Response to Reviewers for manuscript titled:

Brown carbon emissions from laboratory combustion of Eurasian arctic-boreal and South African savanna biomass

A.Mukherjee et al.

RC: Reviewer Comments **AC: Author Comments**

RC 1:

General assessment

This manuscript presents a comprehensive laboratory study examining brown carbon (BrC) emissions from the combustion of diverse biomass types associated with Eurasian and South African ecosystems. The experimental scope is broad, including multiple combustion conditions (smouldering and flaming), analysis of both primary and aged emissions, and optical and chemical characterization of soluble organic carbon fractions.

The work is generally well-structured and systematically documented. The methods are clearly described, and the supplementary information provides useful detail for understanding the combustion setup and analytical techniques. While the study mostly relies on existing methods, the use of the specific fuels and associated findings contribute missing data relevant to the atmospheric behaviour of BrC, in relation to its emission factors and optical properties under different fuel types and aging scenarios.

The manuscript is technically sound, and the results are presented in an organized fashion. A few clarifications and refinements are warranted before publication.

AC: The authors thank the reviewer for his generous and positive comments and feedback.

Specific comments

Line 151: Provide supporting information or references indicating how closely this heating method reproduces the temperature profiles or combustion behaviour observed in real-world biomass burning.

AC: The authors thank the reviewer for the comment. We have now added suitable references (Pokhrel et al., 2021 doi:10.1080/02786826.2020.1822512; McRee et al., 2025 doi: 10.1080/02786826.2024.2412652) in line 157-158 to highlight how an electrical resistor power can be adjusted to create different temperature profiles in order to trigger flaming combustion or smouldering combustion. We didn’t have the instrumentation to measure the exact fuel or flue gas temperature in this study. The resistor settings were adjusted and finalised in trial experiments through visual sighting of flame, as well as from the FTIR signals, analysing the flue gas and corresponding MCE values obtained.

Line 156-159 now reads:

“Combustion was initiated using an electric resistor of which the power was adjusted to generate exclusively flaming or smouldering emissions, similar to previous studies (Pokhrel et al., 2021; McRee et al., 2025). With this open combustion setup (Fig. S2), we allowed instant dilution of the emissions in an aim to simulate real world forest surface fires.”

Lines 186-187: Was this definition based on the authors' own measurements, previous literature, or a combination of both?

AC: Flaming and smouldering dominated burns based on MCE values were defined from the equation of MCE itself, as highlighted in previous literatures. MCE denotes the fraction of CO_2 (which predominantly originates during efficient flaming combustion) in the total emitted CO_2 and CO (which is primarily emitted during incomplete smouldering combustion). The authors have now added suitable references (Yokelson et al., 1996, doi: 10.1029/96JD01800 and Stockwell et al., 2014, doi: 10.5194/acp-14-9727-2014) in Line 195, which have previously highlighted MCE values <0.9 denote smouldering dominated emissions and combustions with MCE values >0.9 are dominated by flaming phase. MCE of 0.9 represents emission with equal (50%) contribution from both smouldering and flaming phases.

Line 199: How was the RH controlled in the chamber experiments? Was a specific humidification setup used?

AC: In this work, we used the same humidification system and procedure as described in Leskinen et al. (2015, doi: 10.5194/amt-8-2267-2015). Briefly, we used deionized water, a Model FC125-240-5MP-02 (Perma Pure LLC., USA) humidifier and Lauda water bath to create humidified or wet air. The humidity of the wet air was controlled by the temperature of the deionized water on the other side of Nafion® membrane tubes. To achieve the desired relative humidity (RH) inside the environmental chamber, we mixed wet air with dry clean air while feeding it into the chamber. RH was only controlled at the beginning of the experiment, when the chamber was filled with clean air and not during the experiments.

We have now modified lines 207-210 (previously line 199) accordingly:

"The relative humidity (RH) inside the chamber was set at 20% for SG and SW emissions and at around 50% for BFS and CP emissions to reproduce typical daytime RH in corresponding environments during the fire active seasons, using a humidification setup described in Leskinen et al., (2015).**"**

Lines 225-226 & 288: The phrase "added externally" refers to direct injection into the chamber?

