

Interactive comment on “LES study of the impact of moist thermals on the oxidative capacity of the atmosphere in southern West Africa” by Fabien Brosse et al.

Anonymous Referee #2

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Summary

This article describes the effect of turbulence on the reactivity of OH and two key volatile organic compounds, isoprene and lumped aldehydes (where there are more than 2 carbons). The authors find that turbulence can reduce isoprene and OH reaction rates by up to 30% for a biogenic environment with low NO_x, and affect reaction rates of lumped aldehyde and OH by 16% or less for an anthropogenic environment. Thus, a box model or regional and global-scale models that assume each grid box is well mixed will potentially be in error of the OH reactivity by 10% or less because of covariance of reactants caused by turbulence.

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Over the past 5 or so years, there have been some very similar studies with similar conclusions as what was presented here (Ouwensloot et al., 2011; Kim et al., 2012; 2016; Li et al., 2016; 2017). As a consequence, the only new advance for atmospheric chemistry science is the potential error to the OH reactivity calculation in models that assume a well-mixed box. Yet this error calculation was done for a limited time and space region. In its current state, this paper is not ready to be published. Most importantly, the paper needs to emphasize its uniqueness. Otherwise it will be viewed as a confirmation of the previous studies.

Major Points

1. The paper needs to emphasize its uniqueness. The reactivity of OH should be discussed more thoroughly as it is the goal of the paper. The title of the paper, the introduction, and even the section heading (3.2 OH budget and reactivity in a convective boundary layer) say that we will learn about the convective boundary layer (CBL), yet only results at 20 m, the lowest model level, are discussed. I strongly recommend presenting OH reactivity results for the entire CBL adding a figure showing the error associated with OH reactivity when turbulence effects are considered, and stating the implications of this error on atmospheric chemistry in general. For this last part, it would be good to learn, besides the point that turbulence could explain the missing OH reactivity sink found in the Amazon, what the expectation of turbulence effects on OH reactivity is for the atmospheric oxidative capacity. Making these changes would very much align the paper's content with its title.

2. One other unique aspect of this investigation is the selected case study, which is a region in tropical West Africa that experiences stratus clouds in the morning subsequently breaking up to form cumulus clouds in the afternoon. Examining segregation of reactants with low-level stratus cloud has not been reported (to my knowledge). This aspect could be emphasized more by including the cloud fraction diurnal profile along with the other variables plotted, and address the question of what impact the cloud has on the intensity of segregation and OH reactivity. The effect is most likely limited

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to the effect on heat and moisture fluxes for the simulations shown, unless effects of cloud scattering on photolysis rates are included in Meso-NH. The authors could also speculate what effect the clouds have on isoprene emissions based on transmittance (cloud optical depth) and temperature effects.

Specific Comments

1. In general, the LES results show that the intensity of segregation is <10%. The 30% segregation that is stated in the abstract and conclusions is overstated, as this high value occurs for a small-time period (~30 minutes) and region (top of boundary layer) of the model domain where isoprene is likely quite small.
2. Although this paper does a good job of citing previous studies, I was surprised that Krol et al. (2000) was not cited. Krol et al. (2000) is one of the first to examine segregation effects on VOC + OH reaction rates.
3. Page 2, line 33. Clouds scatter radiation resulting in regions of less solar radiation and more solar radiation.
4. Page 3, lines 29-30. Could the definition of the thermals be presented in a little more detail? My understanding is that the definition is also based on vertical velocity greater than zero, the standard deviation of the decaying tracer, and for when cloud exists, liquid water content. In addition, I was wondering if radioactive-decay tracer is the correct terminology, as it could just be called a first-order decay tracer.
5. Page 4, section 2.2. How does the ReLACS 3.0 chemistry mechanism compare to that used by Kim et al. (2012)? Just based on number of chemical species, they may be quite comparable, making the statement on p. 3, line 4 inappropriate. A key part is that they both include reactions that allow peroxy radicals to produce hydroxyl radical limiting the segregation effects.
6. Page 5, section 2.3. How is the convective velocity calculated? There are different methods such that characterizing the turbulence is important.

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7. Page 6. In comparing equation 4 to equation 9, should ROH be in the denominator of equation 9?
8. Page 7, lines 10-15, lines 22-24. It would be nice to see the observations overlaid on the figures displaying the model results.
9. Page 8, Is UTC same as local time (LT)? This information would be helpful when examining the diurnal profiles.
10. Page 9, lines 4-6. I am surprised production of HNO₃ was not discussed. It seems a more likely outcome at temperatures near 300 K (as PAN thermally decomposes).
11. Page 10, section 3.1.2. It would be useful to show via figures why the intensity of segregation is negative or positive and why it changes with time as part of the discussion of Figure 6 on page 10. Examples of the isoprene and OH anomalies in the context of the OH production would help quantify and explain the results.
12. Page 10, lines 27-33. It is interesting that there is a positive covariance of ALD2 and OH at the top of the boundary layer from 0700 to 1230 UTC, which is during the time period of the stratus cloud (Figure 1 shows cloud fraction > 0.5). How much of this positive covariance region coincide with the clouds? How might the cloud environment affect ALD2-OH covariance (e.g. high relative humidity, scattering of photolysis rates, etc.). How much would the results differ if aqueous chemistry (or just partitioning between gas and aqueous phases) were represented in the model? Finally, why is there a positive covariance for ALD2 and OH during morning at CBL top, yet a negative covariance for isoprene and OH?
13. Page 11, section 3.2.1. It may make more sense to calculate the OH budget for several model layers to reduce effects of the emissions being injected into the lowest model layer. The lowest model layer is subject to subgrid effects (e.g., Vinuesa and Vila-Guerau, 2003; not only subgrid-scale TKE but also subgrid-scale chemistry) and therefore more uncertainties can arise in these budget calculations.

