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## Reply on RC1

Sanna Saarikoski et al.

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Author comment on "Sources of black carbon at residential and traffic environments obtained by two source apportionment methods" by Sanna Saarikoski et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-231-AC1>, 2021

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### Referee #1

We thank Referee #1 for her/his elaborate and valuable comments. We have responded to all the comments below and the changes to the manuscript have been made in "track changes" mode.

### Specific comments

- Line 168: Why apply a CE of 1 on both datasets? Could more details about NR-PM<sub>1</sub> and rBC quantification be provided (e.g RIE might affect the contribution of rBC reported in Table S1 and S2)? Was the SP-AMS run purely in dual mode?

**Reply:** The quantification of BC by the SP-AMS was not the focus of this study since the results of PMF don't depend on the exact concentrations in general. Therefore, the results reported in this paper were calculated with a constant CE value of 1. However, for the calculation the coating factor, the accuracy of AMS concentrations is more important. Therefore, we have added to supplemental material a comparison of the sum of the SP-AMS species (excluding rBC) and BC from the aethalometer with the concurrent PM<sub>1</sub> measurements (Grimm model EDM 180, Grimm Aerosol Technik, Ainring, Germany) (residential site). The sum of the SP-AMS species and AE33 BC made on average 71% of Grimm PM<sub>1</sub> with a moderate correlation (Pearson's correlation coefficient  $r = 0.888$ ; Fig. S4a). Similar comparison was done also by using the composition dependent CE (CDCE) calculated according to Middlebrook et al. (2012). With the CDCE, the sum of the SP-AMS species and AE33 BC was closer to PM<sub>1</sub> from Grimm (~85% of PM<sub>1</sub>), however, the correlation was slightly poorer ( $r = 0.876$ ; Fig. S4b). For the street canyon, the PM<sub>1</sub> comparison could not be calculated as there was no PM<sub>1</sub> mass measurement at that time. Based on these calculations, CE value of 1 was not changed, however, the discussion on the uncertainty in the coating factor due to the CE = 1 was added to Chapter 3.3. Also a paragraph discussing the PM<sub>1</sub> and CE comparisons was added. The time series of CDCE values at the residential and street canyon sites were added to supplemental material (Fig. S4 and S5).

As suggested by the Referee, the comparison of rBC from the SP-AMS with BC from AE33 have also been added to the supplemental material (Fig S3). It shows that at the residential site the SP-AMS gave roughly half of AE33-BC (48 %) with a strong correlation ( $r = 0.961$ ). At the street canyon, the correlation was poorer ( $r = 0.539$ ), however, the

difference between rBC from the SP-AMS and AE33-BC was smaller (rBC 65 % of BC).

SP-AMS run purely in dual mode.

Additional correction was that the relative ionization efficiency for rBC was changed from 0.1 to 0.05 after the original rBC calibration data was inspected again in detail.

#### Reference

Middlebrook, A. M., Bahreini, R., Jiménez, J. L., and Canagaratna, M. R.: Evaluation of composition-dependent collection efficiencies for the Aerodyne aerosol mass spectrometer using field data, *Aerosol Sci. Technol.* 46, 258–271, 2012.

- Could comparisons between rBC from SP-AMS and eBC from AE33 and MAAP be added to the supplement? Could discrepancies between rBC and eBC and, later on,  $BC_{ff}/BC_{wb}$  and  $BC_{HOA} / BC_{BBOA}$ , be explained by either a low CE of rBC due to poor particle/laser beam alignment and/or the fact that the smaller fraction of BC (< 70nm) is not detected by the SP-AMS?

**Reply:** We believe that the discrepancies between BC detected by the SP-AMS and BC from the AE33 are mostly due to the poor laser alignment and therefore incorrect BC RIE calibration with Regal black. Also, the difference between SP-AMS and AE33 results can be due to the size limit of the aerodynamic lens that misses the smallest fraction of BC in the SP-AMS. That can be specially seen at the street canyon site that has the smallest BC particles and a large difference between  $BC_{HOA}$  and  $BC_{ff}$  (Fig. S39). Its impact of imperfect laser alignment on BC RIE is discussed in detail in Referee #2 comment 3).

