has been proposed that the sources of OH in these high isoprene environments may be underestimated and several suggestions for additional methods of OH formation have been put forward (Lelieveld et al., 2008; Hofzumahaus et al., 2009; Peeters et al., 2009; Whalley et al., 2010). Whilst these methods are successful in increasing modelled  $[OH]^1$  in these regions to within the bounds of the measurements, these increases in  $[OH]$  lead to faster oxidation, and hence lower concentrations, of isoprene. Butler et al. (2008) and Pugh et al. (2010) have shown that the increases in

<sup>1</sup>Square brackets are used herein to indicate concentrations where no averaging has been applied or is specified.

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isoprene emission required to rectify this isoprene underestimation exceed the available isoprene flux in these regions and furthermore lead to a re-suppression of [OH].

Butler et al. (2008) hypothesised that the reason for the discrepancy between modelled and measured isoprene and OH may lie with the rate of reaction between isoprene and OH used in chemical models. The rate of change of isoprene concentration with respect to its reaction with OH can be represented by

$$\frac{\partial \langle C_5H_8 \rangle}{\partial t} = -k_{C_5H_8, OH} (\langle OH \rangle \langle C_5H_8 \rangle + \langle OH' C_5H_8' \rangle), \quad (1)$$

where the angle brackets represent volume averages, and the primes represent deviations from the mean concentration. In a typical atmospheric chemistry model, concentrations are assumed to be uniform within a box and the term containing the primes is neglected. However studies with large eddy simulation (LES) models have shown that the contribution of the prime term can be substantial for atmospheric reactions where the timescale of the chemical reaction is of the same order as the mixing timescale (e.g. Schumann, 1989; Sykes et al., 1994; Krol et al., 2000; Patton et al., 2001; Vinuesa and Vilà Guerau de Arellano, 2003). Using an intensity of segregation metric,  $S$  (e.g. Krol et al., 2000), where

$$S_{C_5H_8, OH} = \frac{\langle OH' C_5H_8' \rangle}{\langle OH \rangle \langle C_5H_8 \rangle}, \quad (2)$$

this effect can be represented by a modified reaction rate constant,  $k_{\text{eff}}$ ,

$$k_{\text{eff}} = k_{C_5H_8, OH} (1 + S_{C_5H_8, OH}). \quad (3)$$

A negative value of  $S$  implies that the two reactants are spatially anti-correlated, whereas a positive value implies a positive correlation, and  $S = 0$  indicates a homogeneous distribution. In their idealised LES modelling study, Krol et al. (2000) found that, under conditions of heterogeneous emissions,  $S_{\text{VOC}, OH} = -0.294$  was simulated for a reaction between a VOC and OH. In their study, the effective reaction rate of VOC

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and OH was 25% of that of the  $C_5H_8+OH$  reaction rate at 298 K (IUPAC, 2009). Similarly, in the development of a parameterisation for segregation intensity, Vinuesa and Vilà Guerau de Arellano (2005) suggest  $S_{VOC,OH} = -0.405$ , where the reactants react at a rate similar to that of the  $C_5H_8+OH$  reaction rate at 298 K. Such segregation can occur for  $C_5H_8$  and OH because, due to the extremely rapid reaction rate between the two compounds, [OH] rapidly approaches a steady state between its loss due to isoprene and its various production processes on a timescale of the order of one second (Appendix A). Therefore if isoprene is not uniformly distributed throughout the model box, OH concentrations will also vary, with the lowest OH concentrations co-located with the highest isoprene concentrations, assuming other OH sinks are uniform. Isoprene itself has a chemical lifetime in the boundary layer which is similar to typical turbulent mixing timescales (e.g. Butler et al., 2008; Pugh et al., 2010), while its flux into the BL is subject to heterogeneities likely influenced by the coupling of the canopy to the turbulent BL (e.g. Patton et al., 2001), the local dispersion of isoprene emitting plants, and variations in light and temperature. Therefore it is highly probable that heterogeneities of isoprene concentration within the boundary layer will occur.

Based upon comparisons between measurements over the Amazonian rainforest and simulations using a global chemistry model, Butler et al. (2008) found  $S_{C_5H_8,OH} = -0.6^2$  was required to reconcile measured and modelled concentrations if the standard IUPAC rate constant for  $C_5H_8+OH$  is used. In a similar experiment, but using a box model and measurements over a south-east Asian rainforest as part of the Oxidant Particle and Photochemical Processes (OP3) campaign, Pugh et al. (2010) required  $S_{C_5H_8,OH} = -0.5$  to attain a good agreement between measurements and their model. Considering that there is also a 20% uncertainty in the IUPAC rate constant, such values do not appear unreasonable in the context of the LES studies above.

Direct atmospheric measurements of segregation require co-located measurements

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<sup>2</sup>Butler et al. (2008) report a rate constant reduction of 50% below the lower uncertainty bound of the  $C_5H_8+OH$  rate constant of 20%, as specified by IUPAC, leading to an overall reduction of 60%.

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of both species at a temporal resolution fast enough to resolve the smallest relevant spatial scales. Butler et al. (2008) calculated a  $S_{C_5H_8,OH} = -0.13$  using aircraft measurements over the Guyanas; however at the speed of the aircraft the temporal measurement resolution resulted in a measurement scale of the order of several hundred metres. Hence smaller scale segregation would have been missed. To date only one study has measured  $S_{C_5H_8,OH}$  at a ground-based station, with Dlugi et al. (2010) finding values of  $S_{C_5H_8,OH}$  as negative as  $-0.15$  over a deciduous forest in Germany, although their study is limited to a single day of measurements.

During OP3, high-temporal resolution measurements of [OH] co-located with those of isoprene were not available. Here we use high temporal resolution isoprene concentration measurements (Langford et al., 2010) made over a south-east Asian rainforest as part of the OP3 campaign (Hewitt et al., 2010), in conjunction with a box model of atmospheric chemistry, to calculate [OH] and hence estimate the intensity of segregation of isoprene and OH in this region. First the measurements are described, followed by a description of the modelling approach used. Results are then presented and discussed.

## 2 Measurements

Measurements of isoprene concentration were made using a proton-transfer reaction mass spectrometer (PTR-MS) during April/May 2008 at the Bukit Atur Global Atmosphere Watch station ( $4^{\circ}58'59''$  N,  $117^{\circ}50'39''$  E). The station is located at an altitude of 437 m a.m.s.l., on a small hill approximately 260 m above the valley floor and the surrounded by primary and secondary rainforest (Hewitt et al., 2010). On top of the hill stands a 100 m tall, open-pylon type tower which was instrumented with a sonic anemometer at 75 m and a low pressure (60 kPa) PTFE gas inlet tube (length: 85 m; OD  $\frac{1}{2}''$ ). For the purpose of turbulence calculations, these measurements are considered to be  $\sim 125$  m above the forest canopy, taking into account that the measurement tower is sited on a hill (Helfter et al., 2010; Langford et al., 2010).

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The PTR-MS was housed in an air-conditioned laboratory at the base of the tower and sub-sampled from the inlet at a rate of  $0.3 \text{ l min}^{-1}$ , via a short length of PTFE tubing ( $\frac{1}{8}$ " OD). The flow in the main inlet line was turbulent, minimising the dampening of the VOC signal (Spirig et al., 2005). Individual compounds were sampled, iteratively, providing for each compound a disjunct time-series with a value every  $\sim 7$  s, that is measured with an integration time of 0.5 s and an overall instrument response time of 1 s. These data are available for a continuous 25 min period out of every 30 min. The remaining 5 min were devoted to calibration techniques and scans of the mass spectrum. A complete description of these measurements and set-up can be found in Langford et al. (2010).

