Review of “Segregation in the Atmospheric Boundary Layer: The Case of OH - Isoprene“ by Dlugi et al., submitted to ACPD December 2018.

Overall Recommendation:

This manuscript attempts to bring together all available measurements (and one modeling study) of the intensity of segregation between OH and isoprene in the convective atmospheric boundary layer (CBL). The objective is not only to better understand this parameter but to present some possibilities for universal parameterization of this coefficient, which directly influences chemical reaction rates based on mean concentrations as applied in most atmospheric chemistry models. The manuscript provides the theoretical development and scale analysis of the most pertinent turbulent statistics (mean concentration, vertical turbulent flux, scalar variance, and reactive chemical trace gas covariance) that underly the physics and chemistry of the segregation coefficient, I_s. This is a very helpful exercise, although half of these equations have been covered in the previous work of Dlugi et al. (2014) – namely, the mean concentration and covariance budget equations. Nevertheless, to have it all done in one place and to include scaling values from the two tower data sets, ECHO & ATTO, is in my opinion the most valuable part of this manuscript as it exists now (although this has already been done for ECHO in Dlugi et al. (2014). The inclusion of the modeling work and the two airborne flight legs are not similar enough to warrant inclusion in this work because the conditions are different and the behavior of I_s is not understood well enough to simply extrapolate them along any of the proposed independent variables presented in this paper. While I believe there is a lot of this work that is worth publishing I believe that the effort to cull it and improve it to the point of acceptance might take more time than the typical review turnaround, and for that reason I recommend to not publish this work in its present form.

The two central faults I find with the work as presently constituted are: 1) there is a troubling inconsistency with negative signs in this work that appears in Dlugi et al. (2014) also, which absolutely needs to be corrected before even considering publication, and 2) the variability in NO_x concentrations of the different environments are mostly ignored in this work and, in my opinion, are likely to dominate the variability of the data sets reviewed here. On the latter point, I realize that there is *some* justification for ignoring the NO_x-dependence based on Kim et al. (2016); however, their simulated segregation coefficients for the surface layer are only about -0.02, which does not agree very well with the near canopy data sets presented here, and their modeling work also shows significant NO_x-dependence in other parts of their domain (“mixed” and “cloud” layers, and even changing sign.)

Some other, less important but serious weaknesses of the submission include:

1) There needs to be consistency throughout the manuscript in the use of “larger” and “increase” when it comes to the covariance which, in principal, can be either positive and negative. Sometimes it seems to refer to greater magnitude (larger negative number) and sometimes greater numerically, and it often confuses the discussion. [see individual comments for specific points in the text.]

2) This manuscript is way too long, and its excessive length is not justified. I suggest removing the inclusion and discussion of Kaser et al. (2015) which is in the bulk of the CBL and as such is not easily compared to the other two experiments just above forest canopies. I also question the similarity of the results of Ouwersloot et al. (2011) that are averaged over the depth of the CBL when the data from ECHO & ATTO are in the roughness sublayer of large forest canopies.

3) Much of this work is a direct reworking of the results presented in Dlugi et al. (2014) including many of the figures (the latter's figures 21, 20, 16, 9, 8). I realize the utility in updating these relationships with the most extant data possible, but there is no indication that all of these figures contain much information. For example, I do not see any convincing relationship between I_s(OH, Iso) and the surface buoyancy production rate, or the correlation coefficient, r(OH, Iso), or the Damköhler number. Thus the authors might want to consider which relationships show the most informative new information and only update those.

Specific line-by-line concerns:

Lines 40-43: Please give an approximate range of NO_x for these conditions (instead of "high NO_x" and "low NO_x" which probably mean different things to different readers.) As stated above, I believe that it may be the most important distinction among the various experimental results.

l. 48-49: I disagree, a direct relation is shown in your equations (11) and (21). The isoprene flux is contained in two leading terms: one is in the TPI of the covariance budget and the other is in the variance budget (GP_{var}). But, as you say here, they may be more or less influential depending on the strength of other competing terms.

l. 51: I realize that this may seem like quibbling, but chemical scalar fluxes do not necessarily always decrease with height. For example, if the entrainment is strong and the CBL concentration high enough, then it is possible for the isoprene vertical flux to *increase* with height (e.g. water vapor fluxes in some cases.)