The comparison between rBC from the SP-AMS and BC from the AE33 have been added to supplemental material (Fig S3). MAAP measured only at the background site in Luukki that had no other BC instrument running at the same time.

- References regarding the coating factor calculation are missing as well as the assumptions behind this estimation and their potential impacts on your results should be discussed. Statistics about the SP-AMS and AE33 concentrations in the supplement could be useful alongside NR-PM<sub>1</sub> diurnal variations.

**Reply:** Coating factor was calculated similar to Drinovec et al. (2017) and the reference has been added. Coating factor was calculated by summing all the SP-AMS inorganic and organic species (excluding rBC) and dividing it by BC from the AE33. The assumptions in the coating factor calculations were: (1) CE of 1 for the AMS species, (2) default RIE for organics and inorganic species and (3) similar particle size for the AMS species and BC from the AE33. We can estimate that the uncertainty for CE=1 is 30% and RIE for the each AMS species is 20%. Based on these uncertainties, the total uncertainty due to CE and RIE was ~40 %. The uncertainty due to the different particle sizes of the SP-AMS and AE33 is difficult to estimate quantitatively. Qualitatively, we can assume that the AMS is missing particle mass below <50 nm and therefore the coating factor can be slightly underestimated. The discussion on the uncertainties in the coating factor has been added to manuscript. The comparisons of SP-AMS results with AE33 and PM<sub>1</sub> from Grimm have been added to supplemental material (Figs S3-S4) and discussed in text.

- Any reason for using only  $C_2^+$ ,  $C_3^+$  and  $C_4^+$ ?

**Reply:** The reason for using only  $C_2^+$ ,  $C_3^+$  and  $C_4^+$  was that the signal was close to the detection limits for the larger carbon fragments due to relatively poor laser alignment and small rBC concentrations at the sites.  $C^+$  was excluded because it can have a significant contribution from organics.

We added to manuscript: "For the larger carbon fragments, the signal was close to the detection limit, and therefore, they were not included in the PMF analysis."

- Lines 279-283: "At the residential site, the contribution of rBC was largest to the mass spectra of BBOA in three and four factor solution while in five factor solution the contribution of rBC was largest for LV-OOA. At the street canyon, the contribution of rBC was largest to HOA independent of the number of factors. The contribution of rBC to HOA was more than double at the street canyon compared to that at the residential site. In contrast, the mass spectra of BBOA had several times more rBC at the residential site than at the street canyon." Why such contrast in rBC contributions from 4 to 5 factors at the residential site? Also, the  $f_{C_{2H_{4}O_2}}$  associated with the two BBOAs differs between the two sites, could it imply that one of the BBOA is more aged and harder to separate from other SOA?

**Reply:** A large contrast in rBC contributions from 4 to 5 factors at the residential site can be explained by the splitting of OOA factors when changing from 4 to 5 factors. Moving from 4 to 5 factors, the rBC contribution in HOA increased slightly and BBOA decreased but those changes were not large. In terms of OOA factors, rBC seemed to be divided differently between OOA factors when changed from 4 to 5 factors as rBC contribution decreased in SV-OOA, increased significantly in LV-OOA and was small in the new factor LV-OOA-LRT. In total, the rBC contribution in OOAs was 0.040 in 5 factor solution that was larger contribution than in OOAs in 4 factor solution (0.029) or LV-OOA in 3 factor solution (0.011) showing that the rBC contribution increased in OOA factors when the number of factors increased.

The Referee is right that the composition of BBOA in terms of  $f_{C_{2H_{4}O_2}}$  differs at the sites, which could be due to the fact that BBOA detected at the street canyon is more aged than at the residential site as it is probably transported further away. Therefore its mass spectra resembles more SOA mass spectra.