AC: Yes, in lines 237-238 (previously lines 225-226) and 305 (previously line 288), the authors intended to convey that the reactants were injected into the chamber. Keeping the reviewer's comment in mind, the authors have now modified the phrase "added externally" to "directly injected into the chamber" in L238 and L305.

Lines 285-286: The current approach injects oxidants (e.g., O_3) into the chamber after the biomass burning emissions have been introduced. This may result in direct reactions between O_3 and primary organic compounds, potentially competing with the intended NO_3 radical chemistry. Discuss whether, in terms of experimental design, preconditioning of the chamber, i.e., allowing O_3 and NO_2 to react before introducing BB emissions, would be feasible and better isolate the target aging mechanism and more closely resemble atmospheric conditions. A brief justification of the chosen protocol, with reference to relevant studies (e.g., DOIs: 10.1073/pnas.2010365117; 10.1039/d2ea00031h;

10.1080/02786826.2024.2412652), would be helpful.

AC: The authors thank the reviewer for this insightful comment. We agree with the limitations of our experimental design as pointed out by the reviewer here. In order to justify our choice and also highlight the potential flaw of our design, we have now added the following sentences in the manuscript:

Line 219-222: "Oxidative reactants were injected into the chamber after the BB emissions, because we first wanted to measure the characteristics of primary aerosols as well as, to study the effect of dilution on the partitioning of the POA fraction without inducing any aging pathways, similar to previous studies (Kodros et al., 2020, 2022)."

Line 240-246: "Furthermore, the addition of O_3 within a small span of time (~10 minutes) after the addition of NO_2 in the chamber might have led to competition between the expected NO_3 radical chemistry and ozonolysis pathways, although the reaction rates of ozonolysis are much slower than nitrate oxidation pathways. Another method for simulating aerosol aging with NO_3 radicals would be to precondition the chamber with NO_2 and O_3 before adding the BB emissions (McRee et al., 2025). However, by doing this, we would not have been able to study both fresh and oxidatively aged aerosol during the same chamber experiment."

We have also modified lines 236-238, to highlight that NO_2 was added before O_3 into the chamber to potentially limit the interference of ozonolysis:

"CP and BFS burning emissions were aged in relatively *'high-NO_x'* conditions in the dark chamber with 100 ppb NO_2 followed by 100 ppb O_3 directly injected to chamber"

Line 350: It is recommended to use the term Mass Absorption Efficiency (MAE) rather than Mass Absorption Coefficient (MAC) when referring to solvent extracts, as MAC is conventionally used for aerosol particles in the particulate phase (e.g., DOI: 10.5194/acp-21-12809-2021).

AC: We thank the reviewer and accept the suggestion. We have changed "MAC" to "MAE" throughout the manuscript.

Line 383: "Eq. 4" appears to be incorrectly cited and may refer to "Eq. 8". Please confirm and revise as needed.

Line 384: Similar to the above, "Eq. 5" may also be misnumbered.

AC: The authors thank the reviewer for pointing out the mistake in labeling the equation numbers in Lines 406 and 407 (previously L383 and L384). The references to Eq. 9 in Lines 405 (previously wrongfully labeled as Eq. 4) and Eq. 11 (previously wrongfully labeled as Eq. 5) in Line 406 have now been corrected.

Lines 577 & 821: Organic carbon (OC) is used throughout as a proxy for organic aerosol (OA) mass in emission factor and absorptivity calculations. This may lead to their underestimation or overestimation, respectively, as OA mass > OC mass. A brief comment acknowledging this and its implications for comparison with other studies is recommended.

AC: We gratefully acknowledge the discrepancy the reviewer has highlighted here. We have indeed mistakenly attributed MSOC as a proxy for overall OA (instead of total OC) in section 3.3 (now lines

602-604).

We have now modified lines 602-604 as follows:

"Since MSOC corresponded to >92% of the total OC in our fresh BB emissions, our estimated MSOC concentrations can be used as a proxy for bulk OC."

And added the following sentence in lines 641-642:

"However, it should be noted that our estimated MAE values need to be divided by a suitable OA/OC ratio before comparing with MAC_{OA}."

We have rewritten the conclusion section and the previous sentence in line 821 no longer exists.

