

## **Responses to Round 2 of Review for Hodzic et al. ACPD**

The authors have done considerably work to address the points raised in review, substantially improving the manuscript. A few points remain to be addressed prior to publication:

We thank the reviewer for the appreciation of the work that went into the previous revision. We have modified the manuscript further to address these additional comments.

R2.1. A2.3: A likely explanation for the overestimate of POA in models (when treated as NV) is that emissions of POA were likely overestimated (i.e. SV emissions reported as POA when estimated under high loading conditions, Robinson et al., 2007), so one possible solution for these models is the need to re-balance this (downgrade POA emissions, increase SV SOA sources). It would be nice to see this history (i.e. the incorrect assumption that emissions were all NV) acknowledged in Section 4.4.

We have modified the text in L806 to read:

*“These seasonal differences suggest that model errors could be partially due to inefficient production of SOA and/or too high POA emissions, although removal errors also probably play a major role (see next section).”*

R2.2. A2.5: The updated tables are clearer, but given that these appear in SI, I suggest that the authors include in the text either the standard deviation or range of values averaged to obtain 1.5 and 1.48 in lines 1950 and 1952.

Neither the manuscript (ending in L1713) nor the SI (ending in L147) have lines 1950 or 1952. Perhaps the reviewer is referring to lines in the posted response to R2, but that file does not have line numbers. In any case, the only mention of “1.48” is on L422, while 1.5 is mentioned two lines before in L420. Therefore we assume the reviewer is referring to that section of the text, which already contains a discussion of the range of ratios shown in the table (L422): *“Mobile source measurements in general exhibit lower ratios (POA/OA ratio 0.5-1.5) while COA determination typically ranges from 2 to 3.”*

For the sake of clarity, we have modified this text to include the standard deviations and modes, and rephrased the last sentence to make the ranges we are discussing more apparent:

*“Based on Table S1 data, we assume POA to be co-emitted with BC for anthropogenic fossil fuel / urban region POA (herein called FFRatio for simplicity, even though much of it is non-fossil, Zotter et al., 2014; Hayes et al., 2015) at a ratio of  $1.5 \pm 0.82$  (average  $\pm 1\sigma$  of all*

*urban ambient air studies that report POA and BC for best intercomparability to the ATom dataset; including all urban studies results in a very similar number,  $1.48 \pm 0.65$ , median: 1.41). Measurements where mobile sources are the main contributor in general exhibit lower ratios (POA/OA ratio 0.5-1.5), while studies with strong COA contributions typically ranges from 2 to 3.”*

R2.3. A2.5: It remains unclear exactly how equation 1 was applied to the data. I believe that the authors applied the average POA/BC EFs that were discussed in Section 3.2 to ALL data, but the text “an emission ratio appropriate to the airmass origin..” on L2301 seems to suggest that there is some sort of back trajectory to identify the origin of air masses applied to determine the EF. Please clarify this process in the text.

Line 370 of the revised manuscript reads: *“For a particular airmass, the mass fraction of biomass burning (BB) aerosol reported by the PALMS instrument  $f(BB)_{PALMS}$  (Thompson and Murphy, 2000; Froyd et al., 2019) was then used to evaluate the degree of BB influence.”*

And then again when stating Eq (1) (Line 440):

*“The PALMS determined mass fraction of biomass impacted aerosol  $f(BB)_{PALMS}$  can then be used to determine a total POA contribution from both types of sources”*

They both make clear that  $f(BB)_{PALMS}$  is used as a proxy for airmass origin. Furthermore, the sentence that the reviewer refers to (L761, not L2301) states this again:

*“POA concentrations were estimated from the BC measurements by using an emission ratio appropriate to the airmass origin (biomass burning vs. anthropogenic), and using the  $f(BB)$  mass fraction from the PALMS single particle instrument (see Section 3.2).”*

We have modified the last sentence to make this clearer:

*“POA concentrations were estimated from the BC measurements by using an emission ratio appropriate to the airmass origin (biomass burning vs. anthropogenic), as quantified by the  $f(BB)$  mass fraction from the PALMS single particle instrument (see Section 3.2), with  $f(BB)=1$  taken as a BC and OA being of pure BB airmass origin and  $f(BB)=0$  exclusively from a non-biomass burning source.”*

R2.4. A2.5: The authors state that they could not perform a similar analysis on model output to test the approach of equation 1 because they do not have model output for BC from various emission sectors – I presume that what they mean here is that they would need  $f(BB)$  from the

model. It seems that the authors could have chosen to output this information as part of the SV-POA simulation that they performed during the review process. Given that the authors have not verified their method with model data, they should explicitly acknowledge that the validity of their analysis approach has not been tested with simulated data, and that future work should verify this approach.

