Anonymous Review
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Review of "Photochemical ageing drives the browning of urban outflows through secondary brown carbon production"

General assessment

This manuscript presents an interesting airborne investigation of the chemical and optical evolution of Paris Paris-influenced air masses during the ACROSS campaign. The combination of aerosol optical measurements, OA and rBC observations, aromatic VOCs, oxidant measurements, model products, and photochemical age provides a valuable dataset for examining changes in light-absorbing carbonaceous aerosol during plume processing. The observed increase in wavelength-dependent absorption, together with aromatic VOC depletion and increasing OA relative to BC, provides a coherent picture of photochemical processing and is potentially an important contribution to ACP.

However, I think several methodological and interpretative issues need to be addressed before the main conclusions are fully supported. In particular, the quantitative separation of BC and BrC depends on assumptions regarding the spectral behaviour of BC that require uncertainty and sensitivity analysis. The conversion of hydrocarbon ratios into an absolute photochemical age also relies on an assumed OH concentration and other kinetic/source-ratio assumptions, which directly affect all rates subsequently expressed in units of h^{-1}.

This is particularly relevant to the reported AAE growth rate of 0.25 h^{-1}. Table S4 indicates that this value appears to be calculated primarily from the difference between the first and last binned median values rather than from a regression through temporally matched observations. The intermediate bin also does not closely follow the proposed linear parameterisation. In addition, the number of observations contributing to individual variables within each O_X/BC bin varies, raising the question of whether the AAE and photochemical-age medians used to derive this rate correspond to the same measurements.

I also have concerns regarding the statistical treatment of several key relationships. Some of the central variables are mathematically coupled, most notably $\Delta O_X/\Delta BC$ and $\Delta OA/\Delta BC$, which share the same BC denominator, and the photochemical-age and C8 aromatics/toluene metrics, which both contain the C8 aromatic signal. Table S1 also shows that the underlying aircraft measurements are available at high temporal resolution and contain thousands of observations per flight. It is therefore important to demonstrate how temporal autocorrelation and the effective number of independent plume observations were accounted for in the reported significance tests.

Finally, the manuscript sometimes moves from well-supported observational associations to stronger statements regarding secondary BrC production. The measurements clearly show that increasing photochemical processing is accompanied by aromatic VOC depletion, increasing OA relative to BC, and increasingly wavelength-

dependent absorption, but increasing AAE or fractional BrC contribution does not by itself demonstrate production of new absorbing material. I therefore recommend that the authors distinguish consistently between directly observed quantities, quantities inferred using optical or photochemical assumptions, and the proposed mechanism of secondary light-absorbing OA formation.

With additional sensitivity analyses, clearer handling of the time-based and statistical aspects of the analysis, and more cautious interpretation of the underlying chemical mechanisms, I believe the manuscript could make a valuable contribution to ACP.

Major comments

1. Photochemical age and conversion to absolute time

The conversion of the hydrocarbon ratio into an absolute photochemical age relies on several assumptions that require greater justification and uncertainty analysis.

Most importantly, the use of a constant [OH]=5×10^6 molecules cm^{-3} directly determines the calculated age in hours and therefore all subsequent rates expressed in h^{-1}. Please provide the basis for this value and quantify how potential variation in OH affects the calculated ages and associated temporal slopes.

Reporting the underlying OH exposure in addition to the converted age would help distinguish what is directly constrained by the VOC measurements from what depends on the assumed OH concentration.

Please also define precisely what is included in the PTR-ToF-MS “C8 aromatics” signal and justify the use of a single reaction rate coefficient with OH (1.4×10^{-11} cm^3 $molec^{-1}$ s^{-1}), since OH reaction rate coefficients for C8 aromatic isomers vary by roughly a factor of 2-3.

Figure S1 clarifies that a value of approximately 0.80 is derived from an upper-envelope fit of C8 aromatics against benzene. However, the physical basis for treating this upper-envelope slope as the zero-age source ratio should be explained. The non-zero intercept also raises the possibility that background concentrations and dilution influence the ratio.

Finally, the chemically derived quantity should be described primarily as an OH-equivalent photochemical age rather than directly as elapsed transport time unless independently validated. Since HYSPLIT trajectories have already been calculated, comparison between trajectory transport times and hydrocarbon-derived ages would provide a useful independent check.

2. Derivation and interpretation of the reported 0.25 h^{-1} AAE growth rate

Table S4 raises an important issue regarding the reported AAE growth rate.

The three reported binned values are approximately:

(t,AAE)=(2.0,1.1);(6.7,1.6);(8.0,2.6).

The stated parameterisation,

AAE=0.25t+0.60

appears to be obtained by connecting the first and last binned medians:

(2.6-1.1)/(8-2)=0.25 h^{-1}.