We have added the following sentence in the methodology section 2.7 (in line 375-378):

"It should be noted that the MAE values obtained in this study for soluble OC will need to be divided by an OA/OC factor (typically in the range of 1.8-2.2 for fresh emissions, Hartikainen et al., 2020) to obtain the MAE of MeOH or water-soluble OA before comparing with previous literature reporting light absorption properties of BB emitted OA."

Line 808: The discussion could be strengthened by referring to recent field or modelling studies on BrC emissions and impacts from boreal and African biomass burning. Highlight how your findings may contribute to improved estimates of radiative forcing or inform regional air quality modelling efforts.

AC: The authors thank and acknowledge the reviewer for this comment. We have now revised and rewritten the conclusions section to better highlight how our numeric findings compare to the relevant parameters used in climate models and can affect regional climate and air quality. The conclusion section in lines 857-900 now reads:

"Our estimated OC and EC EFs suggest that OC generally dominates open BB emissions and specifically smouldering conditions emit higher OC than flaming combustion, in agreement with previously existing knowledge. However, we observed significant variation in EFs among experimental replicates, especially for smouldering burns of the same biomasses (fig. 2a,c). This clearly demonstrates how dynamic and variable open BB emissions are inherently, with many factors, including chemical compositions, fuel moisture content and combustion conditions, playing a crucial role in determining the emissions. Emission inventories for open BB from field and lab measurements are often presented as a single value averaged over experimental replicates (Andreae, 2019) for air quality or regional climate modelling purposes, and our findings highlight the importance of parameterizing EFs as a function of MCE (Fig. S6) or emitted OA/BC (or OC/EC) ratios for accurate modelling. The estimated high EF_{OC} for boreal and arctic peatland burns in our experiments also indicates that these vegetation types can become a major source for OA emissions in the region in response to increased forest fires, which can have drastic effects on local air quality and climate.

To include the effects of BrC in climate models, an important approach is to parameterize BrC k values as a function of the BC-to-OA (or alternatively EC/OC) ratio of the emissions. The estimated eBC/OA ratios for different fresh BB emissions in our study varied by orders of magnitude and ranged from 0.002 to 0.7. For different climate models, different BC/OA ratios such as 0.03-0.06 (Wang et al. 2018) and 0.08 (Brown et al., 2018) have been used, which don't account for the fuel or combustion phase dependent variations of BC/OA or EC/OC. The k_{MSOC_550} for fresh BB emissions in our study varied between 0.002 and 0.011, and fell into the category of W-BrC, as classified by Saleh (2020). The k values of open BB emissions are very similar to those used in existing models, whereas BrC from high temperature combustion is currently underestimated. We also observed a different trend between k_{MSOC_550} and EC/OC in this work (Fig. 5b) compared to previous literature, suggesting the need for an extensive fuel and combustion dependent emission inventory for better parameterization of BB emitted BrC k values for global climate models.

We observed a strong abundance of tarball morphologies of variable sizes for all open BB emissions, especially for smouldering burns. Characterization of the BB emissions in the environmental chamber revealed that the most volatile OC fractions, OC1 and OC2, decreased in the chamber compared to fresh emissions, due to particle-to-gas partitioning. This dilution-induced change of OC volatility distribution resulted in higher fractions of OC3, OC4 and PC (overlapping with SVOC, LVOC and ELVOC), potentially leading to more absorbing BrC chromophores (Calderon-Arrierta et al., 2024) as well as more defined tar balls in the chamber primary samples. We observed a slight decrease in MAE_{MSOC} for wavelengths higher than 365 nm. This contrasting finding is likely because our solvent extraction method cannot resolve the lowest volatility fraction of organics (with tar ball morphology) in the chamber primary samples.

We determined an increase in O:C ratio of the particles upon photochemical and dark oxidation, which resulted in an increase in ELVOC fractions (PC in particular), making it more insoluble in solvents. Dark aged CP and BFS smouldering emissions in particular had the lowest MeOH solubility, probably due to the observed high abundance of highly viscous, low volatility tarballs (Chakrabarty et al., 2023). For the dark-aged samples, MAE_{MSOC} increased for all wavelengths, suggesting the formation of stronger light-absorbing oxygenated compounds and/or nitroaromatics. For photochemically aged samples, k_{MSOC_550} decreased, probably due to photobleaching and breaking down of BrC chromophores. After aging k_{MSOC_550} values ranged from 0.0011 to 0.03 across all studied biomass types, which were significantly lower than the k_{550} values currently used in climate models. However, our estimated k_{550} values don't include the non-soluble and highly light absorbing s-BrC fractions. Consequently, in future it would be important to combine online and offline optical measurements of open BB emitted OA to characterize also the non-soluble organic fraction."