l. 58: You should probably be more quantitative about this statement. How much does I_s increase with measurement bandwidth? It seems that if this is one of the leading findings of the study, worthy of inclusion in the abstract, then it should be elaborated a bit more: what does the cospectrum of <Iso'OH'> look like at low wavenumbers? The increase in lower frequencies that you investigate in this study goes from about 2-10 km (based on a wind speed of about 4 m/s), comparable to the LES domain of Ouwersloot et al. (2011). On the other hand, the scales covered in Kaser et al. (2015) start at about 3 km (30 s OH measurements) and run to 50-100 km, which are dramatically larger scales than even your expanded analysis. This is the main reason that I believe the inclusion of the results of Kaser et al. (2015) is not appropriate for this work.

l. 70: "and" is probably more often the case (buoyant & shear production combined).

l. 160: missing 'g' in Tg.

l. 165: I don't see why the transport has to take place in a cloud-topped boundary layer.

l. 172: I don't think that NO_2 generally determines the OH reactivity in any significant way. Also, whenever there is any significant isoprene, it tends to be the dominant VOC sink for OH. Therefore it doesn't make sense to consider isoprene moving through a static OH field because isoprene *is* usually the dominant sink and determines, in part, the OH field. Of course, this rapid reactivity is what drives the anticorrelation.

l. 178: Doesn't $I_s < 0$ hold only for when the chemical sink of OH is dominated by isoprene or something correlated with isoprene? If isoprene is correlated with a major source of OH (e.g. RO_2 or HCHO) then I_s could be > 0 in principle, no? Come to think of it, this is where I believe the answer to the origin of your observed $|I_s|$ limitation lies: the OH photochemistry is so heavily buffered that while isoprene is a dominant sink it is also correlated with important sources such as isoprene peroxy radicals, Iso-O2, and HCHO. See Kaser et al., 2015 Fig. S9 for estimates of the relative magnitudes of RO_x ($=RO_2 + HO_2$) source strengths.

l. 188: 'caused by' is an odd way to put it because $I_s < 0$ is by definition represents an anti-correlation, but what actually caused it is the broader question that this paper tries to address.

l. 207: The I_s values of Kim et al. (2016), albeit very small, nearly double across the range of NO_x from the experiments you compile (~0.1 from ATTO to ~2 ppb from ECHO) from about -0.02 to -0.035.

l. 209: The UNO run of Ouwersloot et al. (2011) developed an I_s of -0.12 and it was 'homogenous' in heat and isoprene fluxes, whereas without NO_2 (lower NO_x) the control run I_s = -0.07. Do you mean I_s (low NO_x) > I_s (high NO_x) or their magnitudes? Note that Ouwersloot et al. (2011) (from their Section 3.6) "stress the need to take the VOC **and NO_x** conditions into account in future studies that aim at segregation parameterizations." This advice seems to have been overlooked in the present work.

l. 213: Again, I disagree with the statement that most of the results of Ouwersloot et al. (2011) are < -0.1. From their Table 4, HOM $\langle I_s \rangle = -0.07$ which is definitely *not* < -0.1! (see less important weakness (1) above about comparisons of I_s magnitude or numerical values less than zero.)

l. 243: I think you should define this here: $\langle w'c'^2 \rangle$. At this point I did not have any idea what M_{21} represented. Incidentally, this appears to be the best predictor you have observed to correlate with I_s, so why not emphasize that more and show the results for M_{21} vs. I_s in the ECHO & ATTO data sets?

l. 255-257: I think you should point out here that most theoretical treatments show I_s to be of smaller magnitudes in the bulk of the CBL vs. the surface layer (e.g., Kaser et al., 2015; Ouwersloot et al., 2011; Patton et al., 2001.)

l. 316: The measurement of HO_x fluxes and other higher moments from July 25 of the ECHO campaign seems like new material (not covered in Dlugi et al., 2014) so it probably merits some more explication. For instance, how did the cospectra compare to <w'T'> or <w'O_3'> or some other scalars? Does the flux direction and magnitude agree to theoretical predictions (e.g. Gao & Wesely, 1994)? Were these data analyzed in a separate paper? What changed to allow for these measurements, of which I know of no others? See Section 5.1 of Dlugi et al. (2014): "Spatial derivations of mixing ratios of these compounds and their fluxes are not available from this data set". What has changed?

l. 321-323: What seems more directly important than temperature and humidity is the mean concentrations of HO_x on that day relative to the rest of the experiment.

l. 345: If the HO_x data is available at 0.2 Hz, why were there no fluxes reported other than July 25?

l. 378: What was an average background OH value relative to the total? And as far as the second unit is concerned, how are you sure the amount of background OH is the same in both units? It seems that it might be worthwhile to describe some statistics of the backgrounds for both units to understand their variability and similarity.