We have added to manuscript text: "Also the mass spectra of organics in BBOA differed between the residential and street canyon sites as the contribution of  $C_2H_4O_2^+$  (at m/z 60) and  $C_3H_5O_2^+$  (at m/z 73) was much larger at the residential site compared to the contribution at the street canyon indicating that BBOA at the street canyon site was probably more aged with its mass spectra resembling SOA. That can make the separation of primary and secondary OA factors more complicated at the street canyon site."

- Line 469-470: "This suggests that  $BC_{LV-OOA}$  was clearly associated with non-local sources." Can BC size distribution alone lead to such a conclusion? Couldn't SOA be formed by fast processing of locally emitted particles (e.g  $BC_{HOA}$  at 100-150nm)?

**Reply:** That is a good statement. BC size distributions can give some clue regarding the source, but for example in terms of SOA, the size distributions do not give that much information on the original source. It is possible that BC at larger sizes was also related to SOA particles, however, the measurement period was conducted in autumn when the SOA formation in Finland is minor due to low UV radiation and small concentrations of SOA precursors.

Changes to the manuscript: "clearly" changed to "possibly"

- It could be interesting to report the average angstrom exponent when BBOA or HOA dominated periods at both sites.

**Reply:** Calculating average angstrom exponent for  $BC_{BBOA}$  and  $BC_{HOA}$  dominating periods is a good idea and those values were calculated as suggested by the Referee.

Added to manuscript: "Those cases corresponded to large  $BC_{BBOA}$  fraction as the  $\alpha$  values calculated specifically for the periods dominated by  $BC_{BBOA}$  or  $BC_{HOA}$  (>50 % of  $BC_{BBOA}$  or  $BC_{HOA}$ ) were 1.36 and 1.25 at the residential site and 1.24 and 1.12 at the street canyon, respectively."

- Line 511-513: "Biomass burning BC obtained from two source apportionment methods followed very similar time trend, however,  $BC_{wb}$  calculated with the  $\alpha_{ff}$  and  $\alpha_{wb}$  values of 1 and 2, respectively, displayed smaller values than  $BC_{BBOA}$  or  $BC_{wb}$  calculated with the  $\alpha_{ff}$  and  $\alpha_{wb}$  values of 0.9 and 1.68, respectively." How much smaller? Could any fit be done based on the two comparisons presented in figure 7.b? A parallel between the diurnal variations of AE33 ( $BC_{ff}$  and  $BC_{wb}$ ) and concentrations of the BC-PMF-factors – either by adding to figure 1.c and 5.b or having the equivalent of Figure S28 for  $BC_{wb}$  and corresponding diurnal cycles for the residential area in the supplement – could provide a good support to the discussion in section 3.3.

**Reply:** A comparison of  $BC_{wb}$  and  $BC_{BBOA}$  concentrations (in linear scale) with a linear fit have been added to supplemental material (Fig. S36). It shows that for the residential site,  $BC_{wb}$  calculated with the  $\alpha_{ff}$  and  $\alpha_{wb}$  values of 1 and 2 gives only 57 % of  $BC_{BBOA}$  or  $BC_{wb}$  calculated with the  $\alpha_{ff}$  and  $\alpha_{wb}$  values of 0.9 and 1.68, respectively. For the street canyon,  $BC_{wb}$  was approximately 3.8 and 7.9 times larger than  $BC_{BBOA}$  calculated with  $\alpha_{ff}$  and  $\alpha_{wb}$  values of 1 and 2 and 0.9 and 1.68, respectively. Also, the correlation between  $BC_{wb}$  and  $BC_{BBOA}$  was very poor.

Modified in text: "smaller values" has been replaced by "half of the values"

Also the diurnal variation for  $BC_{wb}$  and  $BC_{BBOA}$  at the residential site have been added to supplemental material (Fig. S37). We also added text: "In terms of diurnal variation (Fig. S37),  $BC_{BBOA}$  and  $BC_{wb}$  both had a maximum in the afternoon and a second peak in the morning,  $BC_{BBOA}$  increasing in both cases slightly later than  $BC_{wb}$ . The reason for the delay can be speculated to be due to the fact that organics and BC can be emitted at different ratios at different stages of burning (e.g. Kortelainen et al., 2018), the time behavior of  $BC_{BBOA}$  being determined by biomass burning organics due to the used PMF method."