SI: Please number the pages.

AC: The authors apologise for the inconvenience and have numbered the pages in the SI.

SI Text S1: The rationale for fuel selection could be better contextualized. Please briefly explain, with supporting references, whether the selected biomass types and burning conditions reflect those commonly encountered in wildfires across the targeted regions (Eurasia and South Africa).

AC: We thank the reviewer for the comment. To contextualize the fuel selections for this study, we have now added the following text in section S1, with additional references (Descals et al., 2022, doi:10.1126/science.abn9768; Jain et al., 2024, doi:10.1038/s41467-024-51154-7; Huang and Rein, 2017, doi:10.1071/WF16198; Walker et al., 2020, doi:10.1038/s41558-020-00920-8)

"Finnish boreal forest biomass and Arctic-boreal peats were selected for this study, specifically due to the lack of knowledge regarding aerosol emission from these biomasses. Furthermore, with ongoing climate warming, unprecedented wildfires have been recorded both in the boreal forest and Arctic and are projected to increase in the future (Jain et al. 2024; Descals et al. 2022). Boreal and particularly Arctic wildfires largely consume soil organic matter, in many cases consisting of peat (Huang and Rein 2017; Walker et al 2020). South African savanna biomasses, on the other hand, constitutes a major fraction of wildfire emissions from continental Africa and contributes significantly to global carbon emissions (Vakkari et al., 2018,2025; van Wees et al., 2022). Even though savanna wildfires are open surface fires, yet the emissions contain much more EC (or BC) compared to Eurasian biomasses, therefore allowing us a wider range to study the effects of BB emitted EC/OC on the optical properties of the emission. We also included a few data points in this study from modern European chimney stove emissions, which are classified as residential wood combustion (RWC) emissions. We have previously shown that modern RWC emissions are EC-rich (Mukherjee et al., 2024) due to their high combustion temperatures. Therefore, including these data points in the current study helped us explore the temperature and EC/OC continuum of biomass burning in three regimes such as:

1) the low temperature combustion of Arctic-boreal surface and corresponding OC-rich emissions, 2) the high temperature wood combustion and resulting EC-rich emissions and 3) the woody and grassy savanna fire emissions, which fall in between 1) and 2).

With that background, we then explored how these temperature continuum influence the BC-BrC continuum in the BB emissions along with their corresponding light absorption properties."

In addition, we have also included the following text in the introduction section of the manuscript, at lines 59-64:

"Another important source of open BB emissions is savanna fire, which has been estimated to account for almost 50% of global carbon emissions from forest fires (van Wees et al., 2022), with roughly 30% of the total forest fire induced carbon emissions originating solely from Southern African savanna fires (van der Werf et al., 2017). Yet, relatively limited studies have been carried out to characterize these emissions in recent years (Vakkari et al., 2014, 2018; Desservettaz et al., 2017; Wu et al., 2021; Vernooij et al., 2022, 2023)."

SI Fig. S6: In the legend, the first marker for "SW smouldering" likely refers to "SG smouldering".

AC: We thank the reviewer for pointing out the mistake. We have now corrected the label for the marker corresponding to "SG smouldering" in Fig. S6.

SI Fig. S19: Why is BFS plotted in (c)? Also, its colour may have been incorrectly assigned, when compared with the BFS spectrum shown in panel (a).

AC: The authors are grateful to the reviewer for mentioning this mistake. In Fig.S19c, "CP" was incorrectly labeled as "BFS". Both the labeling and the color scheme have now been modified to be compatible with the rest of the plot.

RC 2:
General comments:

1. It is stated in the abstract and conclusions that the comparison with African savanna biomass is an objective of this manuscript. However, throughout the manuscript, the comparison at least is not clearly stated. I would suggest giving a summary or some statements of comparisons on the main properties. Also, how do these data compare to North American forest fires? A brief discussion would put these data sets in a better context for modeling studies or for atmospheric implications.