Figure 1 shows an example of isoprene concentration measurements for a single day (26 April 2008). Although the diurnal cycle in the measurements is clear, substantial variation is seen around the mean. The inset indicates that these variations in isoprene concentration often have a magnitude similar to the mean isoprene concentration. These fluctuations occur on a timescale of less than one minute. If they are characteristic of the real atmosphere they indicate large inhomogeneities in the isoprene distribution on length scales of  $< 180$  m, considering a wind speed  $< 3 \text{ m s}^{-1}$ .

To test whether these concentration fluctuations are a real feature of the atmosphere, or are due to instrument noise, a statistical analysis was carried out. Hayward et al. (2002) showed that the instrument noise signal for the PTR-MS can be well-approximated by a Gaussian distribution. They show that the standard deviation of noise varies with the signal strength can be reliably predicted by the noise statistic (NS):

$$\text{NS} = \frac{\bar{c}}{\sqrt{\bar{c} \times \delta}}, \quad (4)$$

where  $\bar{c}$  is the mean signal recorded by the PTR-MS in units of ion counts per second, i.e. the number of instances in which that compound is registered at the detector each second. This is later converted into a mixing ratio as described in Langford et al. (2010).

The dwell time,  $\delta$ , is the time spent scanning for each compound. For more information on these terms the reader is referred to Hayward et al. (2002). As NS is analogous to standard deviation, if the rapid fluctuations in the measured isoprene concentration are purely due to instrument noise, 4.4% of recorded values should fall outside  $\pm 2NS$  (Hayward et al., 2002).

Calculating NS for the isoprene concentration data collected between 10:00–18:00 LT on 26 April 2008, using a 10 min running mean to calculate  $\bar{c}$ , reveals that 10.5% of these data lie outside  $\pm 2NS$  (3000 datapoints). This indicates that instrument noise is highly unlikely to be responsible for all of the variation measured and shows that variations in isoprene concentration of this magnitude were present in the atmosphere during OP3. In addition, the distribution is close to log-normal (Fig. 2), which is representative of the statistical distribution of atmospheric concentrations, rather than random ion noise, which follows a Poisson distribution. Although it is not possible to differentiate between the smaller variations and instrument noise, it is the large fluctuations that will be of most importance in the analysis that follows.

### 3 Modelling

#### 3.1 Approach

If a snapshot of the boundary layer is taken in time, a range of isoprene concentrations will be revealed in the spatial domain. Because isoprene is the dominant OH sink in the tropical forest environment, the variability in isoprene concentration induces variability in OH concentration. If isoprene is well mixed within the boundary layer, the variations in isoprene (and thus OH) concentrations will be small, and average concentrations are sufficient for calculations of chemistry. However, a boundary layer in which isoprene is not well mixed will display a large standard deviation of concentrations for isoprene, which will induce a large variation in OH concentrations, resulting in a strong co-variance between isoprene and OH. A coupled LES-chemistry model would attempt

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to describe the evolution of mixing air parcels of various concentrations in space. However, here we argue that the variability in the OH concentration can be estimated on the basis of the variability of isoprene, if (a) the chemistry of OH in this tropical forest is controlled mainly by isoprene, (b) isoprene is measured sufficiently fast to resolve the fastest fluctuations that contribute to the co-variance with OH, and (c) the air advecting past the measurement point is assumed to contain a range of isoprene concentrations representative of the boundary layer as a whole.

The ratio of turbulent timescale to chemical timescale is known as the Damköhler ratio ( $D_a$ ). Turbulence and chemistry interact when  $D_a$  is of the order of 1. For  $D_a \ll 1$  turbulence controls the variability and for  $D_a \gg 1$  chemistry dominates (Vilà Guerau de Arellano et al., 1995). Under near-neutral conditions, the turbulent diffusive time scale ( $\tau_t$ ) can be estimated as:

$$\tau_t = \frac{\kappa(z-d)}{\sigma_w^2}, \quad (5)$$

where  $d$  is the displacement height (defined as the effective height above the ground surface; 20 m in this case),  $z$  is the measurement height (125 m),  $\kappa$  is the von Karmen constant (0.38), and  $\sigma_w^2$  is the variance of the vertical wind component. Thus the typical turbulence timescale,  $\tau_t$ , is 200 s (corresponding to a length scale of  $\geq 800$  m) between 10:00–16:00 LT, whilst the chemical timescale for the reaction between isoprene and OH is fast, of the order one second (see Appendix A). Thus  $D_a$  is of the order of 200 and turbulence is insufficiently fast to interact with the OH-isoprene chemistry, fulfilling requirement (a).

The isoprene time-series represents 1 s average values approximately every 10 s. Assuming that Taylor's frozen turbulence hypothesis (Powell and Elderkin, 1974) holds for reactive compounds, a measured isoprene concentration time-series with a temporal resolution of 1 s is transformed into a length scale, or spatial resolution, of 4 m or less, when measured wind speeds are  $4 \text{ m s}^{-1}$  or less. Little is known about the frequency distribution (and thus the length-scale) of the co-variance between OH and

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isoprene and other chemical systems. In a study utilising a LES model, Vinuesa and Porte-Agel (2008) found that the sub-grid scale mixing term could be neglected when a horizontal resolution of  $\sim 50$  m or less was used. In this study, at the high measurement height of 75 m,  $>90\%$  of the variance and flux were estimated to be carried in eddies slower than 1 Hz (Helfter et al., 2010; Langford et al., 2010) and it is likely that the high-frequency contribution to the OH-isoprene co-variance is even smaller because of the damping induced by the fast chemistry. In addition, the close agreement found between the average of the 75-m isoprene measurements and aircraft measurements made in the boundary layer (Hewitt et al., 2009) gives confidence that the PTR-MS isoprene measurements at 75 m are representative of the boundary layer as a whole. Thus, the isoprene measurement is thought to be both representative and taken at a sufficiently high temporal resolution for requirements (b) and (c) to be fulfilled. Because the isoprene measurement is non-continuous, it only provides a good statistical representation of the distribution of 1 s data points. However some of the information on the temporally organised structure in the variability gets lost. In the present model study we assume that for each 1 s data point a stationary state between isoprene and OH is obtained which is unaffected by the concentration history, since OH concentrations re-equilibrate to a change in isoprene concentration on a timescale of the order of this time (Appendix A). Therefore, given a sufficient time window,  $t_s$ , a representative sample of the population of isoprene concentrations advected past the detector should be obtained, and a histogram can be constructed showing the probability distribution of the measured isoprene concentration (Fig. 2).

By calculating the average sampled isoprene concentration and modelled OH concentration over  $t_s$ , estimates can be gained for  $\langle C_5H_8 \rangle$  and  $\langle OH \rangle$ . Hence Eq. (2) effectively becomes,

$$S_{C_5H_8, OH} = \frac{\overline{OH' C_5H_8'}}{\overline{OH C_5H_8}}, \quad (6)$$

where the over-bars represent time averages. Note we are not directly converting

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a time series measurement into a spatial scale of eddy size (evoking Taylor's frozen turbulence hypothesis). Rather a set of discrete samples recorded in the time domain are used to represent the spatial variation of a population of those samples throughout the boundary layer. An appropriate length for  $t_s$  is discussed in Sect. 3.2.

