Response to Reviewer 1

The authors thanks the reviewers for their thoughtful evaluation of our manuscript and for their constructive comments and suggestions. We appreciate the time and effort devoted to reviewing our work, which have helped us improve its quality and clarity. Below, we provide point-by-point response addressing the concerns raised.

Main comments

1.The black carbon (BC) used through-out the manuscript is derived from the SP2, therefore it should be referred to as rBC. This is relevant since the way BC is reported in the literature changes and marking-out the method it is measured provides context and allows for better comparability.
We agree with the reviewer that using the term refractory black carbon (rBC) is more appropriate and improves comparability with their studies. Accordingly, we have replaced BC with rBC throughout the manuscript when referring to black carbon mass concentration derived from SP2 measurements.

2. Lines 186-190: What is the measurement uncertainty linked with using extinction – scattering for deriving absorption? Especially under the conditions of very high SSA of the measurements. How could it potentially impact the determination of BC and BrC absorption, and the AAE with the aging of the plume, as SSA increases?
As noted, deriving absorption using the extinction-minus-scattering (EMS) method can introduce substantial relative uncertainty as SSA approaches unity. However, during the ACROSS airborne campaign, the sampled urban plume exhibited moderate SSA values, with a median of 0.85 and 90% of observations below 0.91. According to the uncertainty assessment by Yu et al., (2024) the relative uncertainty in the derived absorption remains within 15–20% for SSA values below 0.90, a range encompassing over 75% of our measurements. In the revised manuscript, we discussed (section 2.3, lines 215-219) the propagation errors acknowledging the instrument's sensitivity limit.

3. Lines 196: Although a AAE value of 1 is used across many studies, have the authors considered using a more sophisticated and tailored to their area of study approach as the 1st percentile of the AAE distribution as described in Rovira et al. (2025)?
To address the reviewer's concern regarding the sensitivity of our results to the assumed AAE_{BC}, we conducted a sensitivity analysis by varying the values of AAE_{BC} reported by Rovira et al., (2026) (from 0.9 to 1.11). The sensitivity analysis showed that the estimated BrC contribution varies ~4% across the entire range, suggesting that the choice in the AAE_{BC} value have a minor impact in our apportionment results.

We have included a sentence to the manuscript in section 2.3 (lines 230-232) reporting that BrC contribution was only 4% sensitive to variations in AAE_{BC}.

4. Line 206: “Δ denotes an enhancement above background”. From this sentence, my understanding is that the enhancement is obtained as the measured BC and OA vs the “background” estimation provided by the CAMS database marked as “BC” regional. However, throughout the manuscript “background” is also used for the out-of-plume measurements as shown in Figure 1, or for the categorization of ΔOA/ΔBC in Figure 2e. The use of this nomenclature leads to confusion and impairs the correct understanding of some of the results. In particular when trying to interpret ΔOA/ΔBC, since Δ is the difference between measurement and background, one would assume ΔOA/ΔBC to be 0. This needs to be revised, since otherwise the reader has to be constantly making the adjustment between modeled regional background BC measurements and out of plume background measurements.

We thank the reviewer for highlighting this source of confusion. We would like to clarify that we did not subtract a model-derived background concentration from the measured values. Instead, in-plume and out-of-plume air masses were for each flight using in situ measurements of rBC. In-plume air masses were identified when rBC mass concentrations exceeded the 75th percentile for a given flight, whereas out-of-plume air masses (hereafter referred to as background conditions) were identified by rBC concentrations below the 25th percentile. The numerical model was used exclusively to characterize the spatial boundaries, direction, and extent of the urban plume, rather than to estimate background values for subtraction.
To address the reviewer concerns and improve clarity throughout the manuscript, we have made the following revisions:

- Removed the sentence previously appearing at Line 206 defining Δ where its use could lead to ambiguity.
- Revised Section 2.4 (lines 247-249) to explicitly describe the criteria used to classify in-plume and out-of-plume air masses.
- Revised relevant figures and their captions to ensure consistent terminology.

5. Lines 261-264: Since there are not that many individual flights, and the variation is larger between flights than between the different dominated scenarios, I would also include Figure S3 in the main manuscript. Again, use of background and plume dominated is confusing and it is not completely clear how this is obtained, are whole flights marked as “plume” or "background" according to some weight taking into account the CAMS emissions modeling? Are the different parts of the flights separated? I figure it is the latter, but it is not quite clear.
We thank the reviewer for this constructive suggestion. We agree that Figure S3 provides important information for interpreting the variability between flights and the different plume conditions. Accordingly, we have moved Figure S3 to the main manuscript, where it is now presented as Figure 3.

Regarding the classification methodology, each flight was divided into in-plume and background segments based on high-frequency in situ measurements. As described in our response to Comment 4, this classification was performed separately for each flight using the 75th and 25th percentiles of the measured rBC mass concentration to identify in-plume and out-of-plume conditions, respectively. The numerical model was used to characterize the spatial extent and location of the urban plume, but was not used to weight the classification or to estimate background concentrations for subtraction.

To avoid further ambiguity, we have revised Section 2.4 and updated the terminology throughout the manuscript to explicitly distinguish between in-plume and out-of-plume flight segments.

6. Figure 4: This caption could be easily reduced by changing the description into, "Evolution of aerosol chemical and optical properties through the relationship between the Organic Aerosol enhancement vs oxidation state proxy bins as a function of a) photo-chemical age, b) C8 aromatics vs depletion of toluene and c) mean AAE values (450-635 nm)". More importantly, it should be described why the bins don't match across the subplots. Is it data availability/temporal resolution of the x-axis? “The box plots represent the distribution of data points per each ΔOx/ΔBC bin.” Why are there points outside the box in the y-axis direction? Also, what does the size variation of the points in Figure 4 represent?
We thank the reviewer for this constructive suggestion.

