Referee 1:

We thank the reviewer for his helpful comments helping to improve the manuscript.

Rev: Dlugi et al. present new data on the issue of segregation between isoprene and OH, and put these in context of previously published work. Their data were obtained in the Amazon and largely confirm previous studies on segregation. The paper could provide new insights on the topic of segregation in the Amazon, but there are a couple of issues that should be addressed before any possible publication. The manuscript is unnecessarily long (60 pages) - as it stands, the manuscript could be significantly shortened and more focused on the important findings. Vast parts read like a review article. Detailed descriptions of previous studies (section 2.1.) could be significantly reduced and rather be included as a citation. The lengthy discussion of previous studies keeps the authors from describing important details about the ATTO site itself, which is essential to the interpretation of the presented analysis. Section 2.2 therefore lacks clarity.

In general: We propose to add a Supplement to the revised version of the paper. Here we give figures S1 – S27 for this Supplement as an example to provide information on the micrometeorological and chemical situation at the ATTO site on day 22/11/2015.

Ans: Indeed, it is a review of available results on measurements on segregation for the OH- isoprene system with comparison to available information from modelling. This is described in section 1 and specified in lines 262 – 292.
The results obtained during the ATTO 2015 study are compared to available field studies (ECHO 2003, NOMADSS 2013) and results from modelling. In addition, the revised version will be extended to discuss the possible impact of NOx on segregation intensity in the field and for model results. See also general comments to reviewer 2.
Therefore a short description is given for ECHO in section 2.1 with references to Dlugi et al. (2010) and Dlugi et al. (2014).
We agree that the description of ATTO 2015 is too short with respect to the remarks given in this review. Therefore we add a) additional information in section 2.2., and b) in a Supplement (as done by Dlugi et al. 2014) for general features on micrometeorological and chemical quantities. Graphical examples for the description of micrometeorological and some chemical quantities are given in Figures (Supplement) S1 – S27.

Rev: What is the immediate footprint of the surroundings? What is the main wind-direction, is there a variation in isoprene emissions surrounding the site? Have the authors looked at sector dependent isoprene emissions? From their assumptions it appears the site is characterized by a rather homogenous isoprene emission source, but it would be good to show this. What QAQC criteria were incorporated for the interpretation of turbulence measurements? I would have also expected to see an overview on latent, sensible and momentum fluxes as well as other important micrometeorological quantities such as Bowen ratio, Obukhov length etc.

Ans: Note that we did not make assumptions related to the source distribution of isoprene or other quantities. Instead, we pointed out in section 3 that for ECHO 2003 and ATTO 2015 the influence of advection on the flux as well as also on the variance of isoprene is not negligible (see for example Table 1 and Table 2). Footprints are given in Fig. S6 – Fig. S7 and Fig. S24 – Fig. S25 (see Supplement).
The QAQC criteria that were applied to the field data from ATTO 2015 and ECHO 2003 will be described also in the Supplement, although they are given in sections 3.4 and 3.5 of Dlugi at al. (2010) and by Pfannerstill et al. (2018) for ATTO 2015.
In general all studies in the field are made "at a tower in forests", and therefore are "point measurements", necessitated by the fact that the related instrumentation is very complex and can be operated in a reliable controlled manner only in a way to obtain time series from one measuring volume. Spatially resolved – simultaneous measurements of this kind

at different locations – were not performed up to now. The airborne measurements reported by Kaser et al. (2015) were along a transect sample from a certain volume above ground. They obtain a spatial (and time) average. As for all micrometeorological data processing procedures, the assumption is made that spatial and time averages agree. (See lines 482 - 496 in our paper.)

Rev: The key instrumentation relevant to this article are HOx and isoprene measurements. The frequency of isoprene measurements was 1 Hz, so one would expect a loss in high frequency variability. Further, damping through a 40+ m line has to be expected. The method of inferring a lag-time by comparing water vapor fluctuations through such a long line bears a potential problem, because water vapor retention is expected to be much larger than that of small hydrocarbons. It is also not clear what pressure drop was produced by the 5 um filter. One way to ensure that this analysis is not prone to any substantial bias would be to compare the covariance functions between vertical wind, isoprene and water. I am also missing information on the determined delay/lag time. Overall I am concerned that some (significant?) part of isoprene variability might have been lost due to the experimental setup? Have the authors done any co-spectral analysis?

Ans: The instrumentation to measure isoprene during ATTO 2015 is also described by Pfannerstill et al. (2018) as cited above. We performed the requested calculations of correlations before the field study in many laboratory tests as well as on data obtained 2015 in the field, e.g., on water vapor, CO_2, and isoprene. The concern "that some part of isoprene variability might have been lost" is surely correct for frequencies above 1Hz. Note that we focus on segregation between isoprene and OH. For OH we apply the time resolution of 15 s, so that all covariances $\overline{\mathrm{OH'ISO'}}\ \mathrm{are\ for}\ 0.06\bar{6}$ Hz (0.067 Hz) and smaller for ATTO 2015 and for ECHO 2003 are for 0.2 Hz and below as given on Page 42, lines 1308 – 1313 in our paper. For these frequency ranges the calculation "of ogives for $\overline{\mathrm{OH'ISO'}}$ shows that the loss of variability" is not as important as the loss on the low frequency end of the time window being chosen, as was also discussed by Dlugi et al. (2014) (their Fig. 17). Note that averaging over updrafts and downdrafts may result in small Is as the contributions partly compensate each other (see also their example given in their Fig. 17)
In a Supplement we will give more details on these aspects for ATTO 2015 and also summarize such results for ECHO 2003.