We have already stated that the measured  $[C_5H_8]$  time-series is assumed to give a representative sample of boundary layer  $[C_5H_8]$ . Therefore a corresponding representative sample of boundary layer  $[OH]$  can be calculated using

$$[OH] = \frac{P_{OH} - OL_{OH}}{k_{C_5H_8, OH} [C_5H_8]} \quad (7)$$

Where  $OL_{OH}$  is the sum of all OH sinks other than  $C_5H_8$ , and  $P_{OH}$  is the OH production rate. As  $P_{OH}$  and  $OL_{OH}$  are complex terms, they are most easily calculated using a numerical chemistry model. By constraining a chemistry box model to the measured  $[C_5H_8]$  time-series intervals,  $[OH]$  can be calculated. Note that this method does not produce a continuous  $[OH]$  time-series, but rather a set of  $[OH]$  samples, which correspond to the measured samples of  $[C_5H_8]$  at a given time. If the re-equilibration of OH concentrations occurred over a longer time period than the isoprene sampling interval then the model would not find the new steady-state  $[OH]$  before the next change in  $[C_5H_8]$ , and the model generated  $[OH]$  time-series would not be valid, given that no information exist on the isoprene concentration of 9 s after each 1 s sample. Appropriate values for  $[OH]$  and  $[C_5H_8]$  are provided by taking running means over the time window,  $t_s$ . So effectively a running sample of the population is being taken. This avoids unnecessary and arbitrary discretisation of the segregation signal and is similar to running mean filtering in the calculation of surface exchange fluxes, i.e. co-variances of concentration with wind components (McMillen, 1988).  $OH'$  and  $C_5H_8'$  are then easily calculated from the time series, and hence  $S_{C_5H_8, OH}$  can be calculated using Eq. (6).

An important consideration are the secondary oxidation products of isoprene, which may be preferentially co-located with high isoprene concentrations, depending on the ratio of the turbulence timescale,  $\tau_t$ , to their chemical lifetime,  $\tau_c$ . However, the life-

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times of all secondary oxidation product of isoprene which may impact the OH sink are much greater than the  $\sim 200$  s turbulence timescale ( $D_a \ll 1$ ). Hence it is assumed that the concentrations of secondary oxidation products of isoprene are not co-variant with those of isoprene, and effectively consistute random noise in the  $S_{C_5H_8, OH}$  signal.

Therefore it is better to assume a homogeneous mixture, averaging out the effects of secondary species and limiting our conclusions to the segregation of isoprene and OH only. The use of the constrained box model in the manner described above implicitly mixes all species homogeneously across the modelled boundary layer if they have a lifetime longer than the sampling period.

Running a model constrained to measured concentrations is a typical approach for studying chemical processes in the atmosphere and testing model chemical mechanisms using both ground-based (e.g. Carslaw et al., 2001; Emmerson et al., 2005, 2007; Hofzumahaus et al., 2009; Kanaya et al., 2007, 2009) and aircraft-based (e.g. Ren et al., 2008; Kubistin et al., 2008) measurements. These studies typically use measurements of VOCs,  $NO_x$ ,  $O_3$ , CO and other intermediate/long-lived species, as boundary conditions to attempt to calculate radical concentrations. However they all utilise measurements with a temporal resolution of greater than 1 min for the aircraft based measurements and in the region 5–15 min for the ground based measurements. All these studies are likely to miss much of the fine-scale segregation of species investigated in this work.

### 3.2 Model setup

The CiTTyCAT box model of atmospheric chemistry (Wild et al., 1996; Evans et al., 2000; Emmerson et al., 2004; Donovan et al., 2005; Real et al., 2007, 2008; Hewitt et al., 2009; Pugh et al., 2010) is used to apply this approach to the OP3 measurements. The model is run for the 12 h of daylight between 06:00 and 18:00 LT, and isoprene concentration is constrained by each of the 1 s measured concentrations, run for 10 s. To allow the model to run continuously, gaps in the isoprene time series are filled by replicating a section of the immediately preceding data the same length as the

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gap. This is deemed acceptable as the characteristic spectrum of isoprene timescales is what is of interest in this analysis. If the 12 h data period contains gaps greater than 30 min, data for that day are discarded. In total eleven days of suitable data are available for analysis for the first OP3 campaign (OP3-1) (April–May 2008).

The model is integrated on a time step of 1 s, although the chemical solver itself uses intermediate time steps of a variable size (Brown et al., 1989). As the model has previously been optimised for the OP3 scenario by Pugh et al. (2010), the set-up described in that paper is largely retained, with the model being fed campaign average values of cloud cover (calculated using  $j(\text{O}^1\text{D})$  as a proxy) and temperature. Boundary layer height is set to 800 m throughout the run. However it must be cautioned that LIDAR measurements of boundary layer height (Pearson et al., 2010) indicate that the BL is well-mixed throughout this 800 m range only between the hours of 10:00–18:00 LT. Therefore results before 10:00 LT will not be representative of the BL as a whole. Indeed the first hour must be discarded as spin-up time.

Finally, the length of the time window,  $t_s$ , is of importance. When selecting  $t_s$  it must be considered what elements should be classified as segregation and at what time-scale variations start to reflect changing conditions (non-stationarities). For instance, if  $t_s = 1$  h, then variations in cloud cover and solar zenith angle may make a significant contribution to the variation. However, cloud cover and solar zenith angle changes are typically uniform across the boundary layer and therefore do not contribute to the spatial variation which is the subject of this work. In order to ensure that only factors such as canopy emission and BL turbulence dominate the variation, a shorter  $t_s$  is required. To determine how short, the fast Fourier transform of measured  $j(\text{O}^1\text{D})$  (which implicitly incorporates both cloud cover and solar zenith angle changes) is computed (not shown); this indicates little variation on timescales shorter than 10 minutes, suggesting  $t_s = 10$  min would be sufficiently small to eliminate the effect of these lower frequency variations. Conveniently the BL turnover timescale, as calculated by Pugh et al. (2010), is also close to 10 min, hence a time window of this length should be sufficient to allow sampling of the range of isoprene concentrations within the BL. Dlugi

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et al. (2010) find  $t_s = 10$  min to be appropriate for their measurements of segregation intensity over a forest in Germany by examining the covariances of OH and  $j(\text{O}^1\text{D})$ . As using  $t_s = 10$  min also ignores the effects of slower frequency eddies, test calculations for  $t_s = 10, 30, 60$  and  $120$  min have been computed to give an indication of how the result is affected. Calculations were carried out using isoprene measurements collecting during the OP3 campaign on 30 April 2008. Figure 3 shows that the greatest deviations occur at the ends of the day, when changes in  $j(\text{O}^1\text{D})$  are most rapid. Even when using  $t_s = 120$  min, which clearly incorporates significant non-stationarities, results during the middle period of the day were generally within a factor of two of those generated using  $t_s = 10$  min.

## 4 Results and discussion

### 4.1 Case study of OH-isoprene interactions above a German mixed forest (Dlugi et al., 2010)

Dlugi et al. (2010) appear to have provided the only clear observations of  $S_{\text{C}_5\text{H}_8, \text{OH}}$  to date. Therefore, to test the approach described above before making calculations for the OP3 campaign, the model was run for 4 h between 10:00 and 14:00 LT using an isoprene concentration time series produced by generating random numbers according to the distribution statistics specified in Dlugi et al. (2010). As only limited information about the physical and chemical characteristics of the Dlugi et al. (2010) measurement site were available, the model setup used for OP3 was retained with the following exceptions: The box was positioned at  $50^\circ 54' \text{N}$ ,  $6^\circ 24' \text{E}$ , with NO emissions from the Yienger and Levy (1995) inventory for that location being used. The  $j(\text{O}^1\text{D})$  measurements reported in Dlugi et al. (2010) were approximated by modifying the model cloud cover and the reported temperature measurements were also used. Initial concentrations for  $\text{O}_3$ , NO, HCHO, MACR, MVK and HONO were set as reported in Dlugi et al. (2010) and Kleffmann et al. (2005), the latter measurements were for the same site

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but they were made a month earlier. As CiTTYCAT is currently unable to replicate the magnitude of daytime HONO formation that was observed at this site, the model is constrained to a constant HONO mixing ratio of 150 pptv, following the measurements of Kleffmann et al. (2005).