- Line 517-520: "In general, that trend suggests that the aethalometer model produces more constant BB% than PMF and is likely be less sensitive to the changes in the BC sources compared to PMF. Similar observation was done when the diurnal patterns of  $BC_{wb}$  and  $BC_{BBOA}$  were compared;  $BC_{wb}$  had a rather flat diurnal trend whereas  $BC_{BBOA}$  varied more clearly during the course of the day." Could it mean instead that the constant angstrom exponent used to estimate  $BC_{wb}$  is not really adapted when there are different biomass burning sources (such as  $BC_{BBOA}$  and  $BC_{LV-OOA-LRT}$ ) with potentially different absorption properties influencing the site?

**Reply:** Sentence: "Similar observation was done when the diurnal patterns of  $BC_{wb}$  and  $BC_{BBOA}$  were compared;  $BC_{wb}$  had a rather flat diurnal trend whereas  $BC_{BBOA}$  varied more clearly during the course of the day." was incorrect as " $BC_{wb}$ " and " $BC_{BBOA}$ " should have been "BB% values from the aethalometer model and AMS PMF, respectively". This sentence has been corrected.

Diurnal trends of BB% values from AMS PMF and aethalometer model at the residential site have been added to supplemental material (Fig S27) (see also reply to the previous comment).

It is possible that the constant angstrom exponent used to estimate  $BC_{wb}$  is not really adapted when there are different biomass burning sources (such as  $BC_{BBOA}$  and  $BC_{LV-OOA-LRT}$ ) with potentially different absorption properties influencing the site. We have added this remark to Chapter 3.3. (lines 601-602) and conclusions (lines 648-650).

## Technical corrections and minor comments

- If it is possible, having a more detailed title which is more reflective of the content and novelty of the paper might help.

**Reply:** the title has been changed to " Sources of black carbon at residential and traffic environments obtained by two source apportionment methods"

- The fact that the measurements in Street Canyon and residential areas took place years apart should be at least mentioned in the abstract and conclusions.

**Reply:** This was a good point. We added to abstract: "The measurement campaign was conducted at the residential area in winter-spring 2019 whereas the at the street canyon the measurements were carried out in autumn 2015." We also added to conclusions: "When comparing the sites, it should be remembered that the measurements were conducted at different years (residential site in 2019 and street canyon in 2015) that may also impact the source contributions. For example, Luoma et al. (2021) have shown that BC related to traffic has decreased in Helsinki area in recent years, which may overrate traffic related BC at the street canyon relative to year 2019."

- Even though the two sites are described in other papers, it would also be useful to include in the supplement the map of the two sites and potential surrounding sources, and the distance between the two sites as well as the Luukki site.

**Reply:** A map showing the locations of the three measurement sites has been added to the supplement (Fig S1). The distance between the sites can be seen from the scale given in the bottom left corner. The potential surrounding sources were difficult to include in the map but for example the location of the major roads can be seen in the map.

- Line 22-23: "In general, the aethalometer model showed less variation between the sources within a day than PMF being less responsive to the fast changes in the BC sources at the site." Is it that the aethalometer model shows less variations, or that it cannot distinguish between as many sources as AMS-PMF due to similar optical properties despite different OA sources?

**Reply:** The Referee is correct that the difference between PMF and aethalometer model results can be due to the fact that the aethalometer model cannot separate as many sources as AMS-PMF due to similar optical properties of different OA sources. Therefore we have added to abstract "...or it could not distinguish between as many sources as PMF due to the similar optical properties of the BC sources." We also added to conclusions: "...or the aethalometer model was not able to distinguish between as many sources as PMF due to similar optical properties of the BC sources."

- Line 225: "BBOA concentration was a slightly smaller in daytime", was slightly smaller?