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14. Page 12, lines 11-25. It would be good to see a figure showing the error in the OH reactivity due to turbulence effects.

15. Page 12, line 24. Since segregation happens only for compounds that have chemical lifetimes similar to the turbulence time scale, it seems unlikely that there is a compensating factor described in this line (unless isoprene + OH segregation compensates). Could the authors provide support for this statement?

16. Page 13. I applaud the authors for discussing several previous studies in the context of their results. However, I found that there was often no explanation of why there are differences between this study and the previous work. For example, p. 13, line 1, why are the current segregation values higher than Kim et al. (2016)? Line 8, how are the boundary layer dynamics different between this study and Li et al. (2016)? Lines 20-28, do the previous studies report the same dominant OH production and loss reactions as the current study? If they are different why does that happen (e.g. different emissions causes more VOCs in one study or the other)?

15. Page 15, lines 11-13. This discussion states a 5-15% missing fraction of OH reactivity reported by Nölscher et al. (2016) are similar in magnitude as that caused by turbulence effects on OH reactivity. Although I agree that the assumption of the well-mixed “box” is an issue to be considered for studies like Nölscher et al. (2016), I wonder if uncertainties in the measurements and reaction rate constants are also sufficient to explain discrepancies between model and observation analyses of OH reactivity.

16. Page 15, lines 14-20. The Li et al., 2017 study addresses segregation of reactants with aqueous phase chemistry included.

Technical Comments

1. The paper needs to be proofread carefully and completely to improve the English. There are many places that could be improved, which should have been done as part of the Quick Review Process.

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2. Could “resp.” be spelled out?
3. P. 12, lines 27-30, The first paragraph should cite other papers such as Krol et al., 2000; Ouwersloot et al., 2011; Kim et al., 2012; 2016; Li et al., 2016; 2017.
4. P. 18, There are two Hansen et al. (2015) references that appear to be the same.
5. Table 1. Instead of having the reader find the ReLACS3 paper, it would be helpful to explain the names of the lumped species.
6. Figure 2, I find the title of each plot to be useful. Yet in this case I do not understand “MRC”. It should be defined or rewritten into something meaningful.
7. Figure 4 caption should be improved. That is, NO, NO₂ should be added to a-b) description and OH, O₃ should be added to c-d) description. The ALD2 line needs a scale.
8. Figure 5. What are the black lines contouring? I think thermals, but it does not say in the caption. The vertical profile lines need to be thicker.
9. Figure 6. I assume the results plotted must be an average in space, and needs to be stated in the caption.
10. Figure 8 shows results for OH reactivity at an altitude of 20 m (the lowest model level) for “updrafts”, “updrafts-free”, and all horizontal grid points. I think it would be better to characterize these lines as thermals and non-thermals as vertical velocity is often very close to zero at/near the surface.

References

Kim, S.-W., M. C. Barth, and M. Trainer, Influence of fair-weather cumulus clouds on isoprene chemistry, *J. Geophys. Res.*, 117, D10302, doi:10.1029/2011JD017099., 2012. Kim S.-W., M. C. Barth, and M. Trainer, Impact of turbulent mixing on isoprene chemistry, *Geophys. Res. Lett.*, 43, 7701–7708, doi:10.1002/2016GL069752, 2016.

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Krol, M. C., M. J. Molemaker, and J. Vila-Guerau de Arellano, Effects of turbulence and heterogeneous emissions in photochemically active species in the convective boundary layer, *J. Geophys. Res.*, 105, 6871–6884, doi:10.1029/1999JD900958, 2000.

Li, Y., M. C. Barth, G. Chen, E. G. Patton, S.-W. Kim, A. Wisthaler, T. Mikoviny, A. Fried, R. Clark, and A. L. Steiner, Large-eddy simulation of biogenic VOC chemistry during the DISCOVER-AQ 2011 campaign, *J. Geophys. Res.*, 121, 8083–8105, doi:10.1002/2016JD024942, 2016.

Li, Y., Barth, M. C., Patton, E. G., and Steiner, A. L. Impact of in-cloud aqueous processes on the chemistry and transport of biogenic volatile organic compounds. *J. Geophys. Res.*, 122. doi.org/10.1002/2017JD026688, 2017.

Nölscher, A. C., Yañez-Serrano, A. M., Wolff, S., de Araujo, A. C., Lavric, J. V., Kesselmeier, J., and Williams, J.: Unexpected seasonality in quantity and composition of Amazon rainforest air reactivity, *Nature Communications*, 7, 10 383, doi.org/10.1038/ncomms10383, 2016.

Ouwensloot, H. G., J. Vilà-Guerau de Arellano, C. C. van Heerwaarden, L. N. Ganzeveld, M. C. Krol, and J. Lelieveld (2011), On the segregation of chemical species in a clear boundary layer over heterogeneous land surfaces, *Atmos. Chem. Phys.*, 11(20), 10,681–10,704, doi:10.5194/acp-11-10681-2011, 2011.

Vinuesa, J-F and J. Vilà-Guerau De Arellano, Fluxes and (co-)variances of reacting scalars in the convective boundary layer, *Tellus, Ser. B*, 55(4), 935–949, doi:10.1046/j.1435-6935.2003.00073.x, 2003.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2017-969>, 2017.

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