5 The result of this test is shown in Fig. 4. A reasonable agreement is achieved in terms of the timing and magnitude of the main peaks. The model does not capture all the variability in the observed data and tends to overestimate the depth of the troughs. However, as will be discussed in Sect. 4.3, the concentration of OH sinks other than isoprene has a damping effect on the magnitude of  $S_{C_5H_8,OH}$ . At a site such as this  
10 in Western Europe, the concentrations of background species contributing to the OH sink may be quite high. Hence it is likely that our model will somewhat overestimate the magnitude of  $S_{C_5H_8,OH}$  in this case, without detailed information for the background species. When the distributions of  $S_{C_5H_8,OH}$  from Dlugi et al. (2010) and our model are normalised to a mean of zero, a Kolomogorov-Smirnov test indicates that they  
15 are both from the same distribution at the 99% confidence level. This suggests that the variability of  $S_{C_5H_8,OH}$  is well represented by this modelling approach. Overall the agreement achieved is encouraging, suggesting that the model can effectively estimate  $S_{C_5H_8,OH}$  from the supplied isoprene data.

## 4.2 Application to a tropical forest (OP3)

20 Figure 5 shows the intensity of segregation calculated by the model for each day of available data for the OP3 campaign.  $S_{C_5H_8,OH}$  is much less negative than suggested in the studies of Butler et al. (2008) and Pugh et al. (2010) with a 10:00–18:00 LT mean of  $S_{C_5H_8,OH} = -0.054$  for  $t_s = 10$  min, resulting in  $k_{eff}$  being 5.4% smaller than  $k_{C_5H_8,OH}$ . Figure 6 shows that the distribution of  $S_{C_5H_8,OH}$  during OP3-1 is strongly skewed with  
25 a tail towards the more negative values, with the median slightly less negative than the mean at  $S_{C_5H_8,OH} = -0.049$ . The 5th and 95th percentiles are  $S_{C_5H_8,OH} = -0.104$  and  $S_{C_5H_8,OH} = -0.018$  respectively. A large variation in  $S_{C_5H_8,OH}$  is modelled over the course of each day, but 10 min average values never fall below  $S_{C_5H_8,OH} = -0.25$ .

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Figure 7 shows that  $S_{C_5H_8,OH}$  is not strongly correlated with either the standard deviation ( $\sigma$ ) or the mean ( $\mu$ ) of the isoprene concentration. However the combination of these two statistics,  $\sigma_{C_5H_8}/\mu_{C_5H_8}$ , i.e. the relative standard deviation, correlates strongly with the intensity of segregation. This is likely due to the rate of increase of the overall reaction rate of isoprene and OH,  $dR_{C_5H_8,OH}/\langle C_5H_8 \rangle$ , decreasing with increasing isoprene concentration. Therefore a given  $\sigma_{C_5H_8}$  will produce a greater range of  $R_{C_5H_8,OH}$  over  $t_s$ , when  $\mu_{C_5H_8}$  is low. This indicator becomes less accurate as  $S_{C_5H_8,OH}$  becomes more negative; we can find no simple explanation for this increase in scatter. It could be due to a combination of the skewness and kurtosis of the isoprene distribution, combined with the OH production rate and the size of the non-isoprene OH sink. One feature of the plots in Fig. 7 is that, rather than a quasi-random scatter of data, the data points tend to arrange themselves in trajectories. This is most obvious with some of the outliers. This behaviour is a result of using running means over the input data, meaning that each point is influenced to some extent by the last, and should not be interpreted mechanistically.

The calculation of  $S_{C_5H_8,OH}$  presented in this section is specific to the OP3 measurement site, as the relative deviation of the isoprene concentration will depend strongly upon the strength of the isoprene emission flux and upon the behaviour of the factors that make this flux heterogeneous in time and space, e.g. species distribution, canopy venting, small-scale turbulence. This could lead to a large variation in  $S_{C_5H_8,OH}$  at different sites. However two factors are worth noting here. The first is that the measurements of Dlugi et al. (2010) for a forest in Germany and the modelled values of  $S_{C_5H_8,OH}$  presented here are very similar in magnitude despite their differing locations. The second is that OP3 observed relatively small isoprene emissions compared to studies over the Amazon rainforest (Langford et al., 2010). At higher isoprene emissions the relative deviation will be smaller for a similar amplitude of variation; from Fig. 7 this implies a less negative value of  $S_{C_5H_8,OH}$ .

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### 4.3 Sensitivity

Figure 7 demonstrates that the most important variables for  $S_{C_5H_8,OH}$  identified by this study are the magnitude and standard deviation of the isoprene concentration. To test how much the underlying photochemical characteristics of the atmosphere contribute to  $S_{C_5H_8,OH}$  the model was run using a normally-distributed, pseudo-randomly generated sequence of isoprene mixing ratios with a mean of 2 ppbv and a range of 0–4 ppbv, for a day of meteorological parameters. The result, shown by the blue line in Fig. 8, reveals a relative minimum in the absolute magnitude of  $S_{C_5H_8,OH}$  at ~11:00 LT, coincident with the onset of precipitation, and hence a reduction in the non-isoprene OH sink due to the removal of highly soluble species such as peroxides. This clearly demonstrates that the magnitude of the non-isoprene OH sink can have an impact on the magnitude of  $S_{C_5H_8,OH}$ . In effect the additional sink dampens the size of  $OH'$  caused by a given  $C_5H_8'$ . In these simulations the effect on  $S_{C_5H_8,OH}$  is small relative to those induced by changes in the isoprene distribution (Fig. 5), as isoprene and its oxidation products dominated the OH sink during OP3. However, in a more polluted environment, correctly accounting for other OH sinks would become very important, although of course, in such an environment, the importance of  $S_{C_5H_8,OH}$  would be proportionally smaller.

Plotting  $[OH]$  against  $S_{C_5H_8,OH}$  for the OP3 scenario suggests a correlation between the two variables (not shown). However, this is not real; when the random isoprene time series is used, no correlation is seen with  $[OH]$ . Therefore the apparent correlation in the OP3 scenario must be a result of the shape of the diurnal  $[OH]$  signal being similar to that of isoprene, since both are ultimately controlled by solar radiation. Furthermore, running the model using a constant photolysis rate, and hence constant photolytic OH production, leads to deviation in  $S_{C_5H_8,OH}$  only at the extreme ends of the day compared to a run with normal photolysis. Hence  $[OH]$  cannot be determined to have any significant predictive power for  $S_{C_5H_8,OH}$ .

Several recent papers have suggested that the tropospheric oxidation of isoprene

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might include a hitherto unconsidered OH formation mechanism, especially under conditions of low  $\text{NO}_x$  concentrations (Lelieveld et al., 2008; Peeters et al., 2009). For the purposes of this work, the most important factor in such an OH production mechanism is the time between initial isoprene oxidation and OH formation. If the extra OH was formed very rapidly then it could decrease  $S_{\text{C}_5\text{H}_8,\text{OH}}$ , as the OH loss caused by isoprene oxidation would immediately be balanced to some extent by an OH source. Running the model with the reaction of  $\text{C}_5\text{H}_8 + \text{OH}$  modified to directly produce one molecule of OH for each molecule of isoprene oxidised, as in Pugh et al. (2010), results in  $S_{\text{C}_5\text{H}_8,\text{OH}} = 0$ . However there is no known chemical scheme that could describe such a production mechanism.

