**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "The influence of small-scale variations in isoprene concentrations on atmospheric chemistry over a tropical rainforest" *by* T. A. M. Pugh et al.

T. A. M. Pugh et al.

t.pugh@lancs.ac.uk

Received and published: 5 January 2011

We thank the anonymous reviewers for their comments. However we do not believe their concerns apply to our work, as we will explain below. We have also posted separately a short 'Restatement of the problem' in order to better explain our method. As the concerns of reviewer 2 refer directly to those of reviewer 1, we will address most concerns via the comments of reviewer 1. We also thank R. Dlugi, whose concerns are addressed at the end of this document. A copy of the revised manuscript is appended as a separate comment, with the changes shown in bold face.

Reviewer 1.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

1. RC. Equations (2) and (6) in the manuscript give the definition of the intensity of segregation (Is). The essential contribution of Is is the co-variance between isoprene and OH. This is a turbulent quantity that is calculated as a second-moment of the reactant concentration distribution to quantify concentration fluctuations between both species. As the authors mentioned, currently only fast measurements (Dlugi et al., 2010) or large-eddy simulations (Vinuesa et al, 2003) are able to estimate it directly since they are able (within certain limitations) to capture all the essential spatial and temporal scales.

AC. Only fast, co-located measurements (e.g. Dlugi et al., 2010) can calculate the intensity of segregation directly. However the nature of the measurement techniques means that this value is calculated at a point. Our method also aims to calculate segregation at a point (specifically, the volume associated with a single PTR sample in a 1 Hz datastream).

Large-eddy simulation (LES) models are able to estimate intensity of segregation from measurements indirectly based upon knowledge of various meteorological and emission parameters. Their advantage is that they provide explicit estimates across the volume of the boundary layer. But the number of parameters that must be specified, along with their associated uncertainties, makes their estimates less reliable than direct measurements. Unfortunately very few measurements of the intensity of segregation of isoprene and OH based upon fast co-located observations are available to date. The method presented in this paper is designed to complement existing studies by using high-frequency isoprene measurements, as used to calculate fluxes, to make measurement-based estimates of the intensity of segregation of isoprene and OH ($S_{C5H8,OH}$).

In our submitted manuscript, there may have been some ambiguity over the volume for which we calculate segregation, due to the discussion of box modelling. We have tried to remove any ambiguity by posting our 'Restatement of the problem', and the explanation is incorporated in our revised manuscript. As stated above, we calculate

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

segregation, as advected past the measurement point. However, we argue that the calculated segregation intensity is representative of the boundary layer as a whole.

2. RC. The analysis of the evolution of the co-variance equation enables me to elaborate further into this point ((Vilà-Guerau de Arellano et al., Journal of Atmospheric Chemistry 16, 145, 1993), Verver et al. Journal of Geophysical Research 105, 3983; 2000). Taking Verver et al., (2000) as a reference and by analyzing the co-variance equation (see equations 3 and 4), one can notice that the covariance of C_5H_8 and OH is determined by non-linear contributions of mean and turbulent-chemistry terms. The equation shows also the relevance on the scales interaction in governing the covariance. For instance, on the equation right-hand-side, the first two terms quantifies the role of turbulent flux and mean concentration gradients in determining the $C_5H_8'OH'$. Similar non-linear interactions are present in the chemistry term at equation 4. My main concern with the paper under evaluation is that their methodology misses these important contributions in the determination of the $C_5H_8'OH'$co-variance. By using a box-model in calculating OH two relevant processes are omitted: the influence of turbulence/chemistry (at all scales) and (b) the non-linearity in the interaction turbulence-chemistry. Although the assumption that supported their method (page 18205) are well thought and the use of relative (but discrete) fast isoprene observations captures partially some of this information, in my opinion there are not sufficient to guarantee a proper estimation of Is. As Vinuesa et al. (2003) showed in the budget calculation (Figure 7) all the terms of the co-variance equation contribute to the Is evolution, i.e. either they are measured directly with fast response instruments (>1 Hz), calculated directly with large-eddy simulation models or represent in form of a parameterization the relevant terms.

AC. In all of the above, the reviewer's central concern is that we have not considered all the terms of the covariance budget equation. We wish to remind the reviewer that, strictly, we are calculating the covariance in a small volume sampled by an isoprene measurement, for the special case of reacting scalars where one scalar has a very

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

short chemical lifetime (less than 1 second) and is formed throughout the domain. If both scalars were transported and their chemical lifetime similar to the transport timescale, then we would indeed have to consider all terms in the covariance budget equation.