The variations in data availability or bin counts across subplots arise from differences in temporal coverage and native measurement frequencies of the specific instruments (e.g. 90s vs 1s). Bins were populated based strictly on the availability synchronized data for each specific chemical or optical property analyzed.

Furthermore, the individual points displayed outside the box in the y-axis direction represent data points lying beyond the interquartile range threshold (specifically outside the 25th – 75th percentiles). Finally, the pentagon markers in Figure 5 (before Figure 4) represent the median values for each bin, with an associated color scale indicating each specific chemical or optical property analyzed per bin.

In the revised manuscript, we have updated the caption of Figure 5 following the recommended structure. Additionally, we clarified the meaning of the box and pentagon markers. Finally, we detailed the variations in data availability across subplots in the supporting information (Table S4), where the number of points per bin is explicitly reported.

7. Lines 353 - 358 and lines 416-418: The formation of SOA is estimated by the authors through the changes in the OA/BC ratio and the C8 depletion. The increase of the AAE is linked to the formation of absorbing SOA material, however it could also be due to the changes in the composition and amount of internally mixed OA with the BC cores during the plume aging, not necessarily to the increase in absorption of the formed SOA. Furthermore, soot collapsing and shape changes in the soot particles can also lead to changes in the absorption efficiencies and their AAE (Forasteri et al., 2018; Corbin et al., 2022; Sipkens et al., 2024).
We thank the reviewer for raising this important point regarding the potential influence of changes in the mixing state or morphology of rBC on $AAE_{aerosol}$.

To investigate of the potential contribution of rBC mixing state, we examined the relationship between the fraction of thickly coated rBC particles measured by the SP2, and the $AAE_{aerosol}$ in the in-plume dataset (Figure 2b). We found a weak but statistically significant negative correlation (Pearson coefficient of $R = -0.16$, $p > 0.05$, $N=103$), with the fraction of thickly coated rBC particles accounting for approximately 3.0% of the observed variance in $AAE_{aerosol}$ ($R^2 = 0.03$). Thus, within our dataset, the fraction of thickly coated rBC particles does not exhibit the positive relationship with $AAE_{aerosol}$ that might be expected if variations in coating thickness were the primary driver of the observed $AAE_{aerosol}$ increase. Nevertheless, this relationship alone does not exclude contributions from coating-related optical effects or changes in the composition of the coatings.

Because the available measurements do not allow us to quantitatively separate the contributions of BrC absorption, coating-related enhancement, and morphological changes, we cannot exclude a contribution from these physical processes. We have therefore revised our manuscript to acknowledge these potential effects and to present the formation of light-absorbing organic material as a plausible interpretation rather than the sole explanation for the observed increase in $AAE_{aerosol}$. The additional analysis is provided in Figure 2b, and the corresponding discussion has been added in the revised manuscript (abstract, section 3.1, lines 339-353, section 4, lines 527-533).

8. Line 373: It would be helpful to know to which measurements the different PC correspond to, to which periods in the plumes.
We thank the reviewer for this suggestion. To clarify which specific plume periods correspond to the extracted principal components (PC1 and PC2), we have updated Figure S10a in the supporting information. The individual data points in Figure S10a are now color-coded according to their respective OH-equivalent photochemical age.

9. Lines 386 - 387: It could also be due to the coating of BC with the formed OA and thus making the total BC look more "brown". As the authors also show in Velazquez-Garcia et al. (2026a) using the same dataset, particles become more thickly coated with the plume aging using the particle diameter to rBC core diameter from the SP2, therefore this is a likely possibility.
We thank the reviewer for this insightful observation. As mentioned in the comment 7, we have revised the manuscript to acknowledge this possibility. The additional analysis is provided in Figure

2b, and the corresponding text has been added to the abstract, sections 3.1 (Lines 339-353) and 4 (lines 527-533) in the revised manuscript.

10. Lines 395 - 396: It should be specified that the OA-to-BC ratio is used for the absorption efficiency of the organic material, not total absorption. Also, see latest work on this for pans-european measurements Rovira et al. (2026).
We thank the reviewer for this helpful clarification and for highlighting the recent study by Rovira et al., (2026).

In the new version of the manuscript we removed this sentence as we excluded the analysis of linear changes between AAE and OA/BC (slope of d(AAE)/d(ΔOA/ΔBC) = 0.83) after incorporating the remarks from Reviewer #2.

Furthermore, we discussed the reference of Rovira et al. (2026) in our revised manuscript (section 3.4, lines 509-512) to place our findings in the context of ambient data which represent a complex mix of OA species that may account for the variability observed when studying the properties of BrC.

Minor comments

11. Line 52: A reference to the estimated direct radiative effects of BrC is missing.
We thank the reviewer for pointing out this omission. We have revised the introduction in line 42-43 to include a reference to studies estimating the direct radiative effects of BrC.

12. Lines 202-205: Are there any studies where the dOA/dBC from mAMS and SP2 is also used? Please indicate them if so.
We have revised the discussion in lines 459-464 to precise studies with online measurements.

13. Line 216: In Figure 2b, the emission ratios are shown for plume and background, not for urban and background as written in the text. Which is correct? I would suggest revising the nomenclature through-out the manuscript.

We thank the reviewer for identifying this inconsistency. We have revised section 2.4 (line 244) to ensure that the description of the emission ratios shown in Figure 2 accurately reflects the categories presented in the figure.

14. Line 284: Since plume is not emitting, I would modify the sentence so that it just states that the emissions from the urban area are more concentrated in the plume – as per definition.
In the statistical tests requested by Reviewer #2 (described in section 2.6), the correlations were not significant for either condition. Therefore, the sentence in lines 328-329 has been reworded.

References
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