**Reply:** "a" has been deleted

- Line 272: "HOA correlated strongly with NO and NO<sub>x</sub> r being larger for four and five factor solutions than for three factor solution." Missing punctuation?

**Reply:** comma added

- Line 361-362: "That is a slightly larger contribution that the campaign-average percentage obtained in this study", changed to "larger contribution than".

**Reply:** "slightly" removed

- Line 382: Change (Fig. 23) to Fig. S23.

**Reply:** changed as suggested

- Why are the elemental ratios missing from Figure S6 to S8?

**Reply:** Elemental ratios were missing in Figures S6-S8 because the  $\text{CHO}^+$  fragment at mass-to-charge ratio ( $m/z$ ) 29 needed to be excluded from the PMF data matrix, and  $\text{CHO}^+$  is crucial for the source apportionment. The reason for that was that  $\text{N}_2^+$  at  $m/z$  28 was fluctuating due to the unresolved issue in the instrument. That fluctuation caused a large uncertainty for the determination of the isotope  $^{15}\text{NN}^+$  at  $m/z$  29 and also for  $\text{CHO}^+$  that was overlapping  $^{15}\text{NN}^+$ . The exclusion of  $\text{CHO}^+$  was explained in Chapter 2.3 and in figure captions S6-S8: "Elemental ratios were not calculated due to the exclusion of  $\text{CHO}^+$  from the input matrix."

- Line 87: "the light absorption in different wavelengths", changed to "at different wavelengths"

**Reply:** "in" changed to "at"

- Line 610-614: Barreira, L. M. F et al. 2021., has been accepted

**Reply:** Barreira et al. (2021) has been changed

- Line 393: "LRT episodes observed in Helsinki in April 2019 will be discussed in more detail in the other paper." Are there any references for this paper? Otherwise, you might want to rephrase as "in another paper".

**Reply:** Details on the LRT episodes have not been published yet. Therefore "in the other paper" was changed to "in another paper" as suggested by the Referee.

- Line 394-397: "BCSV-OOA concentration was smaller from 9:00 to 21:00 than at the other times of the day. BCSV-OOA concentrations did not depend on the ambient temperature (Fig. S23)." Any idea of the sources or mechanism leading to the formation of SV-OOA?

**Reply:** The average contribution of  $\text{BC}_{\text{SV-OOA}}$  was quite small at the residential site (9%) and therefore we did not focus that much on its origin. Based on the mass spectra of organics, SV-OOA was rather oxygenated and therefore has probably been formed from the oxidation of HOA and BBOA, and because of its semi-volatile nature, the SV-OOA concentrations were smaller in daytime.

We have added to text: "Based on the mass spectra of organics in the SV-OOA factor and its diurnal trend, it can be speculated that  $\text{BC}_{\text{SV-OOA}}$  was related to the aging of local traffic and biomass burning emissions."

- Line 401 and Figure 2: specifying Luukki background site, instead of background site might avoid confusing it with Street Canyon site.

**Reply:** "Luukki" added to text

- Line 406: "probably caused by the local BC emissions at the background site accumulated in the boundary layer due to the temperature inversion." Any data / references?

**Reply:** Unfortunately, we did not have any data supporting this statement. We know that there are some houses only few hundred meters from the Luukki station, however, there is a forest between so that the impact of the houses is supposed to be rather small.

We have added to text: "Although the background site of Luukki is located in a sparsely inhabited area, there are some houses only few hundred meters away from the site, which can have an impact on the measured concentrations."

- Line 484-486: "n ambient measurements, a can be larger than 485 that measured directly from the emission source as a values for biomass burning emissions have been shown to increase due to the atmospheric oxidation processes simulated with a smog chamber (Tasoglou et al., 2017)." Studies have also reported a decrease of BB angstrom exponent by photooxidation during atmospheric aging (Nicolae et al., 2013, Dasari et al., 2019...), which could also explain the difference in AAE if the BBOA are not locally emitted.