In our method, information on the transport of isoprene is included within the fast isoprene measurements. The OH lifetime, with respect to isoprene at a typical mixing ratio of 2 ppbv, is 0.22 s at 298 K, Median vertical velocity during OP3-1 peaks at approximately 0.2 $\mathrm{m\,s^{-1}}$. Therefore the transport distance of OH during its lifetime is much less than 0.05 m, cf. the scale of a few metres we assume for our measured air parcels (based upon a typical windspeed of a few metres per second and Taylor's frozen turbulence hypothesis). As a result any covariance of isoprene and OH must be due to the OH concentration adjusting chemically to a change in the isoprene concentration. Dlugi et al. (2010) also found transport of OH to be negligible based on both the same logic, and on measurements of OH fluxes. We do not need to concern ourselves here with which processes have caused the variation in isoprene concentration, as the measurements provide us with the net effect of these processes.

Given the reviewer's uncertainty regarding the particular case of reactive scalars that we are studying, we have modified the assumptions laid out on pg. 18205 to contain the following:

<start extract> However, here we argue that the OH time series that would have resulted from a suitable OH measurement co-located with the isoprene measurement, can be estimated purely on the basis of chemistry. For most species such a procedure would not be possible. However, two key simplifying aspects of our system are (a) that OH is produced in-situ everywhere throughout the boundary layer and, (b) due to its short lifetime, OH is always in steady-state with its chemical sources and sinks. This means that the OH concentration at a place and time is independent of the history of the air at that place. The OH concentration is therefore a function of the instantaneous value of chemical production, P, its major chemical sink in the rainforest environment,

isoprene, and other chemical sinks, OL:

$$[OH] = f([C_5H_8], P, OL), (5)$$

and there are no advective terms to be considered. Our knowledge of (and uncertainty in) the chemical source and sink terms for OH is embodied in chemical mechanisms. It follows that our best theoretical estimate of OH mixing ratios will come from integrating chemical mechanisms to steady-state, given adequate empirical data on the mixing ratios of longer-lived compounds that dominate P and OL. <end extract>

3. RC. I have also serious concerns on the calculation of the numerator of equation (7). First, and closely related to the above point, the production and loss terms of OH do not take into account all the chemistry and turbulent fluctuations. Second, the calculation of the bulk values depend on surface dynamic forcing and reactant emissions, the boundary layer depth evolution, the exchange between the boundary layer and the free troposphere and advection. I am therefore very surprised that the authors are able to reproduce the intensity of segregation of the German mixed forest (Dlugi et al., 2010) with almost the same numerical set up as the one imposed to reproduce the tropical forest experiments (page 18210).

AC. We apologise that a mistake was made in the formulation of Eq. 7, which should actually read

$$[OH] = \frac{P}{(k_{C5H8,OH}[C_5H_8]) + (k_{OL,OH}[OL])}$$

This equation appears in the text for illustrative purposes, but is not part of the model calculation, therefore the results of our work are not affected.

We think that the use of the words 'boundary layer' in the sentence preceding Eq. 7 may have misled the reader, for which we apologise also. We have rephrased the sentence beginning line 6 on pg. 18207 to the following:

<begin extract> Because, as explained previously, transport of OH is negligible, an

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

OH concentration can be calculated from an isoprene concentration measurement by expanding Eq. 5, <end extract>

It is not necessary for the production and loss terms of OH in Eq. 7 to take into account all the chemistry and turbulent fluctuations because, as explained above, the timescale over which Eq. 7 is being applied is very short. The most important OH sink is isoprene in both OP3 and the Dlugi et al. (2010) situations, but isoprene is not the only OH sink. By allowing the other species to evolve freely within the box model framework we gain an estimate of the total OH sink, OL. This evolution of longer-lived background species throughout the day is one of the advantages of our method. Increasing the non-isoprene OH sink, OL, reduces $S_{C5H8,OH}$ (see Restatement of problem), this means that our estimates of $S_{C5H8,OH}$ may be a slight overestimation, however this does not affect the conclusions of our paper. We have discussed this caveat in Section 4.1 describing the Dlugi et al. (2010) case study, and in the first paragraph of Section 4.3.