However, this equation predicts an AAE of approximately 2.28 at 6.7 h, whereas the reported median at that age is only 1.6. The three median points therefore do not appear to support a particularly linear growth.

Please clarify exactly how the 0.25 h^{-1} slope was derived. I recommend calculating the relationship directly from the paired underlying observations, with an uncertainty/confidence interval, rather than from the difference between the first and last binned medians.

Table S4 also shows that the number of observations contributing to different variables within the same O_X/BC bin is not consistent across variables. Please clarify whether the photochemical-age and AAE values used to derive the reported slope are based on temporally matched observations. Ideally, the AAE-photochemical-age relationship should be calculated only from matched measurements.

Addressing these points, together with the uncertainty in the assumed OH concentration, I recommend describing 0.25 h^{-1} as an empirical AAE growth slope only if it remains supported after reanalysis. It should not be referred to as a BrC production rate.

3. Mathematical coupling between central variables

Several of the principal relationships involve variables that are not mathematically independent.

Most importantly, the correlation between $\Delta O_X/\Delta BC$ and $\Delta OA/\Delta BC$ uses the same ΔBC denominator in both variables. Variation in BC can therefore induce or strengthen correlations between these ratios. The same issue remains when the data are binned according to $\Delta O_X/\Delta BC$ and changes in $\Delta OA/\Delta BC$ are subsequently examined. Please assess whether the relationship remains when the influence of the common BC denominator is accounted for.

Likewise, photochemical age is calculated from C8 aromatics/benzene while C8 aromatics/toluene is subsequently used as another ageing indicator and as a separate PCA input variable. These two metrics share the same C8 aromatic measurement and therefore do not constitute independent evidence.

I recommend demonstrating that the main relationships remain robust using analyses that avoid these shared variables, for example by examining the relationship between the underlying ΔO_X and ΔOA enhancements while treating ΔBC as a covariate, or using an equivalent partial-correlation.

This issue is especially important because the observed (R=0.71) relationship between O_X/BC and OA/BC is subsequently used as evidence linking oxidation and OA production.

4. Statistical independence and effective sample size

Table S1 is useful in showing the measurement time resolutions and raw data counts per flight. However, it also reinforces the need to address statistical independence.

The underlying instruments generate measurements at 1-90 s resolution and Table S1 reports thousands of observations per flight. Consecutive measurements within a single plume crossing are unlikely to represent independent atmospheric samples because of temporal and spatial autocorrelation.

Please state clearly what temporal matching/averaging was applied before combining measurements from instruments operating at different time resolutions, and report the actual number of observations entering each correlation, PCA, and significance test.

More importantly, please explain how the effective number of independent observations was determined. Treating every high-frequency point as statistically independent may overestimate the nominal sample size and produce very small p-values.

This applies particularly to the repeated ($p<0.001$) results in Figs. 3-4 and the Kruskal-Wallis/Dunn analyses. Analysis at the plume-intercept level, flight level, or using an appropriate autocorrelation-adjusted effective sample size would provide stronger evidence.

Table S2 should also report the Kruskal-Wallis result as, for example, ($p<0.001$), rather than “p-value = 0.00000”.

5. Relative BrC contribution versus actual production of new absorbing material

The manuscript should distinguish more clearly between an increase in the relative BrC contribution and actual production of additional absorbing material.

For example, the manuscript notes that flights with lower BC concentrations exhibit larger fractional BrC contributions. However, because BrC is expressed as a fraction of total absorption, a reduction in BC can mathematically increase the BrC fraction even if absolute BrC absorption remains unchanged.

Similarly, increasing AAE demonstrates increasingly wavelength-dependent absorption but does not by itself demonstrate formation of additional BrC.

If possible, I encourage the authors to examine how the inferred BrC absorption coefficient changes with photochemical age both in absolute terms and after normalisation to an independent dilution tracer (e.g. CO). This would help distinguish the formation of additional absorbing material from changes in the relative BC/BrC contribution caused by plume dilution or varying BC abundance.

The same distinction applies to OA. An increase in (ΔOA/ΔBC) is not equivalent to an increase in OA mass; it represents an increase in OA relative to BC and requires assumptions regarding the behaviour of BC before it can be interpreted quantitatively as SOA production.

6. Association versus causal attribution to secondary BrC/SOA formation

The combined changes in AAE, aromatic VOC depletion, OA/BC, and oxidation state provides compelling evidence for coordinated chemical and optical changes during plume processing.

However, the manuscript frequently goes beyond this observational result and states that SOA formation "drives" the browning or that secondary BrC production has been demonstrated.