The suggested simulation is of interest, but would have required much additional work as one (or several) new BC species would have to be added to the model and modified in multiple locations (emissions, transport, convection, wet and dry deposition etc.). And emission fields would have to be broken down by source. The model would then have to be tested to gain confidence on the simulation and make sure errors were not introduced from the extensive code modifications. Therefore this is a considerable amount of work, that would be justified for a manuscript on source apportionment of BC, but not for the revision of an OA manuscript that already includes extensive experimental data and output from many models. On the other hand, running a case with another standard GEOS-Chem configuration (as for the SV-POA case) was straightforward as it only required changing the model configuration and input files.

In addition, the models have a more accurate internal method to track POA and SOA by applying mass conservation within the model. The measurement-based estimate is well-supported in the revised manuscript, including extensive sensitivity studies, which shows that its conclusions are robust against the uncertainties. It does not seem necessary (or too useful) to us to simulate the measurement-based method with a model. Therefore we refrain from recommending this research.

R2.5. A2.6: The authors have not sufficiently described the inorganic aerosol simulations in the model description section (2.1), including a description of relevant thermodynamic schemes (highlighting which models did not include nitrate and ammonium) and emissions input and schemes (i.e. sea salt and dust). Without such a description, the results of Section 4.6 should not be included as the reader has not been provided sufficient basis for assessing these schemes.

References have already been provided that describe each of the models in section 2.1. We have also indicated which inorganic species are included in each model, and it is clear whether a specific model has nitrates. There is still high value in including an overall comparison including all the species for reference, even if the details of their simulation in all the models cannot be described in great detail, as this provides important context for the relative importance of OA (the main topic of this paper) and other species, and the fact that there is high variability in the simulations of other components as well. The following text provides key references for an interested reader:

*“Specific studies have discussed and continue to investigate the A<sub>Tom</sub> measurements and simulations of different components in more detail, including particle number (Williamson et al., 2019), black carbon (Katich et al., 2018; Ditas et al., 2019), MSA (Hodshire et al., 2019), sulfate-nitrate-ammonium (Nault et al., 2019), and sea salt (Yu et al., 2019; Bian et al., 2019; Murphy et al., 2019).”*

R2.6. A2.16: Are the authors suggesting that the spatial distribution and observed OA magnitudes are the same between A<sub>Tom</sub>-1 and A<sub>Tom</sub>-2?? Visual inspection of Figure 2 and S1 suggest that these are quite different, and thus the original review comment that Figure S1 should be included in the main text should be re-considered.

There are many similarities between the spatial distributions, e.g. a clean Southern hemisphere, high concentrations in the lower equatorial Atlantic, more pollution in the Northern hemisphere etc. Of course there are also some differences. However the data are already shown in the paper in arguably more useful ways (Fig. 2b, 2e, and 4) and Fig. S1 is easily accessible for anyone interested. We therefore prefer to keep Fig. S1 in the supplementary information.

R2.7. A2.13: Could the authors explain the logic of why photolytic removal is not included for isoprene-SOA in the text?

For isoprene SOA formed through explicit chemistry and heterogeneous uptake in aqueous aerosols, we follow the implementation of Marais et al. (2016) in GEOS-chem, where the photolytic removal is not included. Further research is needed to quantify how efficient photolytic removal for these isoprene SOA species is. This is now mentioned in the revised manuscript:

*“As in Hodzic et al. (2016) the GC12-DYN model version includes updated VBS SOA parameterization, updated dry and wet removal of organic vapors, and photolytic removal of SOA (except for isoprene-SOA that is formed in aqueous aerosols, where we follow Marais et al. 2016).”*

R2.8. A2.21: the text “correlates quite well with other gas-phase BB tracers” is not justified in the current manuscript. Please provide plots for the SI, or a reference that shows this (or remove this statement).

A comprehensive description of f(BB) is currently under review on a separate manuscript (in which the main authors of this paper are not coauthors), so we cannot include it here. In lieu of it, we have added the following plots to the SI that shows the correlation:

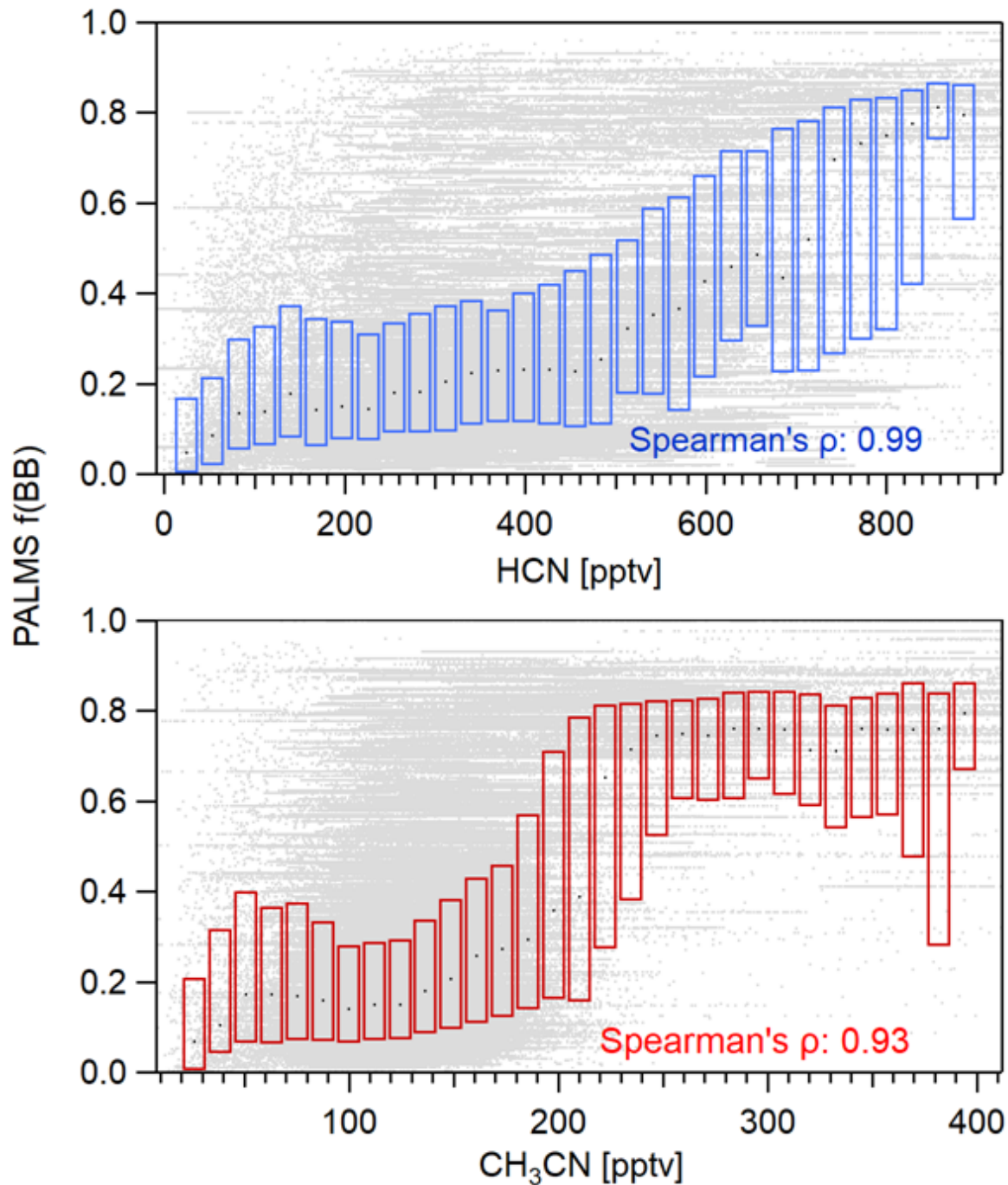


Figure S20: Correlation of  $f(\text{BB})$  from the PALMS instrument with colocated, well characterized gas phase tracers for BB for the full ATom mission (1-4). HCN (top panel) provided by the Caltech CIMS instrument, CH<sub>3</sub>CN (bottom panel) provided by the NCAR TOGA GC-IE instrument (Wofsy et al, 2018).

We are also referring to this Figure now when discussing  $f(\text{BB})_{\text{PALMS}}$  (Line 371):

*“This parameter correlates well with other gas-phase BB tracers (Figure S20), and is more useful as a particle tracer since its lifetime follows that of the particles.”*

R2.9. Line 1934: “documented later” suggests observational confirmation, whereas the POA estimate here is a derived quantity with substantial uncertainties. Recommend this language be modified to “suggested by later analysis..”

Again L1934 does not exist in the manuscript. Those words do appear in L404. We respectfully disagree with the reviewer, and have shown that the low POA is strongly supported by the evidence, as documented extensively in the previous round of responses and the revised manuscript. Therefore we prefer to keep this text as it is.

R2.10. Line 1965: Please discuss in the text how the new numbers from Andreae 2019 compares to other numbers from literature shown in Table S1.

Table S1 only includes urban-focused studies. While three of these did include BB sources (and are listed as such in the table), we see no value in comparing this very small subsample with a review that includes these 3 studies and about 200 more. Especially since, as mentioned in the paper text and illustrated in Figures S9 and S19, the exact value of  $BB_{ratio}$  has virtually no impact on the conclusions of our analysis over the range of values reported in Andreae 2019 (which again, includes the studies in Table S1).

Moreover, we do compare Andreae 2019 with the model emission inventories (Table S2), which in our view is the relevant comparison (L447):

*“On the other hand, for biomass burning, the emission inventories ratios range from ~5 for crop, to ~15 for forest, and up to ~50 for peatland. While generally consistent with the values discussed by Andreae (2019), they are on the lower end of the ranges discussed in that work. The averages and ranges of the measurement and model ratios are similar, and thus no significant model bias on the ratios is apparent”*

Therefore we prefer to keep this text as it is and not discuss Table S1 further.