Figure 1: This figure is probably not necessary since none of the analysis of the OH measurements is covered herein.

l. 453: Equation 4 is a few pages later than this reference, but come to think of it equation 4 does not really give any chemical information other than there is a reaction between OH and isoprene, and as such is probably not necessary.

l. 457: The justification of time resolution invoked by Karl et al. (2013) is for turbulent fluxes (from Lenschow & Kristensen, 1985), which relies on assumptions about the turbulent statistics of *w'*, but the requirements for a covariance with another scalar are different.

l. 489-491: I don't think it makes sense to mention compressible fluids and refer to the various 'α' variables defined by Richardson only to redefine them.

l. 500: I do not think that '$\times$' is the best symbol to use for multiplication? It looks like a cross product and the subscripting *i,j,k* looks like tensor notation. I think a '$\cdot$' or nothing at all is much more conventional and clear to indicate scalar multiplication.

l. 507: Very rapidly after the H abstraction of the OH + isoprene reaction the production of some isomer of an Iso-O_2 radical occurs. These peroxy radicals reacting with NO are usually a very important source of OH (Kaser et al., 2015 estimate it to be of similar magnitude as ozone photolysis.)

l. 508: Is this supposed to mean Eq. 2 subtracted from Eq. 1?

l. 515: What exactly is $C_xH_yO_z$? I recognize the attempt to remain general, but I think the more important general species that is not mentioned anywhere is RO_2.

l. 529: the denominator of term 1 should be r_{wci}.

l. 574: Using the Einstein summation convention with tensor notation confuses your own convention of using a generalized chemical trace gas, c_i and c_j. These look like 3D vectors in tensor notation ($i, j = 1, 2, 3$), and there is no other place in the manuscript where it is beneficial to generalize the chemistry. This is a work centered on the reaction of OH and isoprene and as such there is nothing gained by calling those species c_j and c_i, respectively. For example, k_{ij}, looks like a second order tensor, not a scalar reaction rate coefficient.

Table 1: It would be more clear if you preserved the signs of these terms such that MR & TR are always <0 (that is, act to reduce $<c_i>$ in the budget.) Realizing that you labeled the terms inside the parentheses in equation (7), the terms DMF and DTF have different units because they are not the divergence thus the numbers in the table do not have to sum. I think it would be a lot clearer if you defined the terms to each entire item in the budget equation and keep their signs clear and indicative of how they change $<c_i>$.

l. 603-628: This entire paragraph suspiciously omits any mention of horizontal components of these advective terms. That, in itself, seems like an oversight, and it renders the last sentence (l. 626-628) incorrect: a change in mean horizontal advection (without a change in the wind field divergence) can lead to significant changes in $<c_i>$. It is not clear whether you mean 3D or 2D divergence/convergence in this discussion. Keep in mind that the second term in equation (8) in its full 3 dimensions is zero because of the incompressibility of the mean flow.

l. 707: Doesn't the concentration of isoprene *decrease* with height directly above the canopy making the numbers you report -0.01 to -0.07 ppb m^{-1}? This term then is always negative acting to reduce the steady-state variance, no? This is counterintuitive, but is the nature of your steady-state approximation in equation (11).

l. 717: I think you should be more specific in this reference. I believe it is specifically discussed in Section S3.2 of the Dlugi et al. 2014 supplementary materials.

l. 733: Fig. 1 of Spirig et al. (2005) indicates a tower separation of ~250 m.

l. 740-746: TT_{var} is the *divergence* of a turbulent flux of variance. Speaking of a "vertical change of TT_{var}" sounds like you are now looking at the second derivative of the variance flux. Is that what you're referring to? It would help if this discussion were a lot more clear about what is a turbulent flux of variance (the <w'c'^{2}> term), vs. its vertical change ($TT_{z,var}$).

l. 752: Your term III in Eq (11) is equivalent to IV3 in Table 4 of Dlugi et al. (2014) which states its estimated magnitude as < 3e-5 ppb^2 s^{-1}.

l. 762: It is not clear how you estimate the gradient of a fluctuating scalar directly, but in general variance budget discussions the molecular destruction term is expected to be first order (to balance mean gradient production in the steady-state, flow-integrated condition.) See Section 5.3 of Wyngaard (2010), for example.

l. 805: How did you derive these OH flux values? And are you imply that you have these values for both experiments? Is this not discussed anywhere else in the literature? It seems like a very difficult measurement to directly make by eddy covariance. In any event, you should probably specify the sign of this flux (I believe it should be downward, <0). These magnitudes seem much larger than predicted by Gao & Wesely (1994).

