

Atmos. Chem. Phys. Discuss., author comment AC2  
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## Reply on RC2

Varun Kumar et al.

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Author comment on "Highly time-resolved chemical speciation and source apportionment of organic aerosol components in Delhi, India, using extractive electrospray ionization mass spectrometry" by Varun Kumar et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1033-AC2>, 2022

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## Response to RC2

We thank the reviewer for the helpful comments. Below we provide a detailed point-by-point response to the issues raised by the reviewer. Reviewer comments are provided in *italics* and our responses follow in normal text. Changes to the manuscript are denoted in blue font.

### Comment #1

*Page 8, L25: what is the reason behind removing signals related to CO<sub>2</sub><sup>+</sup>, rather than down-weighting them?*

In standard AMS data analysis, O<sup>+</sup>, HO<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, and CO<sup>+</sup> are not directly measured but are instead calculated as constant fractions of the CO<sub>2</sub><sup>+</sup> signal. This must be accounted for in PMF to avoid overweighting the CO<sub>2</sub><sup>+</sup> variable. Two approaches are possible: (1) downweighting (by increasing the uncertainties) or (2) removing the variables and reinserting them afterwards. The two approaches are nearly equivalent, but may differ in some datasets due to the combination of the requirement of a minimum error for the AMS coupled with the dynamic downweighting routine applied to outliers in the "robust mode" of the PMF. This can lead to small differences in the effective signal/uncertainty ratios between CO<sub>2</sub><sup>+</sup> and its dependent ions, leading in turn to perturbations of these ratios in the output factors. As this is inconsistent with the basic data-processing assumptions for the CO<sub>2</sub><sup>+</sup>-dependent ions, it should be avoided. Although it does not affect all data points, or even all datasets, there is the potential for this problem to occur when the CO<sub>2</sub><sup>+</sup> ions are retained for PMF. However, the remove-and-reinsert approach employed here is always safe, and thus preferred.

This is clarified in the text as follows (Page 9, Line 2):

"Note that this remove-and-reinsert strategy is preferable to downweighting of CO<sub>2</sub><sup>+</sup>-dependent ions as it avoids the potential for small biases induced by the combination of AMS minimum errors and dynamic downweighting in "robust mode" operation of the PMF."

## **Comment #2**

*When taking the HOA profile from the 8-factor solution set, do you mean you used SoFi to constrain the HOA factor? Similarly, on page 9, L 25, do you mean SoFi was used? It may be better to directly mention SoFi in these instances as well.*

We thank the reviewer for this comment. We have made following changes in the text:

(Page 9, line 13): "To get a cleaner HOA profile, we took the HOA factor profile from an unconstrained 8-factor solution and used it in SoFi to constrain the HOA factor in the final 5-factor solution"

(Page 10, line 4): "The reference profiles used in SoFi for these 5 factors were taken from the unconstrained 10-factor solution."

## **Comment #3**

*Page 9, L26: how do we know the 5 factors from the 10-factor solution set were not mixed and reasonable to be assumed as pure reference profiles?*

The 5 factor profiles obtained from a 10-factor solution were obtained from the PMF model. Increasing the number of factors from 10 to 15 did not lead to further changes in the profiles of these 5 factors. This suggests that these factor profiles are robust and unmixed, at least in a mathematical sense. In the absence of evidence to the contrary or pre-existing reference profiles for the relevant sources/processes, these can be taken as stable profiles which are logical to assess for environmental interpretability. As discussed elsewhere in the text, these factors do prove interpretable, and are while perhaps not completely free from mixing, provide our best estimate of the clean source profiles. Note also that the bootstrap/a-value analysis implies that the profiles from the 10-factor solution are only a starting point, with further adaptation permitted.

## **Comment #4**

*Page 11, L7: Equation 7 does not assume that activity coefficient is 1. Do you mean in your calculation of  $C^*$ , you assumed it's one?*

Yes, we assumed it one. We have added this in the manuscript (Page 11, line 25):

"The activity coefficient was assumed to be 1"

## **Comment #5**

*Figure S2 and page 16, L 4-5: Not having worked with EESI-ToF, I'm not sure how much fragmentation one gets. My understanding has been that it's a pretty soft ionization technique. If that's the case, I don't know how to interpret seeing signal at similar ions for both aromatic and biogenic SOA. To reconcile this, do you mean that the common signals are due to fragmentation?*

Since EESI-TOF cannot distinguish between structural isomers, we believe that common ions found in aromatic and biogenic SOA spectrum are actually isomeric compounds originating from different processes/ oxidation of different precursor VOCs. For example, Wang et al. (2021) showed substantial overlap in the molecular formulae between OH

oxidation products of cresol (presumably from ring-opening reactions) and limonene. Similar results have been observed or inferred in other studies (Mehra et al., 2020; Stefenelli et al., 2019).