The present aircraft measurements do not directly identify the molecular species responsible for enhanced absorption. The discussion of nitro-aromatics provides a potential mechanism based on previous laboratory and field work, but CHON compounds or aromatic VOC depletion do not directly establish that nitro-aromatic chromophores account for the observed AAE increase.

Similarly, newly formed OA is not necessarily light absorbing.

I therefore recommend maintaining a clear distinction between:

1. the directly observed increase in wavelength-dependent absorption;
2. the BrC contribution inferred using the optical attribution assumptions; and
3. the proposed mechanism of secondary light-absorbing OA formation.

Wording such as "drives", "demonstrates", "production rate", and "producing new absorbing material" should be moderated unless directly supported by the measurements. A formulation such as "the observations are consistent with an increasing contribution from secondary light-absorbing OA during photochemical processing" would remain scientifically strong while better reflecting the evidence.

7. Plume attribution and interpretation of transport/ageing

The manuscript would benefit from a clearer distinction between identifying air masses influenced by Paris and demonstrating temporal transformation of the same plume.

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The percentile-based plume definition (>75th percentile BC) is operationally reasonable but guarantees a high-BC subset for every flight regardless of absolute Paris influence. In addition, (ΔBC/ΔCO) is not a fully independent validation because BC is used both in the initial selection and the validation metric.

I suggest making greater quantitative use of the WRF-CHIMERE Paris-source attribution across all flights and showing that the selected plume and background populations differ systematically in simulated Paris influence.

The HYSPLIT analysis also requires further clarification. Please specify the forward-trajectory starting height(s), explain what is meant by "arrival heights corresponding to the aircraft altitude", and define the horizontal, vertical, and temporal criteria used to determine an aircraft-trajectory intersection. HYSPLIT is described as a complementary check that the sampled air masses were transported from Paris, but the corresponding trajectory results should also be shown, potentially in the Supplement.

Please also explain whether the aircraft data were screened for possible contamination from the ATR42 exhaust or previously emitted wake, particularly during turns and repeated low-altitude transects. Figure 1 contains repeated BC, CO, and optical enhancements. The spatial agreement with WRF-CHIMERE provides evidence for an ambient Paris plume, but the manuscript should nevertheless describe the self-contamination screening procedure and explain the yellow excluded periods.

Finally, wording such as "tracking plume evolution" and "transport time" should reflect that the analysis represents an ensemble of Paris-influenced plume intercepts from different flights and meteorological conditions rather than continuous tracking of a single parcel.

Minor comments

1. **Introduction, lines 43-45:** Please separate direct atmospheric absorption, snow/ice albedo effects following deposition, and cloud/boundary-layer adjustments rather than grouping these mechanisms together.
2. **Introduction, lines 63-66:** Please broaden the discussion of secondary BrC formation beyond gas-phase VOC oxidation and clarify what is meant by "BrC lifetime". In many cases, this is more accurately a wavelength-dependent absorption-decay or photobleaching timescale.
3. **Introduction, lines ~90-102:** The novelty relative to Yu et al. (2026b) should be made more explicit, since that study already reported SOA formation, increasing AAE, and enhanced BrC contribution using substantially overlapping ACROSS airborne measurements. Please state clearly which analyses and conclusions are unique to the present manuscript.

4. **End of Introduction:** The objective to provide "recommendations for incorporating BrC dynamics into climate models" appears somewhat stronger than what is directly evaluated. The study does not perform a model sensitivity experiment. "Discuss implications for the representation of BrC ageing in atmospheric and climate models" may more accurately describe the scope.

5. **Section 2.1:** Table S1 provides the individual instrument time resolutions. Please explain how these datasets were temporally matched before ratios and multivariate statistics were calculated.

6. **Section 2.1, lines ~127-134:** I suggest using the term refractory black carbon (rBC) for the SP2-derived mass concentration. This would distinguish the SP2 measurement from modelled BC and optically inferred BC absorption used elsewhere in the manuscript.

7. **Section 2.2:** Please briefly explain how Paris-derived BC was tagged or separated from regional/background BC in WRF-CHIMERE.

8. **Lines 190-199:** The BrC attribution assumes, assigns absorption at 630 nm entirely to BC, extrapolates this contribution to 450 nm, and attributes the residual absorption to BrC. A close to unity AAE_{BC} is a reasonable nominal assumption, but BC mixing state and coating can modify its wavelength dependence, particularly during atmospheric ageing. I therefore suggest a sensitivity analysis using a reasonable range of values to indicate how strongly the inferred BrC fraction depends on this assumption. The assumption of negligible BrC absorption at 630 nm should also be acknowledged.