   AC: We thank the reviewer for this valuable comment. In section 3.1, we have previously discussed the OC-EC emission factors of fresh BB emissions, including the African savanna and the North Eurasian biomasses and compared them with previously reported North American forest fire emissions. In section 3.2, we were unable to include a comparison of the broad chemical compositions of savanna emissions, as the detailed chemical analyses of South African biomasses will be discussed in a separate manuscript, which is under preparation. In section 3.4, we discussed the morphology, particle size distribution and effective densities of all the biomasses used in this study as well. In section 3.5, where we had discussed the effect of dilution in the environmental chamber on the volatility and solubility of fresh BB emissions, we had not previously included any discussion about the savanna biomasses since we had not conducted any chamber study of the said biomasses without aging**. However, we have included the data points for savanna experiments in Figure 8 and Figure S11 for better representation.**

We had also tabulated the most important physical parameters (density, MAE and k_{550}) for fresh and chamber aged BB emissions for all experiments of this study in Table S4. However, we agree with the reviewer that we didn't explicitly compare the light absorption properties of the fresh and aged emissions from different biomasses and compared them with North American BB emissions in sections 3.3 and 3.6.4. We have therefore taken the reviewer's comments into consideration and modified the manuscript accordingly:

1. **Section 3.3:**

We added the following text in lines 609-618:

"However, our estimated $AAE_{300-550}$ values were higher than reported values from western-US wildfires for similar wavelength range (1.6-1.8, Chakrabarty et al., 2023) and $AAE_{401-870}$ reported from laboratory burns of canopy (2.69±0.36), litter (1.86±0.20) and mixed (2.26±0.36) coniferous ecosystem from western USA (Selimovic et al. 2018). Interestingly, our reported $AAE_{300-550}$ values matched well with lab burning of rotten logs (4.60±3.73) of Douglas fir (*Pseudotsuga menziesii*) and ponderosa pine (*Pinus ponderosa*) from Western USA and generally fell in the range of previously reported AAE values from FIREX campaigns (FIREX 2016: McClure et al., 2020; FIREX 2019: Zeng et al., 2022) for emissions with OA/BC ratios ranging from 6.6-143 (McClure et al., 2020) or EC/OC ratios of 0.01-0.3, assuming an average OA/OC ratio of 2. All the flaming dominated and full combustion emissions, as well as some smouldering dominated emissions reported in our work, had EC/OC ratios that fell in this range."

We have restructured and added texts to lines 631-642. It now reads:

"In general, flaming dominated BB emissions had higher MAE_{MSOC_365} values compared to smouldering emissions (Fig. 5a). Among open BB experiments, the lowest MAE_{MSOC_365} were generally observed for fresh emissions from BFS smouldering combustions (0.56±0.10 m^2 g^{-1}), while flaming combustion of CP (1.31±0.13 m^2 g^{-1}) and SW (1.06-1.38 m^2 g^{-1}) were estimated to have the highest MAE_{MSOC_365} (Table S4). The MAE_{MSOC_365} for smouldering SG (0.68-0.94 m^2 g^{-1}) and SW (1.05-1.11 m^2 g^{-1}) emissions were in a similar range to the MAC_{OA_370} estimated by Vakkari et al. (2025) and agreed well with of MAC_{370} from African residential biomass burning emissions (0.24 – 2.2 m^2 g^{-1}) as reported by Moschos et al. (2024). Previously estimated MAC_{BrC} (at 405 nm) from In-Situ observations made during WE-CAN campaign (2018) in the US and ORACLES-2016 and CLARIFY (2017) campaigns over Southern Africa ranged from 0.9 to 1.6 m^2 g^{-1} (Carter et al., 2021). However, it should be noted that our estimated MAE values need to be divided by a suitable OA/OC ratio before comparing with MAC_{OA}."

Section 3.6.4:

We have now rearranged and added new text to lines 807-812. It now reads:

"Depending on the biomass type and the combustion conditions, photochemical aging either increased (fig. S19b) or decreased (fig. s19a,c,d) the light absorption efficiency (MAE) at wavelengths below 350 nm, while the MAE_{MSOC} at wavelength range 350-450 nm decreased for all cases. Overall, MAE_{MSOC_550} and k_{MSOC_550} also decreased and in some cases remain unaltered (Fig. 9, Table S4) after photochemical aging, while w_{MSOC} increased. The w_{WSOC} and w_{MSOC} varied between 3.3-3.7 and 4.3-4.5, respectively, for fresh emission of CP, while it increased to 4.0-5.1 and 4.0-6.4 after photochemical aging."