#### **Comment #6**

*Page 16, L 28: My first thought after reading that BSOA was high at night was that it's NO<sub>3</sub>-driven SOA. Later on, you mention that because of the high NO levels in Delhi you don't expect much of NO<sub>3</sub> formation. Are NO levels so high that they titrate O<sub>3</sub> completely such that NO<sub>2</sub> conversion to NO<sub>3</sub> is not possible? Even if that's the case, I think the potential for NO<sub>3</sub>+BVOC oxidation at night should be mentioned here.*

Our investigations suggest that the diurnal cycle for N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> in Delhi differs from many less-polluted urban areas, as discussed in detail in another study based on this campaign (Haslett et al., submitted). Because of very high levels of NO (□200-300 ppbv) in Delhi, the NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> formation is suppressed in the boundary layer during the night-time. As a result, the concentrations of N<sub>2</sub>O<sub>5</sub> during the night are substantially lower than in many other urban centres, while the highest concentrations are during the day. If night-time NO levels are considerably reduced, it can have substantial impacts on the production of night-time SOA. Following the reviewer's suggestion we have modified the text as follows (Page 17, line 6):

"Biogenic VOCs such as monoterpenes and isoprene are susceptible to oxidation by NO<sub>3</sub> radicals which can result in large amounts of biogenic SOA production. In Delhi, however, due to large concentrations of NO (□200-300 ppbv) during the night-time, the production of NO<sub>3</sub> radicals is suppressed and the diurnal cycle of NO<sub>3</sub> is actually inverted with the majority of available NO<sub>3</sub> radicals actually present during the daytime (Haslett et al., submitted)"

#### **Comment #7**

*Page 18, L 17: it is not clear to me what you mean by GBRP-based sensitivities in a relative sense. Please explain more.*

The GBRP-based sensitivities denote sensitivities estimated from the GBRP model, which are normalized to GBRP-based sensitivities calculated for the biomass burning factor. Specifically, the EESI-TOF response factor for biomass burning was calculated by taking the ratio of the summed EESI signal in primary biomass burning to the summed AMS BBOA factors. This was then used to scale the sensitivities of the SOA factors obtained using the GBRP model. We have added the following text to the manuscript (page 18, line 38):

"The GBRP model results were used in relative terms, where the response factors obtained for each EESI-TOF factors using the GBRP model were normalized relative to that of primary biomass burning. The EESI-TOF response factor for biomass burning was calculated by taking the ratio of the summed EESI signal in primary biomass burning to the summed AMS BBOA factors. This was then used to scale the sensitivities of the SOA factors obtained using the GBRP model."

#### **Comment #8**

*Page 18, L 31: case 1 still excludes the data from Jan 3-4, right? If so please indicate that clearly here too.*

Yes, the data from 18:00 LT on 3 January till 12:00 LT on 4 January were excluded. We have modified the text to state this clearly (page 19, line 14):

“Based on the issues mentioned above, the time series was divided into two parts: i.e., part-1 from 31 December 2018 - 3 January 2019 (till 18:00 LT) and part-2 from 4 January 2019 (from 12:00 LT) -13January 2019. The data from 18:00 LT on 3January 2019 to 12:00 LT on 4 January 2019 were omitted.”

### **Editorial:**

#### **Comment #9**

*Page 5, L2: do you mean PM10 and PM2.5, separately rather than respectively?*

We thank the reviewer for pointing this out. We indeed intended to mean “separately” here. We have now changed the text (Page 5, Line 9):

“to measure the mass of 35 different elements in PM<sub>10</sub> and PM<sub>2.5</sub>, separately (Rai et al., 2020).”

#### **Comment #10**

*Page 11, L34: Please change to C<sub>x</sub>H<sub>y</sub><sup>+</sup>. Similarly, Page 13, L 11, please change to SO<sub>4</sub><sup>2-</sup> and on Page 18, L 14, change to C<sub>x</sub>H<sub>y</sub>O<sub>z</sub><sup>+</sup>*

We thank the reviewer for the suggestions. We have now corrected the text.

Page 12, Line 16: C<sub>x</sub>H<sub>y</sub> has been changed to C<sub>x</sub>H<sub>y</sub><sup>+</sup>

Page 13, Line 30: SO<sub>4</sub> has been changed to SO<sub>4</sub><sup>2-</sup>

Page 19, Line 23: C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> has been changed to C<sub>x</sub>H<sub>y</sub>O<sub>z</sub><sup>+</sup>

#### **Comment #11**

*Figure S1: Consider changing SVOOA to LO-OOA to be consistent with other parts of the paper*

We thank the reviewer for the suggestion. We have changed SVOOA to LO-OOA in all parts of the manuscript

#### **Comment #12**

*Page 19, L 34: For completeness, please define ROS*

We thank the reviewer for the suggestion. We have defined ROS in the modified text (Page 20, Line 21):

"It has been recently shown that oxygenated OA contributes a significantly higher fraction of particle bound-reactive oxygen species (ROS) (Zhou et al., 2019) as compared to primary OA"

### **Comment #13**

*Page 21, Line 5: Either change to "...enabled apportioning the ...." Or "...enabled apportionment of the ...."*

We thank the reviewer for the suggestion. We have modified the text (Page 21, Line 30):

"enabled apportioning the"

### **Comment #14**

*Figure 5. Figure caption indicates colors of the background that are different than the real colors for secondary and primary factors.*

We thank the reviewer for pointing this out. We have changed the caption of Fig. 5 to indicate accurate colors of the background shading

"For the ease of viewing, background shading denotes SOA (pink) and POA (blue) factors"

## **References**

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Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2021-1033/acp-2021-1033-AC2-supplement.pdf>