l. 834/5: Again, the gradients of isoprene should be negative.

l. 845: I recommend sticking to a single format for all of these range limits of your scale analysis, and preferably using only one significant digit. For example, '*x*e-3' to '*y*e-1'. Two significant digits for these scale analyses that typically span multiple decades just seems unnecessary and slightly confusing.

l. 859-861: The similarity you are applying to associate the different scalar transport terms needs to be explicitly stated. It seems like you are using some sort of modified Bowen ratio analog to the transport term, but this seems highly speculative. I believe that speculative is fine, but it would be more convincing if you explicitly stated the similarity you are applying.

l. 893: This range of a factor of 5 for the pressure transport term implies that the time scale values have a range of a factor of 6, because the isoprene fluxes mentioned above span a factor of 30 (0.02 to 0.6 ppb m/s). It would be clearer if you presented what the mixing length concept of Poggi et al. (2004) depended on.

l. 973: I have tried and tried and redone the arithmetic on the governing equation (15), because I know how pernicious and elusive sign errors can be, but I just cannot see how the normalized variance term in equations (20 & 21) can have the opposite sign of the C_{ij} term (which is the balance of the terms from R_{ij} outside of the covariance and variance terms that all have the same sign). This same error appears in Dlugi et al. (2014) at their equation (15). This has very important bearing on the analysis because the normalized variance of isoprene ***and*** the RES (Eq. 16) terms both act to ***increase*** the magnitude of the OH and isoprene segregation coefficient, in this case, - I_s, because $I_s < 0$. It seems like this equation will change the authors' calculations of RE_{is} because they solve for it as the residual of equation (21), and will fundamentally change Figure 7.

l. 999: You say that R_{ij} goes *negative* despite terms (b) and (c) which are positive definite. But R_{ij} is defined with a negative (definite) sign (equation 18), so the positive definite terms like (b) and (c) work to make R_{ij} negative. I found this language error typical throughout the manuscript. When revising I recommend being very careful with the language about discussing relative values or magnitudes of values, always retaining the accurate signs of the terms.

Figure 3: 60% of graph has no information on it. Also, why is the total term in one unit ($ppb^2\ s^{-1}$) and the individual components in another (ppb^3). I think it makes the figure less clear to include the reaction rate in one and eliminate it in the others.

Figure 4: Again, why compare these terms of differing units and then put a one-to-one line on the figure? Also why ignore the sign of R_{ij}? If all the values are negative, then label it $-R_{ij}$.

l. 1041: Term (c) is not the only leading term of R_{ij}. The ATTO results could differ because of a substantially different contribution from the <OH'Iso'>[Iso] term (a), especially at higher values of [OH]var(Iso).

l. 1109: "R_{ij} increases [**in magnitude**] with increasing variance…"

l. 1126: It does not seem clear from Fig. 9 that the relationship between r_{ij} and I_s is *non-linear*. You use this term a lot but none of the figures clearly show any distinction among a linear or non-linear relationship.

l. 1219-1221: You do not know for certain that the var(Iso) and flux terms are *only* established near the surface (for example, the entrainment zone can possess high variances and fluxes.) Furthermore, equation (11) also shows that var(Iso) is augmented by a term proportional to [Isoprene]$\langle c_i \cdot c_j \rangle$ (concordant with equation (21) with the corrected sign), which could also be a leading term near the surface. Also note that what you are referring to as GP_{var} actually serves to decrease isoprene variance in the steady-state form you present in equation (11) because $d[Iso]/dz < 0$. In the variance budget, equation (9), GP_{var} produces variance, but in the reactive chemical steady-state of equation (11) it reduces variance.

l. 1243: I am assuming you mean vertical advection by the mean flow. However, just because *W* is larger in magnitude at higher elevation in the CBL does not mean that the magnitude of the scalar gradient is larger. It is much more likely to be turbulent transport that is a large term. If by 'vertical advection' you mean turbulent transport (the divergence of a vertical turbulent flux), then I would specify that.

l. 1244: I_s is related to the isoprene flux by two separate terms of Eq. (21): the *TPI* term of RE_{is} ***and*** the GP_{var} term in the normalized variance, nvar(Iso). This is not made clear in this discussion and consequently these arguments are ambiguous. These two flux terms have different coefficients (OH and isoprene gradients, respectively) so that their coefficients will change with altitude (probably both decreasing with height.) I would suggest eliminating all of this height dependence of variance discussion because it is speculative (for reactive scalars) and it does not really help the overall work in any way that I can discern.

