**Atmospheric
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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.

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Restatement of problem.

In the following, isoprene, C_5H_8, is referred to as I for brevity.

Our aim is to compute $S_{I,OH}$, which is defined as

$$S_{I,OH} = \frac{\overline{OH' \cdot I'}}{\overline{OH} \cdot \overline{I}},\qquad(1)$$

where overbars denote time averaging and the prime symbol (') denotes an eddy term. $S_{I,OH}$ may be calculated using measurements of OH and I, as long as the measure-

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ments of OH and I concentrations are co-located, and sampling is carried out at a sufficiently high frequency to resolve the smallest relevant scale of segregation. High frequency isoprene concentration measurements were made during OP3, and are the basis of our approach. The OH concentration measurements were neither co-located with the isoprene measurements, nor in the same frequency range. Hence the OH measurements made during OP3 were inappropriate for the calculation of $S_{I,OH}$.

In order to calculate $S_{I,OH}$, we consider whether we can estimate the OH time series that would have resulted from a suitable OH measurement co-located with the isoprene measurement. 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 mixing ratio is therefore a function of the instantaneous value of chemical production, P, its major chemical sink in the rainforest environment, isoprene, I, and other chemical sinks, X:

$$OH = f(I, P, X), \tag{2}$$

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 X.

Looking at the method in more detail, we write the continuity equation for OH

$$\frac{dOH}{dt} = P - k_i(\overline{I \cdot OH} + \overline{I' \cdot OH'}) - L, \tag{3}$$

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where,

$$L = \sum_{j=1}^{j=n} k_j(\overline{X_j \cdot OH} + \overline{X_j' \cdot OH'}), \tag{4}$$

and

$$P = \overline{P} + P' = k_a(\overline{O \cdot H_2O} + \overline{O' \cdot H_2O'}) + k_b(\overline{NO \cdot HO_2} + \overline{NO' \cdot HO_2'}), \tag{5}$$

where X is the concentration of a non-isoprene OH sink j, and P is dominated by the reactions of $O(^1D)$ + H_2O and NO + HO_2, with rate constants of k_a and k_b respectively. For the sake of simplicity, other sources of OH are ignored here, although they are included in the model calculations. At steady state Eqs. (3) - (5) can be rearranged to

$$\overline{I' \cdot OH'} = -\overline{I} \cdot \overline{OH} + \tfrac{1}{k_i} \cdot (k_a \cdot \overline{O} \cdot \overline{H_2O} + k_a \cdot \overline{O' \cdot H_2O'} + k_b \cdot \overline{NO} \cdot \overline{HO_2} + k_b \cdot \overline{NO' \cdot HO_2'}$$

$$- \sum_{j=1}^{j=n} k_j \cdot \overline{X_j} \cdot \overline{OH} - \sum_{j=1}^{j=n} k_j \cdot \overline{X_j' \cdot OH'}), \tag{6}$$

or

$$\overline{OH} = \frac{P - k_i \cdot \overline{I' \cdot OH'} - \sum_{j=1}^{j=n} k_j \cdot \overline{X_j' \cdot OH'}}{k_i \cdot \overline{I} + \sum_{j=1}^{j=n} k_j \cdot \overline{X_j}}, \tag{7}$$

hence $S_{I,OH}$ depends on several terms. We discuss the impact of these terms on the calculation of $S_{I,OH}$ below.

If X_j' covaries negatively with OH', then X_j' positively covaries with I', therefore $\overline{OH}$ will be smaller, and $S_{I,OH}$ will be more negative. If there is very little or no covariance between X_j' and I' in an isoprene-dominated environment, such as the one measured during OP3 (Langford et al., 2010), I' will be the dominant control on OH' and

$$\sum_{j=1}^{j=n} k_j \cdot \overline{X_j' \cdot OH'} \to 0. \tag{8}$$

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Those elements of X which are oxidation products of isoprene, are not expected to show significant covariance with I, due to the several-hour lifetime for their reaction with OH. This timescale greatly exceeds the time for which small parcels of air in the convective boundary layer can be expected to maintain coherence. Compounds that may be co-emitted with isoprene from the canopy, such as monoterpenes, could result in an increase in $S_{I,OH}$. However, such compounds can be neglected because the VOC fluxes during OP3 were dominated by isoprene (Langford et al., 2010). For the OP3 case, therefore, the third term of the numerator of Eq. 7 tends to zero.

Therefore, because I is prescribed by measurements in our approach, $S_{I,OH}$ can be correctly calculated if $\overline{X_j}$ and P can be estimated. We show that $S_{I,OH}$ does not depend strongly on $\overline{OH}$ in the main paper. A straightforward way to estimate $\overline{X_j}$ and P is by using a box model which incorporates the details of the known chemistry. Underestimating $\overline{X_j}$, that is not accounting for all OH sinks, would make $S_{I,OH}$ more negative. A positive covariance of NO' or H_2O' with I' would make $S_{I,OH}$ less negative, as the increased OH loss associated with high I would be offset by increased OH production due to high NO or H_2O (or vice-versa). Such a positive covariance might occur due to simultaneous emission of these compounds from the canopy. A negative covariance of these compounds appears unlikely. Therefore the results of this study are expected to be close to upper limits for the magnitude of $S_{I,OH}$ during OP3.

References.

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