Lines 824-836 has been slightly modified so it now reads:

"The effect of dark aging on the optical properties was more non-trivial in our study. We noted that for flaming dominated emissions, the NO_x dominated dark aging led to higher k_{550} values and decreasing w values (fig. 9) in accordance with Saleh (2020). This suggests an increase in light absorption towards the visible wavelength range, which was also seen in the absorption spectra (fig. S19b,d). On the other hand, dark aging seemed to have a minor effect on the smouldering emissions of BFS (Fig.9, Fig. S19a). One explanation for this observation could be the prevalence of tarballs in the smouldering dominated emissions of both peat and other biomass samples, which have been shown to be quite resistant to oxidative aging (Chakrabarty et al., 2023). Additionally, nitroaromatics are reactive, and certain fractions of them may have degraded at the end of the chamber experiments or during filter collection from the chamber, making it difficult to distinguish the effects on optical properties. Owing to very limited NOx concentration in the chamber during the "low-Nox" dark aging, we observed very limited effects of aging on the savanna biomasses. In general, the MAE and k decreased after aging (Table S4), most likely aided by the ozonolysis pathways in the presence of externally injected O_3 into the chamber."

2. What are the aerosol loadings in the aging experiments? At high loading, ozone could readily react with the gases and be lost onto particles, so the observed photochemical aging is mainly by ozone resulting in a low equivalent time (less than 2 days, Table 1)? Please comment on this issue.

AC: The authors thank the reviewer for the comment. We agree with the reviewer that for high aerosol loading, there could be significant scavenging of the oxidants in the chamber, thus stopping OH radical formation and further oxidation after a certain time period of exposure. As mentioned in Lines 205-206, the aerosol loadings in the chamber ranged only between 20-50 ug m^{-3} in our experiments. We also observed from the PTR-MS that the OH exposure continued to increase throughout the whole experimental period.

Minor comments:

1. There are too many abbreviations which lead to more confusions and less readability. It would be convenient to have a table or list. Some terms are only used for less than a few times, so it is not necessary to use abbreviations. For example, DMF, MeOH, PRD, etc. Define the variables or abbreviations when they are first used, then use the symbols or abbreviations, duplicated definition is not necessary, for example, L35,36,39, 117,140, 235.

AC: We thank the reviewer for the comment. We have now provided a list of abbreviations for the ease of the future readers.

We agree that some of the abbreviations used in the manuscript were repetitive. We think it is important to define certain terms and their abbreviated forms in both the Abstracts and the Introduction section for the convenience of the readers. However, we have now removed the abbreviations that were used in the Abstracts section without defining them beforehand.

The abbreviations that were only used once (e.g. PRD) in the manuscript, as the reviewer had kindly pointed out, have also been removed. Although we would like to keep the abbreviation for organic solvents like dimethylformamide as DMF and methanol as MeOH. These abbreviations are generally more recognized among the scientific community.

Some of the abbreviations lacked consistency across the manuscript (methanol and MeOH were being used interchangeably and so on) and we have rectified that as well. For example, methanol has been referred to as MeOH throughout the manuscript other than the abstracts section (methanol soluble organic carbon).

2. L28, it would be better to use "determined" than "defined".

AC: The authors agree with the reviewer's recommendation. The word "defined" has now been changed to "determined" in L28.

3. Figure 3, what do the bottom right squares with lines indicate?

AC: We thank the reviewer for the query and acknowledge that it is important to clarify the figure for the convenience of the broader readership. Therefore, we have now added additional text to the figure title as well as the figure itself to help understand the so-called "upset plot". Fig. 3 and its title now read (L561-567):