If additional OH is produced further down the isoprene oxidation chain, then the additional OH source is unlikely to be co-located with isoprene, instead being spread much more homogeneously across the boundary layer. To date, only Peeters et al. (2009) have proposed a detailed mechanism for how extra OH of the quantity apparently required by models might be formed. They point out a number of places in the oxidation scheme where possible extra OH yields may occur. By far the most important route is by the photolysis of hydroperoxy-aldehyde compounds formed as a secondary oxidation product of isoprene. Peeters et al. (2009) estimate the photolysis frequency for these compounds to be  $J = 3 \times 10^{-4} \text{ s}^{-1}$ , with a quantum yield of 100%, giving a lifetime of approximately 1 h. This suggests that OH formation via this route will not be preferentially co-located with isoprene, as air parcels are highly unlikely to remain undiluted over this time period. In this case, as it has already been demonstrated that the OH concentration cannot be shown to have any direct effect on  $S_{\text{C}_5\text{H}_8,\text{OH}}$ , OH recycling on the timescale of an hour in the isoprene oxidation scheme is not expected to make any difference to  $S_{\text{C}_5\text{H}_8,\text{OH}}$ . To test this, the model was run for data from 30 April 2008 with an additional OH source one step further down the isoprene oxidation chain. The result yields virtually no change in  $S_{\text{C}_5\text{H}_8,\text{OH}}$  (not shown).

Another issue of potential importance is the inhomogeneous distribution within the boundary layer of species other than isoprene. Krol et al. (2000) found that heteroge-

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neous emission of NO, in addition to that of isoprene, led to a decreased magnitude of  $S_{\text{VOC,OH}}$ , as an OH gradient formed as a result of the NO fluctuations counteracting the effect of the VOC and OH segregation. NO is likely to be heterogeneously distributed as its principal source at the OP3 measurement site is biogenic below-canopy emissions. Therefore a spatial and temporal variation in both its original source, and its release from the canopy is likely. No high temporal resolution measurement of NO concentration were made during OP3, but 1 Hz measurements of NO<sub>2</sub> concentration made at 75 m on the measurement tower, show variations in NO<sub>2</sub> concentration with an amplitude of the same magnitude as the mean concentration, on a timescale of less than 1 minute. As NO and NO<sub>2</sub> are quickly inter-converted in the daytime boundary layer, this suggests a heterogeneous distribution of NO within the boundary layer.

To test the effect of heterogeneous NO concentrations, three further runs were carried out constrained to a randomly-generated normally distributed isoprene time-series. The first of these runs, N1, was constrained to a NO mixing ratio of 50 (10) pptv if isoprene mixing ratios were greater (less) than 2.5 (1.5) ppbv, and 30 pptv if isoprene mixing ratios were between 1.5 and 2.5 ppbv. This produced an effect where high NO concentrations were more typically co-located with high isoprene concentrations; an effect that may well occur if coupling of the canopy to the BL is the primary reason for heterogeneous concentration distributions. The second of these runs, N2, was identical except a NO mixing ratio of 10 (50) pptv was used if isoprene mixing ratios were greater (less) than 2.5 (1.5) ppbv, resulting in a scenario where high NO concentrations were typically anti-correlated with high isoprene concentrations. Finally N3 was constrained to a randomly-generated NO time-series that was entirely independent of isoprene.

Figure 9 shows the results for runs N1, N2 and N3, compared to the standard run for that day. Run N1 shows a substantial decrease in segregation, with much less negative  $S_{\text{C}_5\text{H}_8,\text{OH}}$ , as found by Krol et al. (2000). Indeed, at the ends of the day, when OH production via photolysis is relatively small compared to production via the reaction of peroxy radicals with NO,  $S_{\text{C}_5\text{H}_8,\text{OH}}$  can even become positive as the effect on [OH]

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caused by increased [NO] dominates over the effect caused by decreased isoprene.

Run N2 has the opposite effect, showing that NO concentrations anti-located with isoprene concentrations could yield significantly more negative values of  $S_{C_5H_8, OH}$ . This latter scenario appears unlikely in reality as, unless canopy-coupling proves to be the primary driver of heterogeneities in the BL leading to an N1-type scenario, it is likely that the distributions of NO and isoprene in the BL will simply be different, showing no kind of correlation. Run N3 demonstrates that if any heterogeneities in the NO concentration are independent of those in the isoprene concentration, then the typical value of  $S_{C_5H_8, OH}$  should not be affected.

## 5 Conclusions

An approach has been described to model the intensity of segregation of isoprene and OH using high temporal resolution isoprene concentration data. The approach shows good agreement when compared with the only observations of isoprene and OH segregation available in the literature. When the method is applied to measurements made over the south-east Asian tropical rainforest during the OP3 campaign, an intensity of segregation typically less negative than  $-0.15$  is calculated. This is much less negative than the  $-0.5$  required by global and box models of atmospheric chemistry to reconcile their OH and isoprene concentrations with measurements.

The model-calculated intensity of segregation for the OP3 rainforest scenario described in this paper appears robust, both to inhomogeneous concentrations of NO and to potential OH recycling, unless NO anomalies are strongly correlated with those of isoprene or OH recycling happens virtually instantaneously following initial isoprene oxidation. Given that rapid isoprene concentration measurements have been made during several other field campaigns, it is suggested that the approach described here might be applied to estimate the intensity of segregation in those regions.

Both Butler et al. (2008) and Pugh et al. (2010) have demonstrated that additional OH recycling in the isoprene oxidation scheme can only improve model fits to measured OH

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concentrations at the expense of the fit to measured isoprene concentrations/fluxes. In order to attain an acceptable fit to both OH and isoprene concentrations a reduction in  $k_{C_5H_8,OH}$  was required. However this work shows that, at least for the rainforest conditions observed during the OP3 campaigns in Malaysia, segregation of isoprene and OH can only be responsible for a minor fraction of the rate constant reduction required to resolve the measurement-model discrepancy; hence either another justification for this  $k_{C_5H_8,OH}$  reduction must be made or an alternative solution found.

In the light of the results presented here, it is suggested that the highest temporal resolution measurements for isoprene available are utilised in constrained modelling studies of atmospheric chemistry in areas where isoprene dominates the OH sink. If high temporal resolution measurements of other species are co-located with the isoprene measurement (i.e. sufficiently close that they are very likely measuring within the same air parcel) then it may prove advantageous to use these also.

## Appendix A

The timescale for the OH concentration to reach a new steady state following a perturbation in the isoprene mixing ratio from 2 ppbv to 3 ppbv (assuming no other OH sinks), is found by integrating the volume average conservation equation:

$$\frac{\partial \langle OH \rangle}{\partial t} = P_{OH} - k_{C_5H_8,OH} \langle OH \rangle \langle C_5H_8 \rangle \quad (A1)$$

where,

$$P_{OH} = k_{O^1D,H_2O} \langle O^1D \rangle \langle H_2O \rangle + k_{NO,HO_2} \langle NO \rangle \langle HO_2 \rangle \quad (A2)$$

to yield

$$t = \left[ \frac{-1}{k_{C_5H_8,OH} \langle C_5H_8 \rangle} \ln |P_{OH} - k_{C_5H_8,OH} \langle OH \rangle \langle C_5H_8 \rangle| \right]_{\langle OH \rangle_0}^{\langle OH \rangle_t} \quad (A3)$$

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where  $\langle\text{OH}\rangle_0$  is the OH concentration at  $t=0$  and  $\langle\text{OH}\rangle_t$  is the OH concentration at time  $t$ , when the system is in steady state. At steady state  $\partial\langle\text{OH}\rangle/\partial t=0$ , therefore,

$$P_{\text{OH}} = k_{\text{C}_5\text{H}_8,\text{OH}}\langle\text{OH}\rangle\langle\text{C}_5\text{H}_8\rangle \quad (\text{A4})$$

Hence the  $\langle\text{OH}\rangle_t$  limit of Eq. (A3) is zero. When a  $P_{\text{OH}}=3.0 \times 10^6$  molecules  $\text{cm}^{-3} \text{s}^{-1}$  is used,  $t=3$  s. This value of  $P_{\text{OH}}$  is based upon midday typical midday values of the components of Eq. (A2) during the OP3 campaign Hewitt et al. (2010). As the approach to steady state is exponential in nature, the majority of this change in [OH] due to a perturbation in  $[\text{C}_5\text{H}_8]$  will occur within 1 second. This is demonstrated in Fig. A1 which shows an extract of the model time-series for  $\text{C}_5\text{H}_8$  (blue) and OH (green). Each mark represents a model timestep of one second. It is clear that the OH response to a change in  $\text{C}_5\text{H}_8$  concentration occurs nearly entirely within the first timestep following the change.

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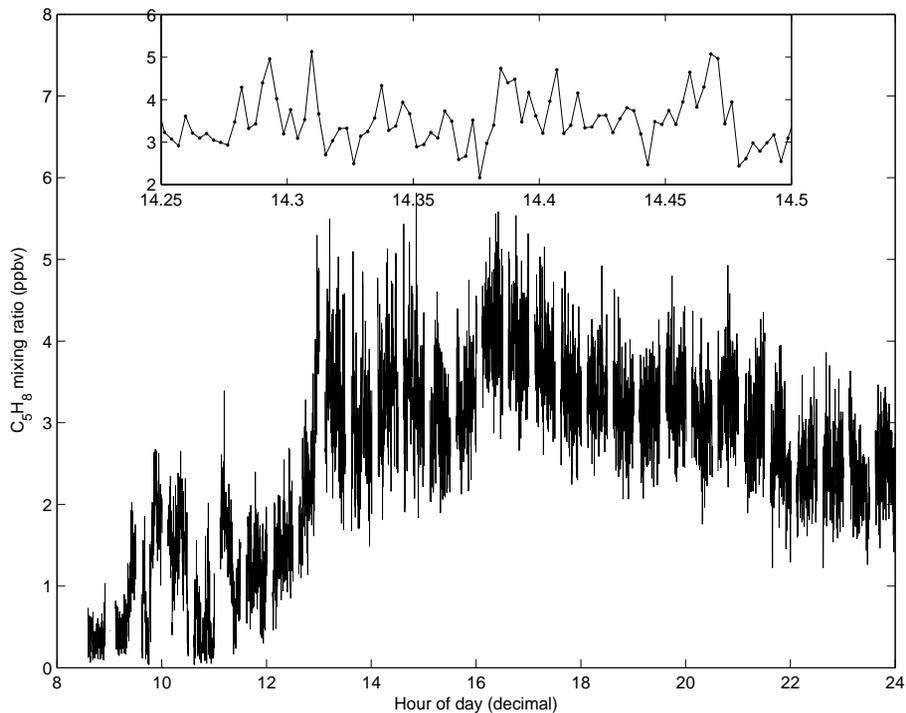
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**Fig. 1.** Isoprene concentration data measured by PTR-MS for 26 April 2008 showing 1 data point every 10 s. The inset shows a 15 min extract (note hours given as decimal fraction) indicating the short timescale over which large variations can occur.

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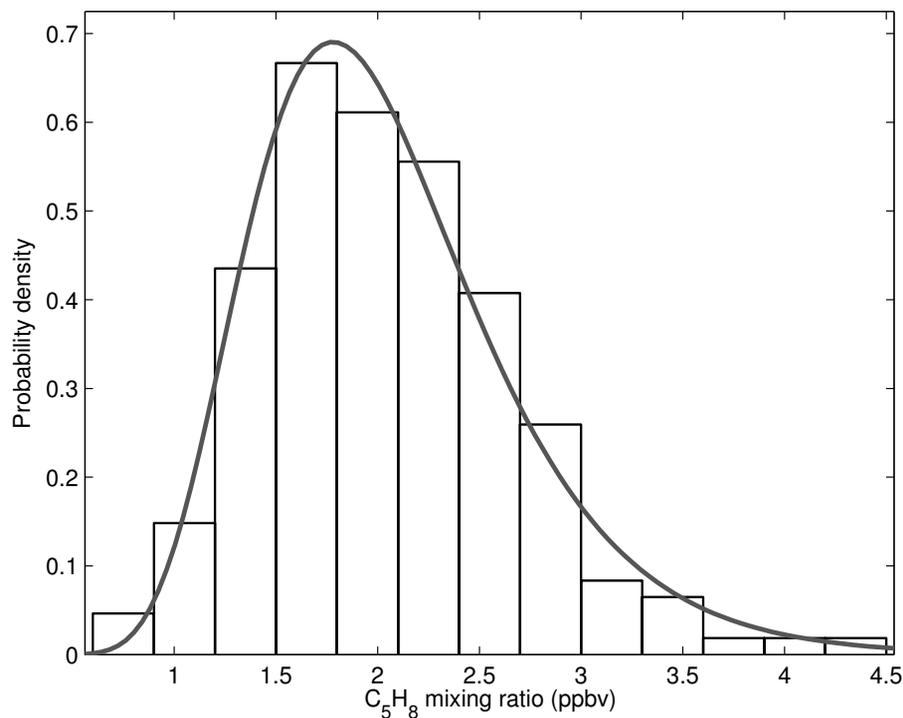
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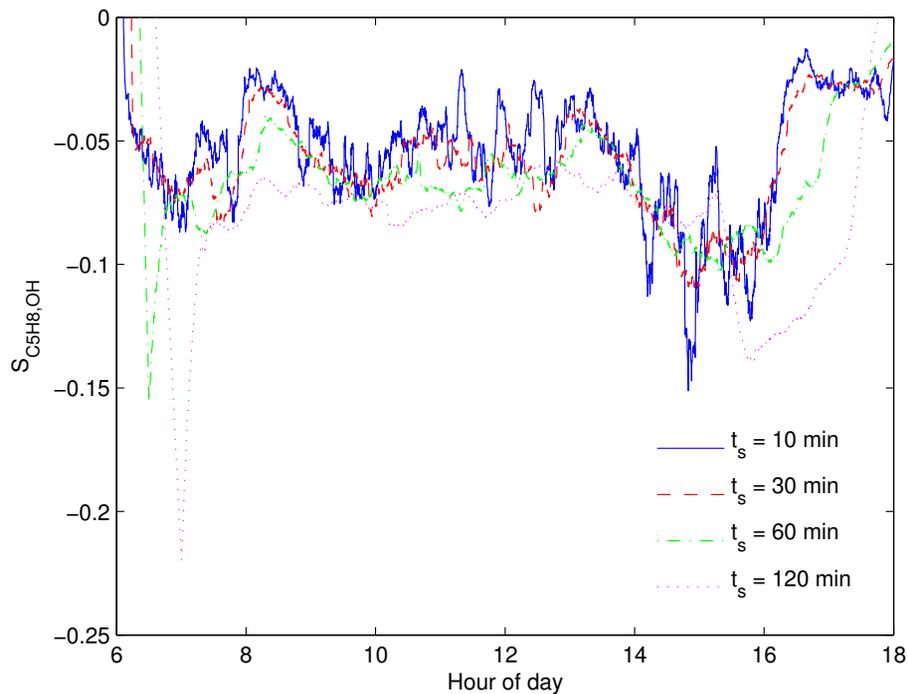
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**Fig. 2.** Histogram showing distribution of isoprene concentrations between 11:00 and 12:00 LT on 30 April 2008. The line shows the probability density function for a log-normal distribution.

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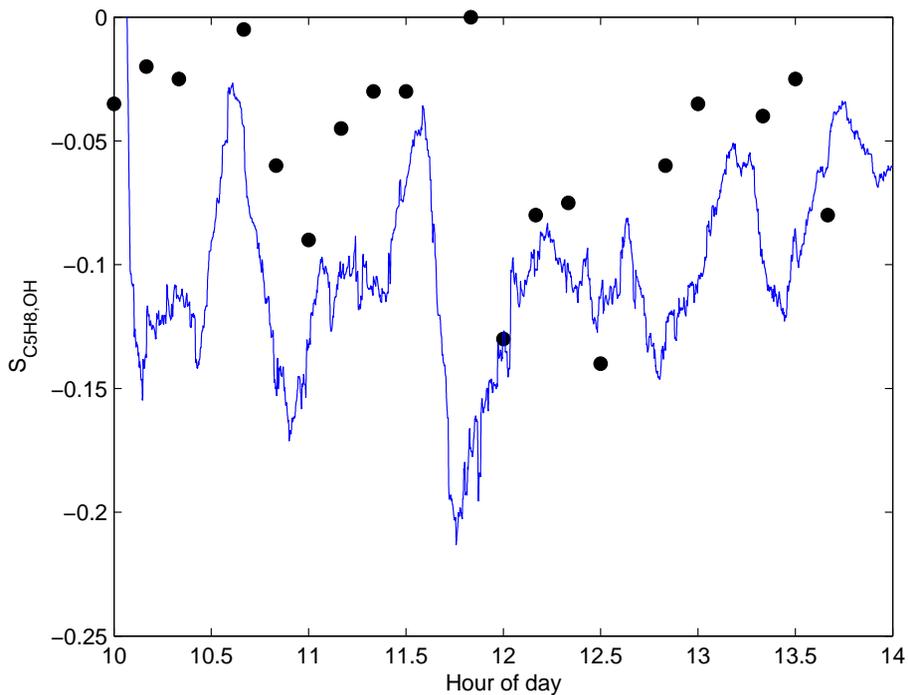
**Fig. 3.** Variation in  $S_{C_5H_8,OH}$  due to using  $t_s = 10, 30, 60$  and  $120$  min. Carried out using OP3 isoprene measurements collected on 30 April 2008.

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**Fig. 4.** Comparison of the observed  $S_{C_5H_8,OH}$  of Dlugi et al. (2010) (black dots), with the model estimate using the approach described in this paper ( $t_s=10$  min) (blue line).

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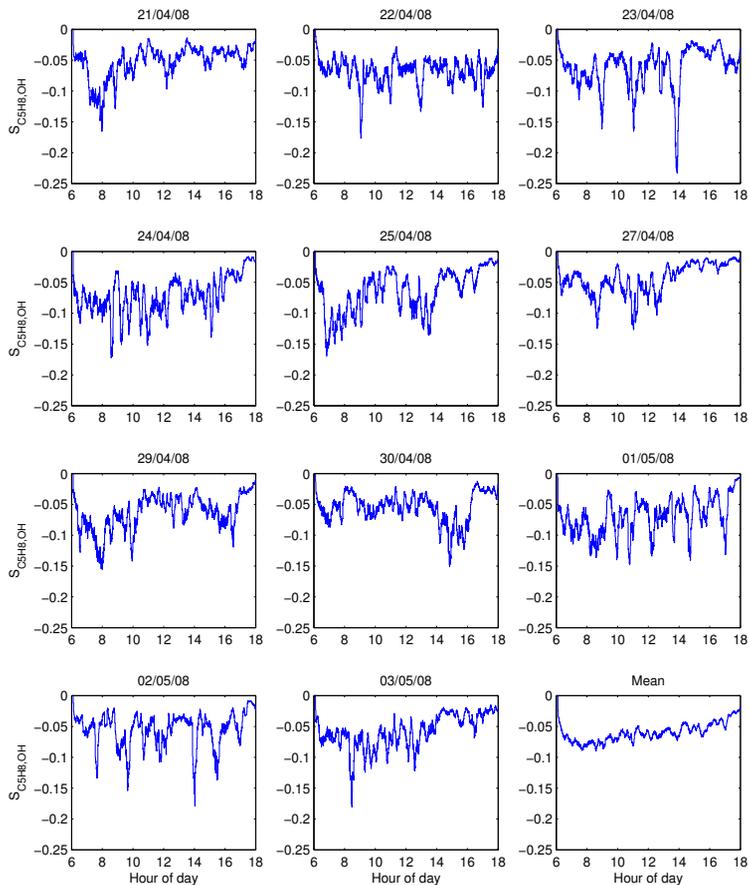
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**Fig. 5.** Model calculated intensity of segregation for  $t_s=10$  min, showing each day during OP3-1 and the overall mean. Note that results before 10:00 LT are not representative of the boundary layer as a whole.

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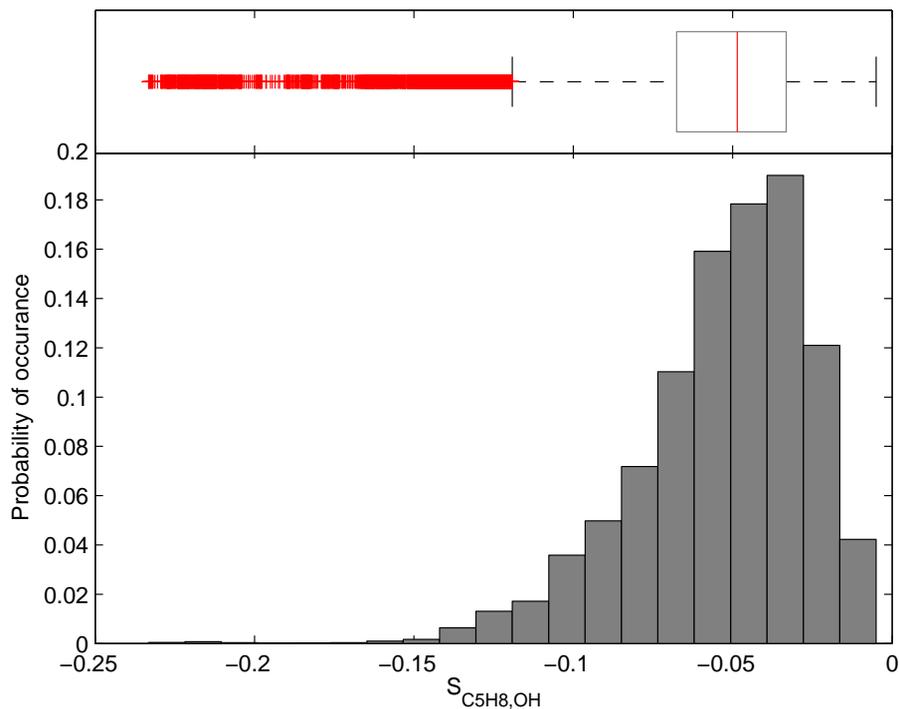
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**Fig. 6.** Lower panel: histogram showing probability of occurrence of  $S_{C_5H_8,OH}$  based upon all 10:00–18:00 LT calculations for the OP3-1 campaign. Upper panel: box and whisker plot showing median (red line) and upper and lower quartiles (box). The upper (lower) whisker encompasses the region within 3 times the region between the upper (lower) quartile and the mean. Outliers are shown by a red cross.