**Reply:** That is a good addition from the Referee.

Added to text: "However, studies have also reported a decrease of a in biomass burning emissions by photooxidation during atmospheric aging (Nicolae et al., 2013, Dasari et al., 2019), which can explain the difference in a if the biomass burning particles are not locally emitted."

- Line 518-520: "Biomass burning BC obtained from two source apportionment methods followed very similar time trend, however,  $BC_{wb}$  calculated with the  $\alpha_{ff}$  and  $\alpha_{wb}$  values of 1 and 2, respectively, displayed smaller values than  $BC_{BBOA}$  or  $BC_{wb}$  calculated with the  $\alpha_{ff}$  and  $\alpha_{wb}$  values of 0.9 and 1.68, respectively." As mentioned before, the comparison between the diurnal profiles of  $BC_{wb}$  and  $BC_{BBOA}$  could be presented in the supplement.

**Reply:** diurnal profiles have been added to supplemental material (Fig. S37).

- Figure 2.b: Y axis legend should be corrected from " $\mu\text{g} (\text{m}^{-3})$ " to  $(\mu\text{g m}^{-3})$ .

**Reply:** changed as suggested

- Figure 3.b and Figure 5.c: As mentioned in the caption, the two size distributions correspond to the BC size distribution under BBOA influence and background conditions respectively. The legend should reflect the same information, as  $BC_{BBOA}$  and  $BC_{LV+SV+OOA}$  size distributions cannot be completely deconvolved. Also, what about adding the size distribution under LRT conditions? Could the corresponding size distribution of organic and  $C_3^+$  for the same period be presented in the supplement for those periods? It could provide some information on the mixing of particles, and help interpret the difference in coating factors observed between the two sites.

**Reply:** Unfortunately, the size distribution for the  $C_3^+$  fragment needs the analysis of high resolution PToF and that data is not available. Instead, we could present the unit mass resolution size distribution of m/z 36, however, that has an interference from  $\text{HCl}^+$  fragment at m/z 36 that, based on the high resolution mass spectra, contributed 60, 54 and 88% of total signal at m/z 36 in  $BC_{BBOA}$  dominated,  $BC_{LV-OOA\_LRT}$  dominated and  $BC_{LV-OOA + SV-OOA}$  dominated periods, respectively. Therefore, the size distributions for the m/z 36 were not included in this article.

We have added "dominated" to legends in Figs 3b and 5c in order to make them more clear. The size distribution of rBC in the LRT dominated period has been added to Fig. 3b as suggested by the Referee.

The average size distributions of organics in  $BC_{BBOA}$ ,  $BC_{LV-OOA-LRT}$  and  $BC_{LV-OOA + SV-OOA}$  dominated periods at the residential site and  $BC_{HOA}$  and  $BC_{LV-OOA}$  dominated periods at the street canyon have been added to supplemental material (Fig. S31). We also added text regarding residential site: "The size distributions of organics were very similar to those of BC during the three periods (Fig. S31a) indicating that BC was mostly internally mixed with organics." and regarding street canyon site: "During the  $BC_{LV-OOA}$  dominated period, the size distributions of BC was similar to that of organics (Fig. S31b), but in the  $BC_{HOA}$  dominated period, there was slightly more BC in the first mode (at  $\sim 130$  nm) relative to organics than in the second mode (at  $\sim 300$  nm)."

In terms of coating factors, the size distribution of organics did not provide that much new information. We can see that rBC and organics from the SP-AMS are mostly in the same particle size indicating that they seemed to be internally mixed, however, due to e.g. aerodynamic lens in the AMS, we may miss smaller ( $< 50$  nm) particles especially at the street canyon site. These small BC particles are included in eBC measured by the AE33 that may result in the underestimation of coating factor. Uncertainties in coating factor calculation has been discussed in comment 3) in more detail.

- Figure S22: Could you add in the caption that the data corresponds to the residential site?

**Reply:** "at the residential site" added

### **Additional corrections**

the citation details of Helin et al. (2021) has been changed