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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The balances of mixing ratios and segregation intensity: a case study from the field (ECHO 2003)" *by* R. Dlugi et al.

Anonymous Referee #2

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General Comments:

This manuscript describes an analysis of data from the ECHO2003 field campaign, focusing on the intensity of segregation (I_s) between isoprene (C_5H_8, herein referred to as ISO or c_i) and the hydroxyl radical (OH), i.e. $I_s = \frac{\overline{ISO'OH'}}{\overline{ISO}\,\overline{OH}}$, and the mechanisms responsible for the production/destruction of I_s. The results are novel since most efforts investigating I_s thus far have hinged on using numerical models to test the concept and evaluate its importance.

- I find this manuscript extremely difficult to read. I find that the presentation lacks focus. The authors provide a high level of detail without clearly guiding the reader through the reasons that understanding the results at that detail level yield impor-

tant interpretation. I am unable to ascertain the manuscript's testable hypothesis - rather, the introduction's final paragraph simply states the final conclusions. The text also regularly refers the reader to future sections of the manuscript and makes repeated statements. It is therefore my opinion that the manuscript needs a relatively broad overhaul for the ACP readership to properly take home the message; I think the same information could be thoughtfully presented in about half the length and about half the figures.

- For the manuscript to stand on its own, it is my opinion that the reader needs to know more about the actual measurements considered; it therefore seems that there should to be a section outlining items such as (location, time, canopy/vegetation type, canopy density, canopy height, instruments deployed, configuration that the instruments were deployed, pros/cons of that deployment for this analysis, etc. I find it terribly remiss for the reader to need to wait until Section 4 before learning that the canopy's 30m tall and that the single level of instrumentation is located 7m above the canopy. How was the data quality controlled? Were there any stationarity criteria used? Was there any detrending or coordinate rotations imposed? How are averages defined? Why are certain data points missing? What were the overall weather conditions this day? In my opinion, referring the reader to a separate manuscript for these details is insufficient.

- I recognize that making measurements of ISO' and OH' is a difficult task, but as presented I find that a single day's data from 10am-2pm with missing data strewn throughout is insufficient to be able to put forward statistically significant conclusions.

- I find the level of effort expended to try to 'shoe-horn' individual data points lying outside the expected range extremely tedious; a feature that implies to me that the campaign failed to measure the quantities necessary to concretely interpret the data presented. I am most disappointed that the effort to massage the data

points into the expected range focuses mostly on 'modified' chemistry, and only in the last section does the fluid mechanical aspect really come into the discussion. How is it that things like the potential influence of species entrained from aloft (e.g. Ganzeveld et al, ACP, 2008; Vila et al., JGR, 2011) or spatially organized motions on the scale of the boundary layer depth (e.g. Molemaker and Vila, JAS, 1998; Krol et al, JGR, 2000; Vinuesa and Vila, AE, 2005) are not discussed?

- Due to the limited data available from the ECHO2003 campaign, the authors lump nearly every term in the conservation equations into a residual while attempting to explain the mechanisms controlling $\overline{c}_i$ and I_s; although I usually don't take issue with this practice, I find that the numerous terms being lumped into the residuals are affected by such a wide variety of influences, that interpreting these residuals becomes extremely convoluted and hides the important ideas.

- I find that the manuscript regularly shifts or neglects to document its notation, an additional feature making the reader's interpretation extremely difficult. What's the meaning of $\sigma(ISO)$ vs. σ_{ISO} vs. σ_{Iso} vs. $std(ISO)$ vs. σ_i? How do $[OH]$ and $\overline{OH}$ differ? How are the $'$'s defined? Where are $I3$-$V3$ defined? How can the reader be expected to take home the manuscript's primary message when the notation wanders all over the place and/or is never defined?

- I also find the English and sentence structure throughout to detract from the manuscript's readability, i.e. commas in incorrect places, heavily strewn with prepositions, run-on sentences, single sentence paragraphs, passive voice, etc.

There are certainly aspects of this manuscript that might be useful for the ACP community, but the authors have failed to guide the reader down a clear and convincing storyline. I also question the the robustness and applicability of their conclusions across a range of atmospheric stability conditions or chemical regimes. I therefore find myself unable to recommend publishing this manuscript as it was submitted.

Specific Comments:

Lines 165-168 I don't understand the lefthand/righthand value commentary. Write down the approximation as an equation so the reader can see exactly what's being done.

Line 181 *...significantly smaller...* How much smaller?

Line 186 *...shows that the mean contribution is not significant in our case...* I disagree. I think it shows that the sum of the storage and advective terms is approximately 20%.

Line 208 *... have to be ...* in order for what? I find this discussion terribly circular.

Line 213 *on average an inverse relationship (Fig. 5).* To me this inverse relationship is difficult to see in Figure 5.

Lines 234-235 Isn't this simply stating that for these data points, the reaction with isoprene the dominant sink?