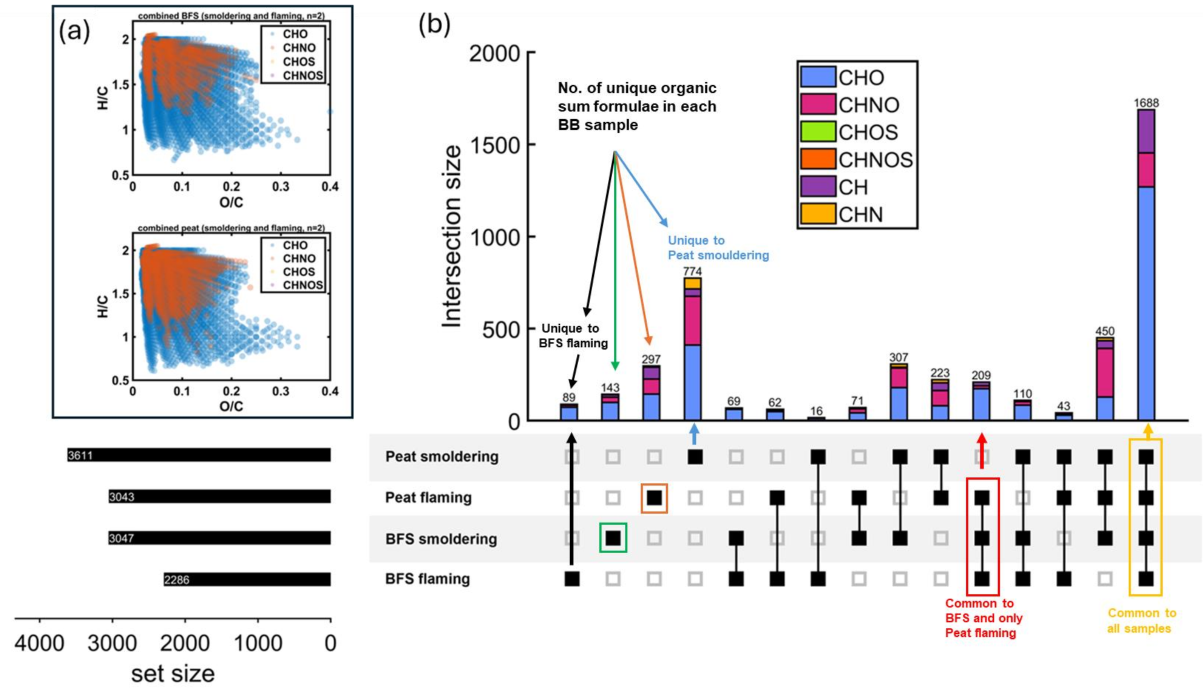


Figure 3: (a) Van-Krevelen diagrams of oxygen-containing compounds and (b) upset plot intersections (combined CP and BFS) with compound class indicated by colour. Samples were analyzed by positive-ion DIP-APCI FT-ICR mass spectrometry. Upset plot of four organic aerosol datasets (flaming and smouldering emissions of CP and BFS) with the number of measured molecular formulae in each dataset (bottom left) and the individual intersections (top right) indicated by color (CHO-light blue, CHOS-green, CH-purple, CHNO-magenta, CHNOS-orange and CHN-yellow). The compared samples are shown in the lower right corner and the common organic sum formulas they contain in the panel on the upper right.

4. L669, how do you determine the OC1-4, Pyrol C and EC?

AC: In line 275 (previously Line 259), we have mentioned that the OC-EC from filters were determined using the IMPROVE-A protocol. This measurement protocol is widely used and is very well characterized. The original method, along with its details, has been previously described by Chow et al. (2007), as referenced in the manuscript. We decided not to describe the whole procedure in the manuscript for the sake of brevity, but keeping the reviewer's valuable comment in mind, we have now included a description of the analytical procedure in the supplementary information.

We have added the following sentence in the manuscript in lines 277-278:

"The details of the measurement protocol have been described in the supporting information (Section S2)."

In S2 of Supplementary Information, we have now included the following paragraph:

"Thermal–optical carbon analysis with the IMPROVE-A protocol was carried out by placing a filter punch in the sample oven of a carbon analyzer. The filter punches were first heated in completely inert (100 % He) condition where various OC subfractions gradually volatilized at temperature ramps of 140 ºC (OC1), 280 ºC (OC2), 480 ºC (OC3), and 580 ºC (OC4). The system then switched to an oxidizing atmosphere (He with a fixed amount of O_2) where EC subfractions combusted at 580 ºC (EC1), 740 ºC (EC2), and 840 ºC (EC3). The released carbon compounds were converted to either carbon dioxide (CO_2) or methane (CH_4), followed by infrared absorption (CO_2) or flame ionization (CH_4) detection. During the thermal analysis, a fraction of OC pyrolyzed or charred (Pyrolyzed Carbon, PC) under the inert He atmosphere into EC-like substances and were accounted for using optical correction by reflectance. Specifically, the instrument monitored the sample filter reflectance throughout the analysis using a laser source. The filter reflectance decreased in response to the formation of PC and then increased as the PC was combusted off the filter. The split between OC and EC is defined as the point at which reflectance returns to its initial reading before the heating started. OC and EC data discussed in this work refer to those after the correction as per the following equations:

$$\text{Corrected OC} = \text{OC1}+\text{OC2}+\text{OC3}+\text{OC4}+\text{PC}$$
$$\text{Corrected EC} = \text{EC1}+\text{EC2}+\text{EC3}-\text{PC}$$

"

5. L509, how was the solubility determined?

AC: The authors thank the reviewer for highlighting the need to mention how solubility was determined in this study. We have now added the required equation (Eq. 5) in Line 366, and added the following text to the manuscript in Line 364-366:

"The solubility of organics in each solvent were estimated as:

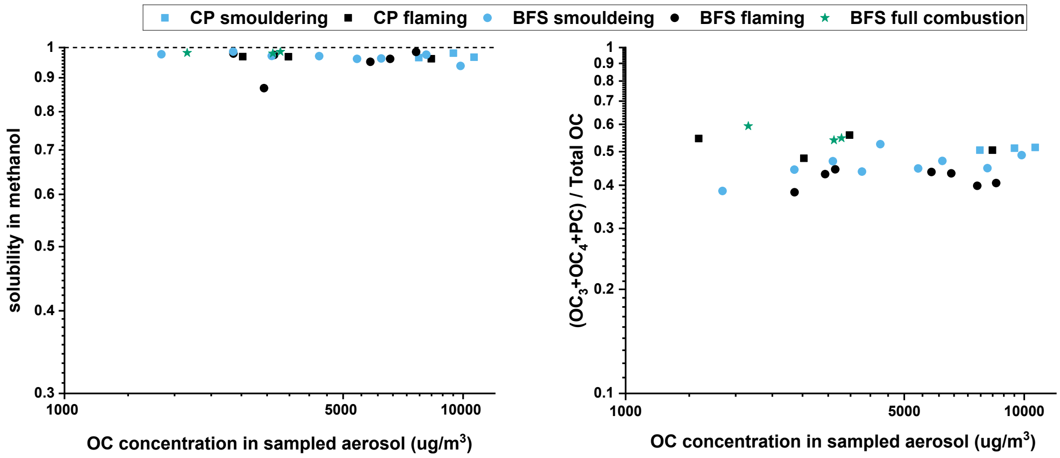
$$\text{solubility} = \frac{(\text{OC in original filter}) - (\text{OC in extracted filter})}{(\text{OC in original filter})} \qquad (5)$$"

6. L603-605, Figure 5, I don't see a clear correlation between EC/OC and MAC if excluding the RWC data.

AC: We thank the reviewer for the comment. The authors acknowledge that there is no correlation between EC/OC and MAE (previously referred to as MAC). The authors intended to highlight the trend between EC/OC and MAE in Figure 5, hence the word "correlation" has been changed to "trend" in line 645 (previously line 603).

7. L684-685, how does the trend look like if excluding the chamber data? or how does it look like if it is plotted on a log scale?

AC: No clear trend was seen between OC concentration and its methanol solubility or (OC3 + OC4 + PC)/Total OC for fresh BB emissions, although we generally observed higher non-volatile fraction in the diluted samples in the chamber as a result of dilution related partitioning. For visual reference, we have added the following plots showing the relationships between solubility and non-volatile OC fractions as a function of the OC concentrations in primary emissions, in log-log scale.



Without the chamber data, the OC concentration range for different experiments was relatively narrow (one order of magnitude). This might be influenced by the fact that fresh BB emissions were directly collected from diluted exhaust with minimal residence time (less than a second). Thus, there was no time for partitioning of organic compounds, whereas in the chamber, the residence time was up to 5 hours before the particles were collected on filters.