l. 1319: No, OH and O_3 do not *necessarily* have a large positive covariance (presumably someone could check if there were O_3 fluxes being measured on the tower), but the principal source of OH (on the ~1 s time scale) is the photodissociation of O_3 so it is very likely that they are, in fact, correlated.

l. 1331-1333: That is patently incorrect. First, E_{i0} ***is*** directly related to the flux at any height in the CBL (you used such a relationship yourself earlier to extrapolate their observed fluxes at z/z_i ~ 0.4 to the surface). Furthermore, as stated previously, I_s is correlated to the isoprene flux through both the GP_{var} (where it serves to diminish the variance, and thus $|I_s|$, right above the canopy where the flux is upward and the gradient is negative), and in the TPI term of RE_{is} in (21) where it tends to be a source of negative covariance because the OH gradient is likely positive (due to preponderance of sinks effusing out of the canopy.)

Figure 12: Why are there are not the same number of blue diamonds (spectrally extended) as there are black circles? They should be 18-27% larger according to line 1391. Also, the blue diamonds all lie exactly on top of the circles showing no spectral change in <OH'Iso'>. Also, the two points on the lower left ($I_s < -0.2$) do not seem to exist on Fig. 14.

Can you explain what the blue dashed curves represent? Are they a power fit with n=2 and n=3?

60% of this central figure has no information on it aside from a legend.

l. 1409-1410: I_s never becomes independent of [Iso][OH] because that product resides in its denominator. The covariance may become independent, but not I_s.

l. 1460: According to Dlugi et al. (2014) Eq. (17) M_{12} were considered the "ejections", and M_{21} the "sweeps"?

Figure 14: This figure is nearly identically the same as Dlugi et al. (2014) Figure 20, save for the three modeling results and two Kaser et al. (2015) points. Why do you not present any of the ATTO data on this figure? Why plot both BP and kinematic heat flux? As far as I can discern there is no appreciable difference in the underlying relationship and plotting both just clutters the figure.

l. 1545: It is very challenging to find an empirical relationship in Fig. 14 as stated. You should propose one if you think it exists. Is looks to me like a nearly vertical line would fit through the points of BP > 3e-3? I wonder what the *p*-value of such a fit would be, because it does not look great by my eye.

l. 1597-1601: If M_{21} vs. nvar(Iso) & RE_{is} shows a strong relationship as in Fig. 18 of Dlugi et al. (2014) why not show it? If this finding is worthy of a paragraph in conclusion, then it seems it should be represented in a figure. Earlier you state the sweeps only weakly correlate with nvar(Iso) and RE_{is}, and here you state that only ejections contribute to I_s. This all seems to beg for a figure of both M_{21} and M_{12} to see how much they each correlate to nvar(Iso) & RE_{is}. This could be a micrometeorological parameter that is readily measured in canopy field studies that could be used to estimate I_s for chemical modelers, for example.

l. 1621: The bandwidth of the Kaser et al. (2015) measurements were out to nearly 100 km. For typical winds speeds of, say, 5 m/s this would require a 5.5 hr integration time at a tower site. Thus the measurements, aside from being made several hundred meters higher than the ECHO & ATTO datasets, represent a much larger spectral band.

The 'hypothesis' of scale dependence is established explicitly in Ouwersloot et al. (2011), why bring this in as a hypothesis from this work? There is currently no easy way to disentangle the isoprene surface source variability from the scale of the measurements in terms of their effects on I_s, so it is not a hypothesis that is truly tested in this work.

l. 1625-1627: This is an interesting idea, but not very well explicated in the body text of the manuscript, and only sprung on the reader in the last sentence of the work. The diurnal source correlations (which in and of itself would promote a *positive* species covariance) occur on long time scales relative to the chemistry and the TKE dissipation and the 10-40 minutes averaging used in this study. In order for this to be a reason for the "limits" of I_s suggested on the 10 min scale the sources would need to correlate on this restricted time scale, and/or there would need to be some sort of downscale cascade at play. This speaks to the absence of any cospectral representation of I_s in this work (something like Fig. S4 of Kaser et al., 2015), which would help understand its spectral dependence. In any event, I suspect the compensating chemistry of OH sources that are correlated with isoprene (e.g. isoprene peroxy radicals) are the most likely culprits for limiting the magnitude of I_s.

Reference Su et al. (2015) I was not able to find. It seems better to use: Atmos. Chem. Phys., 16, 7725–7741, 2016. www.atmos-chem-phys.net/16/7725/2016/. doi:10.5194/acp-16-7725-2016.