Lines 236-254 Need to explain why this is effort is being undertaken. I understand that the authors are attempting to account for other chemistry contributing to the production/destruction of OH locally at this measurement location, but as written the reader isn't provided the necessary guidance leading them to this fact. As it currently reads, one is directed to look back into Appendix A to understand f and what it means. Personally, I think the information in Appendix A is brief enough that it should be included here for improved clarity.

Lines 257-259 How do the authors know there's a mean sinking motion during this ten minutes? Was the sonic anemometer deployed perfectly level? Without providing the reader further information describing how the vertical velocity measurements

were made and/or how the vertical velocity measurements were processed (coordinate rotations, etc), I'm unable to determine how $\overline{w}$ is observed. If there truly is a mean downward vertical velocity for these two 'points', where's the compensating period with a mean upward vertical velocity as one would expect from passing organized turbulent motions? If there's some intent to suggest that land-surface heterogeneity is impacting this location, please explain why the results don't see this downwelling vertical motion throughout the six-hour period.

Line 261 *... cause only a small contribution to* I_s*...* How is small defined in this context?

Lines 265-266 How is this *direct influence of the emission source* detected?

Lines 270-278 What's the take-home message from this paragraph?

Line 284 With the limited data available, how do the authors know that this *upper limit* is in any way meaningful? What controls this limit? Will the limit be the same tomorrow, or the next day?

Line 308 How do the authors know this is the *lowest possible value*?

Lines 312-317 I highly disagree with making these comparisons without explaining why I_s differs across each study. I_s is not just a parameter (as the authors discuss later in Section 4). All these examples represent different chemical regimes, different atmospheric forcing, different emission/deposition.

Lines 320-321 Should one expect this result? How does this relationship vary with chemical reaction rate? or a reactant's source distribution? or atmospheric stability? or turbulence intensity?

item[Line 338] I don't understand this comment: *... below the assumption made for model calculations*. Please explain. What is the typical assumption? Reference?

item[Line 342] Again, *... often assumed for model studies*. Reference?

Line 350 *... two branches ...* What branches are we discussing? Branches of what?

Equation 8 Something's awry with this equation. The term A_{1k} also contains $\overline{c_i' c_j'}$, see Equation 5. Please explain.

Lines 450-451 *... and the mean gradient of OH above canopy - from unpublished measurements - ...* Unpublished measurements? From where? I was under the impression that only a single level of OH was observed at ECHO2003.

Lines 452-453 What second term is obtained if isoprene and OH are replaced? Replaced with what?

Line 457 What product is the same order of magnitude as TPI_k? How do the authors know this? This entire paragraph seems like conjecture.

Lines 466-469 *According to the ergodic theorem we may assume that this spatial gradient is comparable to the time derivative* S*.* It is my opinion that the authors should be required to provide the reader further clarity and explanation regarding application of this theorem to their particular situation. Also, I think the reference should be Liepmann (1952), not Lippmann.

Line 469 *... and in Fig. 10* S *is small.* If you're going to refer to the time derivative as S, then S needs to appear somewhere in the figure or in the figure caption.

Line 477-479 *The turbulent transport is also one term in the chemical part of the flux balance and is calculated directly from measured quantities at* z_R*=37m. This term is generally below* $\pm 10^{-5}$*ppbms*$^{-1}$ *...* A couple points: 1) The turbulent transport term involves the vertical gradient of the third-order moments. How are these calculated from a single observation level? 2) Where's the figure showing that these data are shown to be in the stated range?

Lines 500-503 What's $I3$? $II3$? $V3$?

Line 507 *... higher by a factor of two respectively four in the morning hours ...* I don't understand this sentence structure.

Lines 534-535 *... many features of I_s ...* What features? What are we talking about here? Given that most everything being discussed is calculated as a residual from the other, I'm not surprised that ups and downs of one are reflected in the other.

Line 539 *Two branches ...* Again, what kind of branches are we discussing?

Line 585 *The latter can only be determined as a mathematical residuum ....* Perhaps this is true for the experimental data being discussed here, but otherwise I must question the validity of this statement.

Lines 711-714 What point is being made by presenting this linear regression? Is there some implication that this functional form should apply above all canopies? Or for all chemical regimes? Please inform the reader what they should take home.

Line 734 *This is done...* To what does 'this' refer?

Lines 754-755 Why can't a typical sweep/ejection cycle be established for this current data set? What's different?

Lines 806-810 *A comparable spatial variability of H_v may be possible for ECHO2003...* Does this sentence intend to state that the ECHO2003 measurements are affected by heterogeneous sources of heat and isoprene? If so, this leads back to my earlier comment regarding mean vertical velocity.

Lines 827-829 Patton et al. (2001) reported a value of the stability parameter (h_c/L, where L is the Obukhov length) of -0.4 for their simulations. This seems far from what the community would call 'free-convection', i.e. shear production remains important. Also, for the 'average' case presented here (using the reported values

of u_* = 0.39 m/s and H = 0.085 mK/s), I calculate that h_c/L is approximately -0.5 – not terribly different from that presented in Patton et al. (2001). Something therefore seems awry with this entire discussion.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 12913, 2013.