

Review of Ouwersloot et al., "On the segregation of chemical species in a clear boundary layer over heterogeneous land surfaces."

Atmos. Chem. Phys. Discuss., 11, 18927–18978, 2011

by Ian Faloona

General Comments:

The authors present a series of LES simulations that begin to elucidate the influence of boundary layer turbulent mixing on the chemical reactivity of the isoprene-OH system under conditions of surface heterogeneity. The investigation is interesting and worthwhile, and many of the figures are of exceptional quality. My general concerns regard the undescribed role of NO_x in this photochemical system, and the importance of the effect of incomplete mixing in light of the many large uncertainties remaining in HO_x photochemistry in elevated hydrocarbon environments.

The role of NO in this study is kept in the shadows. It was shown by Krol et al. (2000) that the flux and variability of NO_x in these reactive systems are extremely important in influencing the segregation coefficient, yet this is given no mention in the current work. While I understand that modeling studies need to shy away from letting too many parameters run free, NO_x seems to be one of the most important components in the system under investigation, and yet its behavior is completely elided.

The significance of the results remain somewhat difficult to fully appreciate. I think it would be worthwhile for the authors to mention a few baseline uncertainties in chemical box modeling. For instance, the uncertainties of reaction rate coefficients are typically 5-15% (Atkinson, et al., 2006); those of critical reaction yields such as RO₂ + NO → NO₂ have uncertainties of about ± 10% (Karl et al., 2006). Furthermore, such physical chemical specifics pale in comparison to the fact that complex photochemical mechanisms routinely fail to match OH measurements to within a factor of 2-3 in such high hydrocarbon, and relatively low NO_x, environments (Tan et al., 2001; Lelieveld et al., 2008). This is not to mention instrumental uncertainty of field measurements and the standard lack of detailed 3d concentrations above a forest in any experiment which will limit the accuracy of a bulk reactivity estimate in the first place. While I realize this may be well beyond the scope of this work, I do believe it behooves us all to bear in mind these gaping craters in our understanding of this photochemical system when considering theoretical claims about ~10% changes in isoprene due to turbulent segregation.

Specific Comments:

p. 18930, l. 7: I learned a lot early on from the work of Sykes et al., 1992. It might be an appropriate reference here.

p. 18933, l.13: It seems that the unrealistically low level of water vapor used in this study will affect the HO_x production rates (via R2) in a significant way. The 6 g/kg specific humidity used is at least a factor of two below actual Amazon PBL values.

p. 18943, l. 2: I understand why the differing signs of the changes at 1350 m are due to entrainment of air aloft, but I do not see why they should be smaller in magnitude due to entrainment as this sentence implies. And if the sentence is not meant to imply that, it might be worthwhile explaining why one change is larger in magnitude than the other. For example, does it imply that entrainment and detrainment are unequal?

p. 18943, l. 10-11: Isoprene is higher over the savannah only above the surface layer according to Fig. 4b. So I think this discussion needs to be a bit more careful about what height is being described. Are you referring to a vertical average?

p. 18943, l. 19: $z_i/w^* \sim 12.5$ minutes, so whence the 30 minutes transport time?

p. 18944, l. 3: Fig. 4 seems to indicate that the entrained air (low isoprene) is transported downward over the forested areas. Is that somehow what is meant by "transported towards the savannah areas"?

p. 18944, l. 4-5: Is it true that mixing is less effective over the forest? Isn't the turbulent mixing nearly equally strong over both patches due to the efficient transport of TKE? Are there significant differences in eddy diffusivity or TKE over the forest vs. savannah patches?

p. 18944, l. 8-12: It is difficult to ascertain the significance of these mean concentration changes without knowing how the average entrainment rate is different between the HET and HOM runs. As discussed later in the text, the HET condition enhances overshooting thermals thereby increasing entrainment. It might be helpful to inform the reader by how much this important parameter changes?

The previous comment and inspection of Fig. 4 brings up two issues that appear odd to me. First, the drop off of more than a factor of two in isoprene in the lowest ~50 m above the canopy seems excessive, especially in light of the muted vertical gradients above the savannah. Is that consistent with any observations? From Fig. 3 of Arellano et al. (2011) it seems that isoprene falls by only ~1 ppb (~15%) in that same region.

Second, your model has 4-5 times less OH in the free troposphere than in the PBL, which is highly unlikely given that there is such a large source of its principal sink in the PBL. Lelieveld et al. (2008) indicate OH levels ~50% higher in the free troposphere above the tropical forest. The cause of this reduced OH in the LES free troposphere is probably due the zero NO_x boundary condition up there. I do not suspect that this introduces significant artifacts into your study, but it does underscore the importance of NO_x in the OH budget, and it is the commanding and silent behavior of NO_x that is sorely missing from this work.

p. 18946, l. 18: How do you know this is the only cause? It seems that the strong NO gradient near the surface is going to contribute to OH variability as well. OH concentrations are strongly modified by sinks, but they are also strongly modified by rapid sources, which in this case would be the HO₂+NO reaction (R11). Again, ignoring NO_x seems to be an oversight.

Fig. 7: It is interesting to note how the downdrafts appear strongest on the edges of the savannah, directly adjacent to the thermals. This seems akin to downdraft shells around cumuli, without the evaporative cooling.

p. 18949, l. 4-5: This is a somewhat surprising result which may be worth exploring in greater depth. When you investigate the causes of segregation in section 3.1.3 you do so without considering the second moment covariance budget equation, the specific data for which you should have in your LES results. See Section 3c of Moeng & Wyngaard (1984) for the general idea, albeit for unreactive scalars. With this type of analysis you could get a sense of the root causes of the covariance (e.g., how much is due to mean-gradient production, buoyancy production, and subgrid chemical reaction.) Also, it might be helpful to provide an estimate of the subgrid contribution to the segregation coefficient if possible. How do we know that the LES is capturing the majority of scales of segregation?

p. 18949, l. 28: How can you be certain this is the case? Why exactly does entrainment not intensify with increasing thermal diameter? And what is the threshold size at which this holds true? Perhaps there is a reference that can shed some light on this point.

p. 18950, l. 10: I do not understand how this statement can be true. You mention that you initialize your LES with a 0.8 K jump at 1000 m, and impose a free tropospheric lapse rate atop of that. So how can there be "no distinct temperature jump over the forests"? There is, in fact, a definite inversion observed in Fig. 2a.

p. 18952, l. 28-29: You say that the concentration of short-lived radicals is governed by the chemical reaction rates, but the concentration of isoprene is also governed by its chemical reaction rate (along with the surface and entrainment fluxes). As you just explained, isoprene is enhanced by ~10% because of the reduction in the overall R9 rate. So what is the difference exactly between the response of OH and that of isoprene?

p. 18954, l. 22-24: I do not understand this reasoning. It seems that smaller (thinner) regions of high forest isoprene are going to lead to *less* horizontal segregation, not more. Perhaps it would be helpful to calculate the two segregation components independently (horizontal and vertical) to obtain a better understanding of which is affecting the overall result more strongly.

Technical Corrections:

p. 18929, l. 28: Syntax needs to be corrected.

p. 18941, l. 12: "Halfway the boundary layer" should be rephrased.

p. 18945, l. 3-4: The reaction of OH+Isoprene proceeds by H abstraction, thus the two compounds do not truly 'combine'.

p. 18949, l. 22: 'lower length' is an awkward combination. Perhaps 'smaller' or 'shorter' would be more appropriate. This phrase is repeated throughout but first appears here.