That we were able to reproduce the Dlugi et al. (2010) measurements of $S_{C5H8,OH}$ is not at all a surprise to us, as once again isoprene is the dominant reactive VOC emitted at their site. Therefore the model is constrained to the primary OH sink. All the variables mentioned by the reviewer are only of importance in this study for the calculation of OL and for the production of OH via photolysis. We have shown on pgs. 18213 and 18214 that the magnitude of OH production is not important for the calculation of $S_{C5H8,OH}$. Clearly the rough estimate of OL provided by our model set-up is sufficient in this case. If, for example, isoprene accounted for 60% of OH destruction, then a 50% error in OL would lead only to a 20% error in the total OH sink. As can be seen from Fig. 4, our method tends to result in more negative values of $S_{C5H8,OH}$ than those produced by Dlugi et al. (2010). This is consistent with an underestimation of OL, as we have discussed in the second paragraph of Section 4.1.

4. RC. Third, in my opinion, reaction C_5H_8+OH accounts for approximately 60% of the OH destruction, and therefore it is not sufficient to account for all the the effects since the potential chemistry-turbulence fluctuations by other reactions are neglected.

AC. The reviewer is quite correct in asserting that isoprene is not the only sink of OH. However, as stated in our Equation 1, we calculate the isoprene-OH segregation only; we do not try to assess the total effect on OH of segregation processes. Such analysis is beyond the scope of this work. It is likely that some other species will also undergo some segregation with OH, but as we explain the the Restatement of the problem, we believe these effects to be minor in our case. For instance, Dlugi et al. (2010) found evidence for some minor segregation of monoterpenes and OH. We would further note that we are yet to see a LES study which accounts for all possible sinks of OH.

We will make more explicit in our revised manuscript that we are considering only segregation of isoprene and OH.

5. RC. Another strong drawback in using the box model is their independence of height. As shown by Patton et al. (1997) at figure 4, the co-variance depends strongly with height due to its dependence on fluxes and mean concentrations (co-variance budget equation). I understand that this is partially included in the isoprene concentrations, but still the box model omits all the height dependent fluctuations related to OH (and other related species at equation 7) and the non-linearties between turbulence and chemistry. This dependence of height is more pronounced close to the canopy and therefore needs to be included.

AC. Our method relies on calculating OH for a small volume associated with isoprene measurements. The box model is a convenient computational framework within which to calculate OH because it provides a consistent set of OH source and sink terms. The parameters in the box model do affect $S_{C5H8,OH}$, in as much as they change these OH sources and sinks. However the dominance of the OH sink by isoprene in these environments means that the error introduced is relatively small. For instance, if we halved the BL height used for the Dlugi et al. case study then a 4% reduction in magnitude of $S_{C5H8,OH}$ results.

6. RC. As a closing example of one of these doubts, at lines 5-10 at page 18214, I

think the result of Is=0, in the particular numerical experiment of the OH-recycling, is an artifact of the method used, and in consequence requires further confirmation.

AC. The $S_{C5H8,OH}$=Is=0 result is indeed a logical outcome of the reasoning we apply throughout the manuscript and defend above. We have established the dominance of chemistry over transport for OH. The chemical scheme dictates that OH' is dominated by C_5H_8', so long as isoprene is a sink for OH. If the reaction of isoprene and OH immediately produces an OH radical, then OH is effectively not consumed in the reaction with isoprene, and hence isoprene induces no perturbation in OH.

7. RC. In my opinion, and in absence of fast response simultaneous observations of isoprene and hydroxyl radical, the authors should use methods to represent/parameterize the co-variance between isoprene and OH (see Verver et al. (2000) or section 6 in Vinuesa et al. (2003)). Notice that Verver et al. (2000) used a combined approach using a box-model and second-order closure modeling to reproduce the intensity of segregation between isoprene and OH in the Amazonian region.

AC. We maintain that our method produces a useful value of $S_{C5H8,OH}$ for the reasons outlined above, because we use the chemical scheme as a virtual instrument to generate a synthetic OH series with exactly the temporal and spatial resolution of the isoprene measurement. Therefore we do not need to represent explicitly the other terms in the covariance budget equation.

Reviewer 2.

RC. Actually, recognizing the work by Verver et al. already being done in 2000 one needs to also mention that this implies that the presented work does not appear to be novel.