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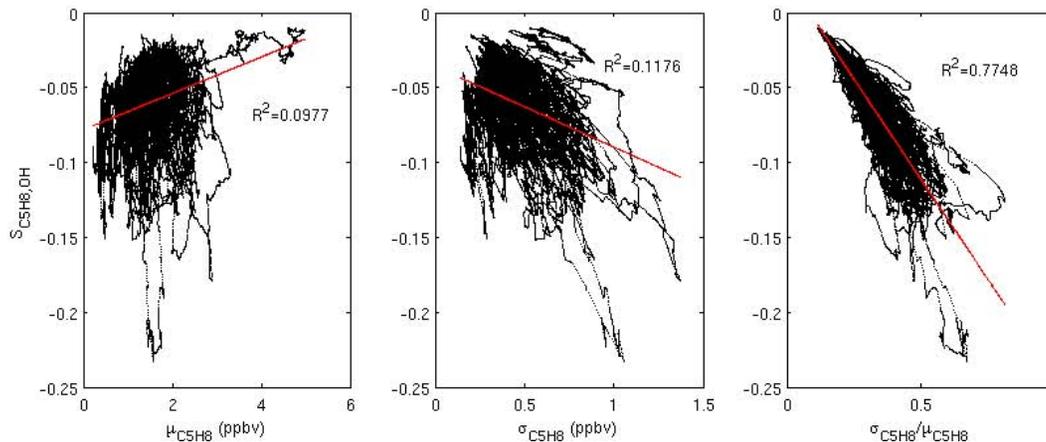
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**Fig. 7.** Correlations between  $S_{\text{C}_5\text{H}_8,\text{OH}}$  and the mean isoprene concentration (left panel), standard deviation of isoprene concentration (centre panel), and relative deviation (right panel). Values between 10:00–16:00 LT are used and  $t_s=10$  min.

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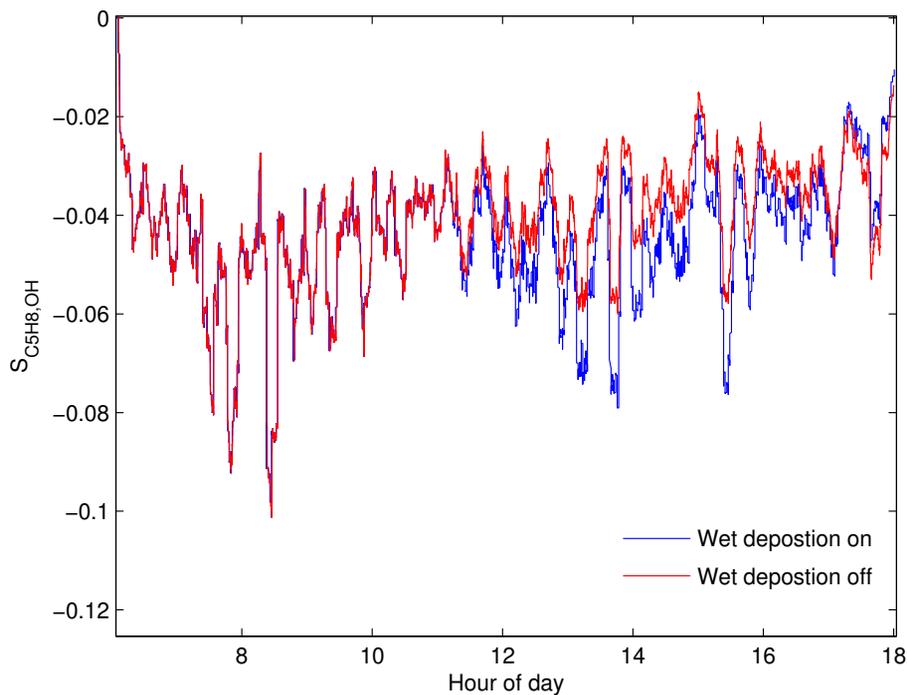
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**Fig. 8.**  $S_{C5H8,OH}$  modelled using a normally-distributed, randomly-generated isoprene time-series. The red line shows a run in which wet deposition was turned off.

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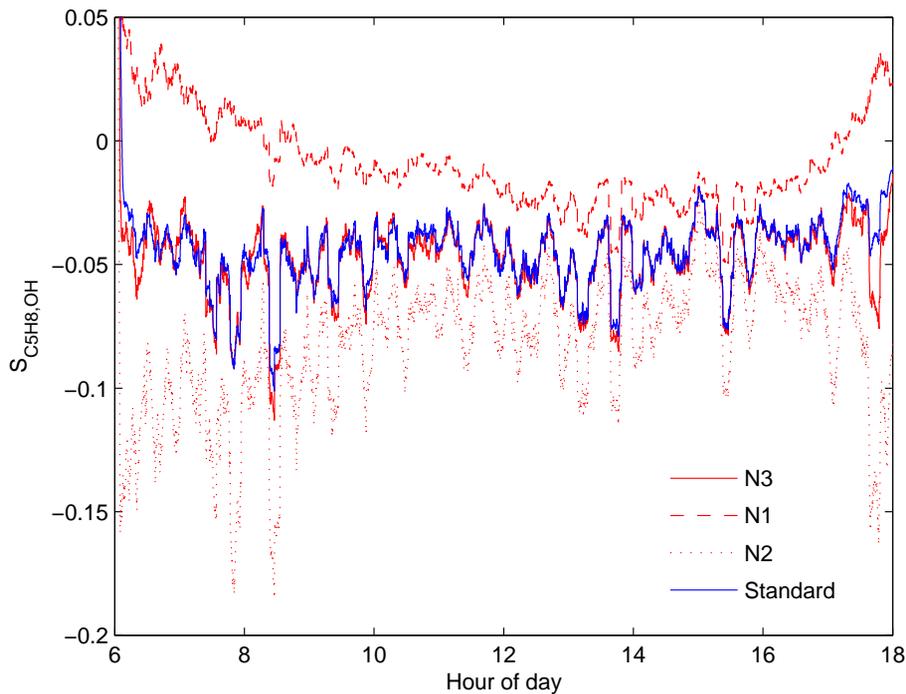
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**Fig. 9.** The effect of heterogeneous NO concentrations correlated with those of isoprene (N1, red dashes), anti-correlated with those of isoprene (N2, red dots), and showing no correlation with isoprene (N3, red line), compared with a standard run (blue line) for a randomly-generated isoprene time-series.

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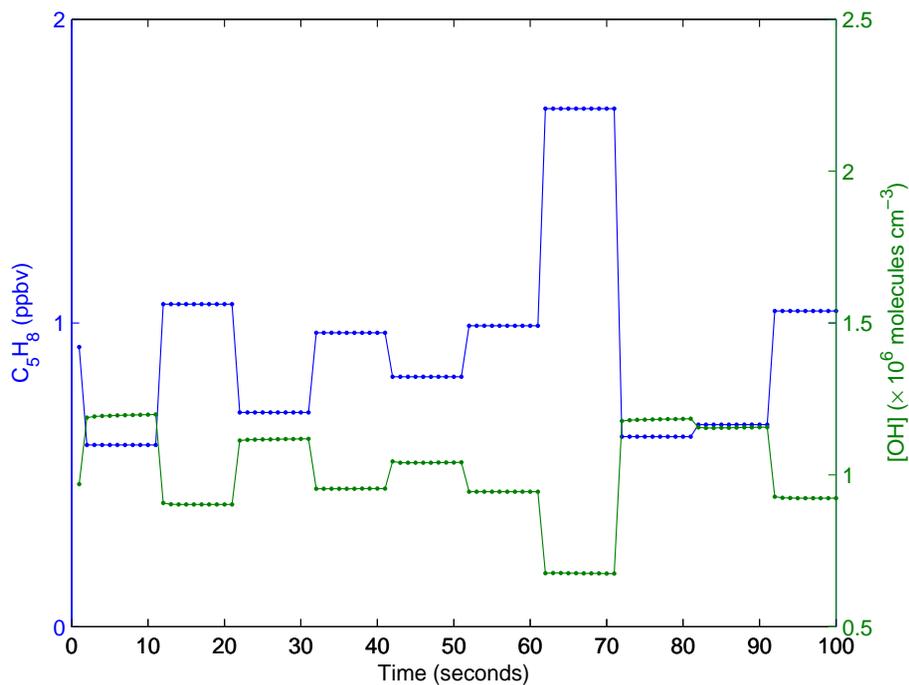
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**Fig. A1.** Response of modelled [OH] to a change in the supplied C<sub>5</sub>H<sub>8</sub>. Each model time-point is marked by a dot.