Rev: The authors present the issue of underestimating modelled OH in the tropical atmosphere as a main cause to look into the subject segregation. There are some reports of a possible overestimation of OH inferred from LIF instruments. Several recent studies (e.g. Liu et al., 10.1126/sciadv.aar2547 2018) have concluded that there is no gap between modelled and observed OH in Amazonia within the experimental uncertainty. The cited study by Kaser et al. actually also shows this, as the total impact of different chemical recycling schemes in their study seemed to be quite small. It would strengthen the manuscript to point out differences in OH measurements during this and previous campaigns, as well as commenting on conclusions of the above papers. In this context it is not clear whether there have been any changes to the presented LIF OH measurements since Lelieveld et al., 2008. At least a reference to a recent validation or intercomparison paper would be warranted. A recent chamber study (Kanaya et al., 10.5194/acp-12-2567-2012, 2012) suggests about a 50% uncertainty (bias) for the measurement of OH in low NOx, isoprene dominated environments. If for example LIF OH measurements were subjected to an offset problem, it would probably not impact the presented analysis of this paper, but if there was a problem associated with a sensitivity bias it certainly would. I am wondering whether this could explain some of the different trends shown in Fig. 4.

Ans: In our studies and the related paper we are analyzing data on the mean reaction rate between OH and isoprene $kij \cdot OH \cdot ISO$ and the potential deviation from mean conditions by fluctuations of mixing ratios of both compounds. If the fluctuations are correlated to a certain extent, the quantity $Is=(OH'ISO')\cdot(OH\cdot ISO)^{-1}$ describes the deviation from mean reaction conditions. The possible underestimation of modelled OH or related topics are, therefore, not of relevance to our study. But as mentioned by referee 1, Liu et al. (2018) found “no gap between modelled and observed OH in Amazonia within the experimental uncertainty”. Here it is important to note that these researchers did not measure OH directly but inferred OH from other measurements of VOC and NOx.

Therefore the paper by Liu et al. (2018), which is cited by the referee, cannot be used to draw conclusions about the agreement of modeled and measured OH. Liu et al. neither operate a model, nor do they carry out a model-measurement comparison. They show that OH inferred from VOC observations increases with NOy, which would be consistent with predictions by old (MCMv3.2) and new (MCMv3.3) mechanisms as well.

We find NOx<0.6 ppb on 22 November 2015 at the ATTO site. For such conditions Liu et al. (2018) inferred $\mathrm{OH} \approx 6 \cdot 10^5\ \mathrm{molecules\ cm^{-3}}$ which is comparable to OH ≈ 0.03 ppt for ATTO 2015 in Fig. S15 – Fig. S16. The total OH reactivity on this day is published by Pfannerstill at al. (2018) and is not only given by isoprene and its oxidation products which, combined, contribute 62 % ± 29 % of the total OH reactivity on this day. Kaser at al. (2013) found a smaller influence of different chemical recycling schemes on mean OH (an average over space and time) but published mean segregation intensity in the range 0.06<$|Is|$<0.15 with maxima up to abut $|Is|$≈0.3. Their mean reaction rates $\overline{\mathrm{R_{ij}}}$ become reduced by 6% up to 15% (and by about 30% at maximum $\mathrm{I_s}$).

Kaser et al. 2015 find that their OH observations tend to be higher than what they calculate by MCM v3.2 and that the implementation of isoprene RO2 recycling in their model and segregation can fill the gap between modelled and observed OH in their campaign. This is also consistent with the most recent isoprene chemical mechanism developments. However, even the most advanced chemical mechanisms cannot explain the high OH observations, which were reported, for example, in Lelieveld et al. (2008) or Hofzumahaus et al. (2009). I think, we need more research and this should include studying the role of segregation between biogenic VOCs and OH.

"Old" mechanisms (e.g. MCMv3.2 and earlier) predict significantly smaller OH concentrations in forest environments compared to "new" mechanisms, which contain additional OH recycling by isomerization of isoprene RO2, such as the MCMv3.3, the Caltech mechanism (Wennberg et al., 2018), or the modified isoprene mechanism proposed by Novelli et al. (ACP, 2020). As Novelli et al. point out, the implementation of the isomerization chemistry can lead locally to an OH enhancement of a factor of 3 at 20 pptv NO. However, if OH is also removed by other VOCs, or when recycling by reaction with NO becomes more relevant, the impact of the isoprene RO2 isomerization is getting smaller. It is essential to note that Kanaya et al. studied the OH measurements in ambient air outside of the chamber, which was the second part of the HOxComp campaign.