9. **Lines 120-126 and 185-190; Table S1:** Please provide or propagate the uncertainty associated with the A2S2-derived absorption through the AAE and BrC calculations, since absorption is obtained from extinction minus scattering before the subsequent spectral attribution. Table S1 also indicates missing/problematic A2S2 450 nm measurements for some flights. Please clarify which flights are included in the AAE/BrC analysis and whether the missing optical data systematically alter the range of conditions represented in this part of the study.

10. **Sections 2.3-2.4:** Please define explicitly how the background concentrations used for each Δ quantity were determined, particularly for observations already classified as "background" using the lower BC quartile.

11. **Section 2.6:** PCA describes covariance rather than causal "drivers"; please revise the corresponding wording.

12. **LOWESS analysis / Fig. S6:** The apparent plateau at advanced ageing should remain explicitly tentative. The data are sparse in this regime and LOWESS

behaviour at the edge of the dataset can depend strongly on the smoothing parameter.

13. **Section 3.1:** Higher SSA supports a more scattering-dominated aerosol but does not by itself demonstrate that the aerosol is more OA-rich.

14. **Section 3.1:** A weak relationship between (ΔBC/ΔCO) and BrC absorption does not by itself establish a secondary origin for BrC.

15. **Section 3.2, lines ~305-310:** The quantity described as an "oxidant production rate" is more accurately the slope of BC-normalised O_X enhancement against inferred photochemical age. Please revise the terminology and retain the BC normalisation in the reported units, including in the Conclusions.

16. **Section 3.2, line 308:** The statement that oxidant production remains "highly efficient" is stronger than supported by the metric. The data indicate continued O_X enhancement relative to BC but do not quantify efficiency.

17. **Section 3.2, line 305 and Section 3.3, lines ~340-342:** Figure 3 appears to span photochemical ages up to approximately 12.5 h, whereas the AAE change and reported 0.25 h slope are based on the 2-8 h interval. Please clarify why the optical analysis is restricted to this shorter age range (e.g. due to availability of temporally matched optical and VOC measurements) and state this distinction explicitly when discussing the 6 h processing interval in the Abstract and Conclusions. In addition, "photochemical lifetime" at line 305 would be better replaced by "photochemical age" or "age range".

18. **Section 3.2:** Temperature and RH correlations should be interpreted more cautiously. These parameters likely covary with time of day, photochemical age, solar radiation, boundary-layer evolution, and flight-to-flight variability.

19. **Figure 4 caption:** A decrease in C8 aromatics/toluene should not be described as "depletion of toluene". It represents preferential depletion of the more reactive C8 aromatics relative to toluene.

20. **Section 3.3 / Table S2:** The statistical analysis demonstrates a significant difference between the lowest and highest O_X /BC groups, whereas adjacent groups are not statistically different. I therefore suggest replacing "statistical progression" with wording describing an endpoint difference across the oxidation range.

21. **PCA / Table S3:** OA/BC loads strongly on PC2 (0.893), whereas the primary photochemical-processing metrics dominate PC1. Please discuss what this indicates about OA variability rather than presenting OA production as completely coincident with the principal ageing axis.

22. **Table S4:** The final sentence describing the different AAE "sensitivities" appears to contain copy/paste errors in the derivative labels. Please check the labels for OA/BC, O_X /BC, and C8 aromatics/toluene carefully.

23. **Table S4 / main text:** Please clarify the units/scaling of C8 aromatics/toluene. The main text refers to ratios of approximately 0.2-0.3, whereas Table S4 reports values of 351.5, 115.7, and 70.9. If these values are scaled, this should be stated explicitly.

24. **Conclusions, line 411:** The statement that photochemical ageing "leads to higher SSA values" does not appear to be directly demonstrated by the ageing analysis. Please either show this relationship or soften/remove the statement.

25. **Conclusions/model implications:** OA/BC and SSA are useful observational covariates but are not yet demonstrated to be transferable model parameterisations of BrC ageing. I suggest describing them as observational relationships that may inform future model development.

Overall recommendation

The manuscript presents a valuable airborne dataset and identifies combined changes in aromatic VOC depletion, OA relative to BC, oxidation state, and wavelength-dependent aerosol absorption in air masses influenced by emissions from the Paris metropolitan area. I believe the study has clear merit and could make a valuable contribution to ACP after the points above are addressed

However, the quantitative BrC attribution and photochemical-age estimation require additional sensitivity analysis, the derivation of the reported rate of 0.25 h^{-1} in AAE should be revisited using temporally matched observations and appropriate uncertainty, some key correlations should be reassessed because the variables share common measurements and the data are autocorrelated, and the causal interpretation should be brought into closer alignment with what is directly constrained by the measurements.

Addressing these issues would, in my view, substantially strengthen both the scientific interpretation and the broader relevance of the manuscript.