

## Anonymous Referee 2

We thank the referee for their constructive comments which have helped to improve the manuscript.

**Reviewer comment 1:** I wonder why black carbon measurement was mentioned in this MS which was not used for analysis, and would suggest that the authors provide more discussion on VOCs speciation for OH reactivity closure purpose, e.g. key species that were not measured from previous studies;

Response: The reason why black carbon measurements are mentioned is because black carbon was used to identify the periods influenced by biomass burning as described in Sect. 2.7 and used in Sect. 3.3.4.

The key species not included in previous studies are discussed in Sect. 3.2.1. However, our analysis shows that there are not only few key species that mainly explain the previously missing fraction. Instead, it is rather the sum of many small contributions, in particular from OVOC. For a comprehensive overview of VOCs which were included in the previous study by Nölscher et al., we now added markers to these VOCs in Table S1. The following was added in Sect 3.2.1:

“As a comparison to a previous OH reactivity study at the ATTO site, the compounds included in Nölscher et al. (2016) were marked with a “\*” in Table S1.”

And

“Our analysis shows that the previously unattributed OH reactivity cannot be explained by few key species, but rather that a multitude of relatively small contributions, in particular from OVOC, explains the sum of OH reactivity. As illustrated in Fig. S4 and Table S1, no VOC exceeds an average OH reactivity of  $1 \text{ s}^{-1}$  except for isoprene, and its oxidation product measured on  $m/z = 71$  (MVK/MACR/ISOPOOH).”

**Reviewer comment 2:** I believe that the contribution of VOCs groups to total OH reactivity could be very different during normal condition (day and night), precipitation, or biomass burning events. The inter-comparison for major VOCs species attributing to OH reactivity would be important and useful;

Response: Thanks for this suggestion. Day and night differences in speciation were already analyzed in Sect. 3.2.3. However, in light of this comment we have now added an analysis of the biomass burning impact on OH reactivity speciation to Sect. 3.3.4. The following was added to Sect. 3.3.4.:

“The OH reactivity speciation differed between biomass burning and low or no biomass burning periods. Under biomass burning influence, the share of OVOCs in total OH reactivity increased on average by 8.1 %, while the isoprenoids fraction decreased by 3.5 %. Biomass burning is a well-known source of both aromatics and nitrogen-containing VOCs [1], which, however, both have low reaction frequencies with OH. Therefore, the OH reactivity fraction of aromatics and nitrogen-containing VOCs increased by only on average 0.05 % and 0.03 %, respectively. “

We were hesitant with showing comparisons of the speciation associated with rain events to “normal” periods because the rain-associated behavior of VOCs is relatively complicated with sharp increases at the beginning of a rain event followed by strong decreases, as shown in Fig. 9 (Fig. 8 in

the previous version of the manuscript). The behavior of OVOCs is discussed in Sect. 3.3.3., with a significant decrease in OVOCs following the rain. However, we now also include the influence of rain events on monoterpenes and isoprene. The following was added to Sect. 3.3.3.:

“When averages of daytime periods without rain are compared to periods associated with daytime rain events, OH reactivity attributed to isoprene and monoterpenes decreased from  $36 \pm 19\%$  and  $6 \pm 4\%$  of the total, respectively, to  $32 \pm 18\%$  and  $3 \pm 1\%$ , respectively (Table S2). This can be attributed to the lower irradiation and temperature during rainy periods, which leads to lower primary BVOC emissions from plants. “

The following table was added to the supplement as Table S2:

OH reactivity contributed by	Rain (daytime, n= 18, $\pm$ standard deviation)	Dry (daytime, n=81, $\pm$ standard deviation)
Isoprene	$32 \pm 18\%$	$36 \pm 19\%$
Monoterpenes	$3 \pm 1\%$	$6 \pm 4\%$
OVOC	$16 \pm 6\%$	$22 \pm 10\%$
GLV	$6 \pm 2\%$	$9 \pm 4\%$
SQT	$1 \pm 0.3\%$	$1 \pm 0.9\%$
Inorganics	$3 \pm 0.1\%$	$3 \pm 0.1\%$
Others	0 %	0 %
Unattributed fraction	$39 \pm 19\%$	$23 \pm 25\%$

**Reviewer comment 3:** The major concern was the main parameters influencing OH reactivity and the approach to quantify the parameters. The MS did not provide explanation why OH reactivity varied with precipitation process, and I wonder why authors use only temperature to parameterize OH reactivity from biogenic emissions, fig 6 showed clearly the regressions were not linear for temperature, and MEGEN model quantified already the role of temperature and PAR in VOCs emissions.

Response:

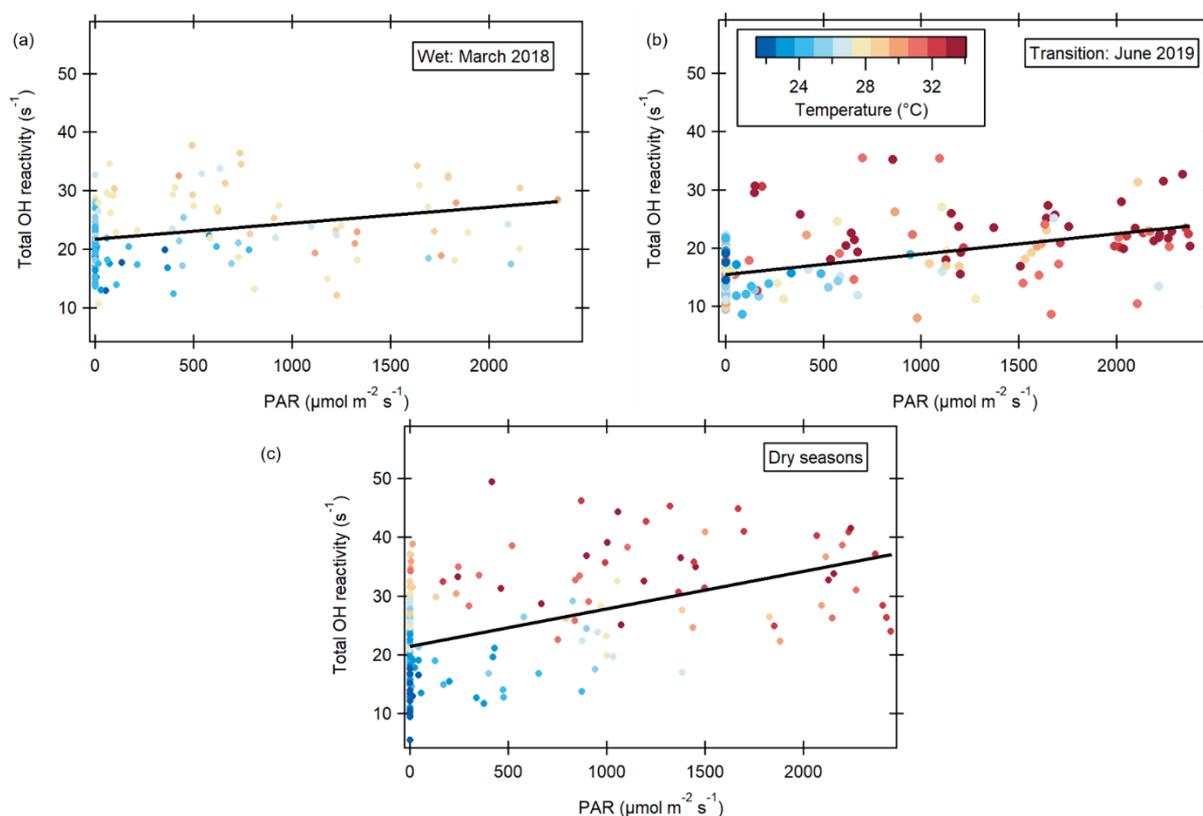
Thanks for this comment. It is true that it is difficult to disentangle PAR and temperature impacts on OH reactivity from one another. The best graphical solution to this problem we found was to also show OH reactivity vs. PAR plots, now in Fig. S5. These illustrate that the correlation of OH reactivity with PAR is weaker than with temperature, and that there is a large range of OH reactivity at PAR=0. We have three reasons to use temperature rather than PAR to parameterize OH reactivity: 1) There is a nighttime temperature dependence of OH reactivity (i.e. see datapoints with PAR = 0) which we could not explain by using a PAR-dependent parameterization. We added plots of OH reactivity vs PAR to the supplement for illustration of the large OH reactivity range at PAR = 0. The correlation of OH reactivity with temperature is, as the comparison with Fig. 7 shows, better than its correlation with PAR. 2) Temperature is, during daytime, strongly influenced by PAR and therefore should be a proxy for it. Thus, we assume that PAR influences on OH reactant levels at the ATTO tower will be sufficiently captured by using a temperature-dependent parameterization. 3) The parameterization

here is not intended to describe emissions, because OH reactivity is a result of VOC concentration levels. It is intended to allow comparison of model generated data with this measurement dataset. Just like the VOC concentrations and not the VOC emission fluxes, OH reactivity follows the diel pattern of temperature, not PAR, in the rainforest, as it is broadened towards the evening [2,3].

The parameterization suggested in our manuscript is by no means intended to replace emission models such as MEGAN. We intended this parameterization as an offer to modelers to compare their results with OH reactivity.

Regarding the rain influence, the wet and transition data show that despite the relatively regular occurrence of rain events, the correlation between OH reactivity and temperature remained strong. This may be because the effect of rain on OH reactivity was very variable as discussed above. The potential reasons for the observed influence of precipitation on OH reactivity was discussed in Sect. 3.3.3. The main effects were suggested to be changes in upwards transport of VOCs due to the convective nature of these events, and a suppression of plant emissions with decreased irradiation and temperature.

We rephrased L. 433ff as following: “As illustrated in Fig. S5 and by the color scaling in Fig. 7, higher temperature and OH reactivity often co-occurred with higher PAR because temperature is driven by PAR at daytime. PAR is a driver of reactive emissions in the rainforest (Kuhn et al., 2004a; Jardine et al., 2015). However, there is a PAR-independent temperature dependence visible at PAR = 0, i.e. during the night, and the correlation of OH reactivity with PAR was weaker than with temperature (Fig. 7, Fig. S5). This is why we chose to parameterize OH reactivity based on temperature rather than PAR. Air temperature can serve as a proxy for the combined effects of direct light- and temperature-dependent emission as well as transport, which all influence observed total OH reactivity. Thus, in this simplistic approach, we assume that any PAR- and transport-related influences on OH reactant levels at the ATTO tower will be captured indirectly by using a temperature-dependent parameterization. The relationship is not intended to be used as an emission algorithm but to facilitate comparison with model generated results. “



**Figure S1.** Hourly averages of total OH reactivity at 80 m a. g. l. at the ATTO tower as a function of photosynthetically active radiation (PAR). Temperature color scale shown in (b) for all panels. (a) Wet season (March 2018), fit function:  $R = 21.7 - 0.003 \cdot [\text{PAR}]$ ,  $r^2 = 0.08$  (b) Transition season (June 2019), fit function:  $R = 15.4 - 0.004 \cdot [\text{PAR}]$ ,  $r^2 = 0.27$  (c) Dry seasons (October 2018 and September 2019), fit equation:  $R = 21.4 - 0.006 \cdot [\text{PAR}]$ ,  $r^2 = 0.27$ .

## References

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