For additional information we give in a Supplement in Fig. S15 the OH mixing ratios for ATTO 2015 and ECHO 2003 as function of NOx and further relations in Fig. S16 – Fig. S17.

The way how OH measurements were performed is described in Section 2.2 and will be discussed in more detail in the revised version in this section 2.2 and in a Supplement. Here we will also refer to the background signal and the topic of an “offset problem”.

As mentioned above, despite the nice review article of Wennberg et al., 2018, there are still new findings emerging regarding the OH + isoprene chemistry. Novelli et al. (2020) concluded from their chamber measurements in Jülich: “It was found that the MCMv3.3.1 for isoprene degradation initiated by OH radicals is not able to reproduce the measured trace gas concentrations in the experiments despite the inclusion of the isomerization reaction for isoprene-RO2 following the LIM1 mechanism for NO mixing ratios <0.2 ppbv. Large discrepancies are observed, in particular for OH radicals, with a ratio of modelled to measured OH of 0.7±0.07and of almost a factor of 2 for the sum of MVK, MACR, and ISOPOOHs (all isomers)."

Anyhow, since 2010 we operate the ground based as well as the aircraft based instrument using a 'IPI' system for the chemwave technique (Hens et al. 2014 , Novelli et al. 2014, Mao et al. 2012) to remove ambient OH and to quantify the chemical OH background signal. We did compare our measurements using the IPI with the CIMS in Hyytiälä (Hens et al.) as well as with the CIMS on the Hohenpeissenberg (Novelli et al. 2014) and concluded that the usage of IPI does get our instrument into agreement with the CIMS instruments, which also use a OH scavenger to quantify the chemical OH background signal.

In the introduction we describe some results from literature on OH measurements and their comparison to modelling. We will refer to mean mixing ratios of OH (and NO_x) in section 1 and section 2 and in a Supplement (see Figs. S11 – S17) and also in the discussion and comparison of results from the field to results from modelling including the suggested literature.

One possibility for the discrepancy between measurements and modelled mean mixing ratios is the influence of segregation that we directly experimentally asses in this paper. Even if measured and modelled OH is said to be equal in any of the papers mentioned, their difference is in the range of ±20% to ±40% (and often a systematic deviation is given). Note that I_s influences the mean reaction rate; to what extent a mean mixing ratio is influenced can only be stated if the complete balances are considered.

But our studies on segregation were performed basically to find out a) if this phenomenon occurs in the atmosphere and b) which atmospheric processes may be related to I_s especially for OH + ISO.

Note that Liu et al. (2018) did not perform measurements of OH as discussed above. The results given by Kaser et al (2015) are compared to mean box calculations and allow I_S in a range up to about 15% (and even 30%) (see also above).

Here we discuss deviations from purely homogeneously mixed cases for a chemically reactive compound (isoprene) with OH, as derived from instrumental determination at that time and that specific location, and also compare to results from modelling. We only take published information. The deviation is given by the normalized covariance in Eq.1. To further illustrate our comparisons, we will compare I_s as function of height from different studies (experiments / models) in a Supplement and give a comparison with respect to the NO_x environmental mixing ratios (see our Figs S15 – S17 and Fig. S22).

In addition, we will give errors for the measured quantities in revised Figures in our paper (Fig 5, Fig.6, Fig.7), so that the reader can get information for ECHO 2003 and ATTO 2015. "Commenting on conclusions of the papers by Lin et al. and Kaser et al." will be given in section 1 in a way that we mention what is given in their publications and what is needed to draw a certain conclusion.

Rev: The derivation of some of the simplifications is poorly explained – eq. 19: why would only one triple term be important in the analysis here? RES, RE and REis are not well explained – I assume REis refers to term I in eq. 21. In general, I miss a thorough analysis of error propagation in context of the presented equations (e.g. eq 21). Many terms are dropped because they are supposedly small, yet the impact of the experimental limitations is not rationalized well in context of the variance budget of isoprene. I suspect that a significant amount of variance of isoprene might not be accounted for due to spectral attenuation. It also appears that the data availability is rather thin – I only count about 16 individual data points for the analysis presented in Fig3. Within the uncertainty of the analysis, I wonder whether this is enough to draw some of the presented conclusions after considering a thorough analysis of the propagation of errors (ie. systematic and random).

We will refine our explanations in the revised version. These are the data existing so far.
To our knowledge, there are not more data points available.

Ans: Eq. 19 has a sign error and, therefore also Fig. 5 – 7 have to be corrected. The correct Eq. 19 reads:

$$\mathrm{I_s} + \mathrm{CH_{is}} + \mathrm{nvar(ISO)_{is}} + \mathrm{RE_{is}} = 0$$

This revision of figures is given in the Appendix: „Revised Figures“. In addition term $\mathrm{RE_{is}}$ needs to be corrected in the revised version.

Errors (from „Error Propagation“) for $\mathrm{I_s}$ are given for ECHO 2003 and ATTO 2015 results in Figs. 5-7. Following the procedure which was described in Dlugi at al. (2010/ 2014).

Each data Point is for a 10 minute interval and describes one data point of $\mathrm{I_s}$ for this interval.

References:

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