AC. We recognise that the explanation of how the model has been employed in this study was not entirely clear in our manuscript. As explained above, we have taken steps to remedy this. We would argue that the novel aspect of our work is the use of

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

measured C_5H_8' to infer OH'. We do not believe this approach has been used before.

R. Dlugi.

RC. In the following we refer to some further aspects not explicitly discussed by the reviewers. The data for the case study by Pugh et al. are taken from the OP3 campaign on 30 April 2008 at the Bukit Atur tower 75 m above its base and situated in a 50m*150m large clearing surrounded by trees of about 10 m height as described in the cited literature and the paper itself. The station is situated on top of a hill 260m above valley floor. Note that under such conditions the determined covariances are only related to the emission in the surrounding area by strongly nonlinear relations (e.g. J. Finnigan (2004), Agr.For.Met. 127, pp 117-129; A. Sogachev et al, (2004), Agr.For.Met., 127, pp 143-158) also influenced by mesoscale motion (Stull, 1988).

AC. We apologise that we have allowed confusion to develop here regarding the height of the forest canopy in the footprint of the OP3 measurements. The measurements were made on a tower in a clearing on top of a hill, as described in Pugh et al. (2010) and Hewitt et al. (2010). The trees surrounding the hilltop clearing rose to approximately 10 m above this clearing. However 10 m is not a typical height for the canopy in the footprint of the tower; this being $\sim$25m (N. Chappell, Lancaster University, pers. comm.). We will make the canopy height explicit in a revised manuscipt.

RC. But we refer now to the relation $z_R = h_c$ during the OP3 campaign. The boundary layer height z_i is on average 800 m. On page 18205 a displacement height $d =$20m is given for a canopy. Compared to the canopy of the surrounding trees d is larger than h_c by a factor of 2. This, by the definition of d, is not possible. If one instead takes $d =$20m for the trees in the footprint area, where most of the isoprene is emitted, and which is given to be about 1400m away, one can estimate h_c from relations given by Raupach et al. (1991, 1996) or Kaimal and Finnigan (1994) as cited by Dlugi et al. (2010). One find $d = a$ * h_c with 0:6 $<= a <=$ 0:9 for 2 $<$ LAI $<$ 10. This leads to 22m $< h_c <$ 33m for this forest in the footprint area.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

AC. In the light of our explanation of the canopy height above, these numbers now agree well.

RC. From the cited reference by Helfter et al. an effective measuring height of 125m is given but it remains unclear, if this is considered to be above valley floor or canopy top in the source area or another reference height. With this height we get a relation $z_R = h_c > 5$ which is above the surface roughness layer and with $z_R = z_i => 0:16$ in the CBL. Therefore surface layer scaling to estimate a time scale should not be applied. The loss of high frequency contributions in turbulence, as cited in the text, also points to towards measurements in the CBL where spectra of all quantities are shifted to lower frequencies compared to surface near measurements (H.A. Panovsky, J.A. Dutton (1984), Atmospheric Turbulence, Wiley, N.Y.).

AC. The effective measuring height is taken to be 125 m above the canopy top. However we emphasise that there is considerable uncertainty on the effective measurement height (Langford et al., 2010 quote an estimate of 100-150 m, and we took 125 m here as a central value). We accept that the use of surface layer scaling is probably inappropriate in this case, and will remove this from the revised manuscript. In addition, we have concluded that the paragraph beginning on line 8 of pg. 18205, and dealing with the turbulent timescale, is misleading. The important mixing scale here is relevant to the size of the air parcel the isoprene measurement is integrated over. Therefore this paragraph has been replaced with the following:

<start extract> The OH lifetime, with respect to isoprene, at a typical mixing ratio of 2 ppbv, is 0.22 s at 298 K. The median diurnal profile of vertical velocity during the OP3 measurement period considered in this paper peaks at approximately 0.2 m s^{-1}. Therefore the transport distance of OH during its lifetime is less than 0.05 m, cf. the scale of a few metres we assume for our measured air parcels (based upon a typical windspeed of a few metres per second and Taylor's frozen turbulence hypothesis, Powell and Elderkin, 1974) and therefore Da $>> 1$. As a result any covariance of isoprene and OH must be due to the OH concentration adjusting chemically to a change in the

isoprene concentration. Dlugi et al. (2010) also found transport of OH to be negligible based on both the same logic, and on measurements of OH fluxes. <end extract>

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 18197, 2010.

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper