

Peer Review File

Cloud processing and weeklong ageing affect biomass burning aerosol properties over the south-eastern Atlantic



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16th Nov 21

Dear Dr Che,

Your manuscript titled "Cloud processing and weeklong ageing significantly affect the biomass burning aerosols over the south-eastern Atlantic" has now been seen by 3 reviewers, whose comments are appended below. You will see that they find your work of some potential interest. However, they have raised quite substantial concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication, but would be interested in considering a revised version that fully addresses these serious concerns.

We hope you will find the reviewers' comments useful as you decide how to proceed. Should additional work allow you to address these criticisms, we would be happy to look at a substantially revised manuscript. In particular, we ask that you present sufficient further evidence and analyses to ensure your measurements are robust and that your conclusions on organic aerosol formation are compellingly supported by the data presented in the manuscript.

If you choose to take up this option, please either highlight all changes in the manuscript text file, or provide a list of the changes to the manuscript with your responses to the reviewers.

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If the revision process takes significantly longer than three months, we will be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

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We are committed to providing a fair and constructive peer-review process. Please do not hesitate to contact us if you wish to discuss the revision in more detail.

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Please do not hesitate to contact me if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

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REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

This study investigates the evolution of BB aerosol as it transports westward over the southeastern Atlantic.

They use in situ measurements data from two field campaigns CLARIFY and ORACLES.

They compare the composition, organic fraction, size distribution, and optical properties of the BB aerosol upwind and downwind along the trajectories.

The study provides interesting information on BB aging however, I miss supporting information from satellites.

Remote sensing observations of the aerosol properties (AOD, SSA, AE, effective radius, aerosol height (from LIDAR) could all give a better perspective on what is measured and where.

On the same note, their results suggest that cloud processing is one of the main factors controlling changes in BB. Therefore I would recommend explaining the cloud processing estimations in more detail. Using reanalysis information for estimating the cloud properties along the trajectories is a good first approximation but I am not sure how reliable it is on the scales needed for this analysis. What if the cloud fraction is not uniform? Then the liquid water content values will be different than the mean.

Geostationary satellites could be used to follow cloud properties along the trajectories and polar-orbiting (that usually provides more detailed microphysical information) could be used to have a better perspective on the type of clouds and expected LWC.

Finally, I may miss information but It is not clear why only the last 24 h are considered for cloud processing. What if the aerosols passed through clouds before that.

Reviewer #2 (Remarks to the Author):

In their paper, Hoachi Che and colleagues link through lagrangian trajectories aerosol and BB emission tracers measured on flights during a campaign over the south-eastern Atlantic, in order to derive aging characteristics of organic aerosol mass, and its oxidative, size distribution and optical properties. They present interesting results which I think merit publication in Nature Communications Earth and Environment. The results are somewhat explorative due to relatively small number of cases, but observations over this area are scarce. However, several major questions need to be answered before publication.

1) How to make sure that the encountered air parcels during the linked flights are indeed affected by biomass burning emissions. The only criterion given is that a back trajectory passes over fire pixels, but is this sufficient ? This requires that fire emissions are transported up to the trajectory height (often in the mid-troposphere). To make sure this point, absolute BB emission tracer concentrations, here CO, should be given and compared to background unaffected by fire emissions. The main paper and also the SI only show tracer ratios or differences required for the aging analysis, but no absolute concentrations.

2) The organic aerosol aging analysis differentiates dry and wet trajectories, with cloud processing for the latter ones. It should be noted that the dry cases usually occur at much higher mid-tropospheric altitudes, why the wet ones are located at lower altitudes where they meet the lower atmospheric stratocumulus cloud. Thus the discussion of results should recognize that there are correlated discerning factors, including height and temperature in addition to cloud processing. How would this affect the discussion ? For instance, lower temperatures at higher altitudes affect the phase distribution for SVOC species.

3) The quasi linear increase of the oxidation status (f_{44}) with respect to photochemical processing time is an interesting result and puts confidence on the method. However, the discussion of the larger Δf_{44} values is unclear (« thus, OA with higher f_{44} can be assumed to have a higher hygroscopicity and can be more effectively removed by cloud droplets. Therefore, it seems likely that the increase of f_{44} results from SOA formation by cloud processing »). The second statement can not be concluded from the first one, as the first one talks about removal processes and not formation. Please clarify.

4) The increase in size distribution during aging is attributed to coagulation. Are the authors sure that this is a relevant process ? At my knowledge this process more affects very small particles. For illustrating my purpose authors can look at figure 2.7, p48 of the thesis of Hilel Dergaoui (2012) that can be downloaded at <http://www.theses.fr>. It shows that particles larger than 100 nm diameter are not affected by coagulation.

5) At several occasions (for exemple page 10, from line 13 on), authors indicate removal by clouds as an important process. This would imply that clouds are present at the arrival points, otherwise cloud evaporation would reconstitute processed aerosol. In one example shown, clouds are present at the end of the trajectory, so removal is certainly an important process. But is this true for the other « wet » flights also. Rain would lead to irreversible removal. Did rain events happen, were they included in the analysis ?

6) The paper lacks a finalizing step. There are numerous typos or English grammar errors, sometimes formulations are awkward, figure legends unclear. The paper needs a thorough rereading. There should be no problem with many native English speakers among the co-authors, and which are hopefully ready to re-read the paper.

I annotated typing and some minor or technical remarks directly in the paper.

Reviewer #3 (Remarks to the Author):

Review for Che and co-authors: Cloud processing and weeklong ageing significantly affect the biomass burning aerosols over the south-eastern Atlantic

Che et al. report measurements of biomass burning emissions off the coast of Africa using upstream and downstream aircraft measurements to compare organic aerosol mass changes as well as changes in the optical properties (SSA and AAE) of the transported aerosol. Upstream and downstream measurements are linked via HYSPLIT analysis. The authors also try to estimate the effects of cloud processing on SOA formation and on changes in optical properties of the aerosol. The presented measurements are valuable, and the analysis technique used to probe the effects of aerosol aging by linking trajectory is valid. However, I found that there are major inconsistencies in the reported measurements that are not fully addressed in the manuscript. For instance, the authors hypothesize that the decrease in OA mass (using the OA/CO ratio) for air mass that spent some time inside a cloud is due to wet scavenging. Yet, the higher the cloud processing intensity the higher was the measured aerosol hygroscopic (as approximated by increasing f_{44} with increasing cloud processing intensity). This is inconsistent since the more hygroscopic aerosol would likely be scavenged first. Also, the authors present conflicting results regarding the role of cloud processing on changes in aerosol optical properties. For instance, the authors reported that photochemical aging decreases AAE, and the decrease is more pronounced when the air mass spent some time inside clouds. This means that cloud processing made the aerosol less absorbing. Yet, the authors also show a negative correlation between cloud processing intensity and SSA, meaning that cloud processing made the aerosol “look” more absorbing (the authors attribute this to potential wet removal of thickly coated BC particles). Obviously, changes in particle size impacts both SSA and AAE, as rightly pointed by the authors, which could explain the apparent contradiction. However, the effect of size is only briefly discussed and not fully explored in the manuscript leaving the reader to guess what the actual role of the size distribution on optical properties is. Mie theory predictions

could yield insight into the role of the size distribution to changes in SSA and AAE. Unfortunately, this is also not explored in the manuscript. More detailed comment can be found below.

Minor comments:

P4 L11: “Launched” and not “lunched”

P4 L26: “By only considering the cloud processing within the last day of the air mass transportation, the immediate effect of cloud processing on the aerosol can be studied.” This doesn’t make sense to me. You are not making measurements just before cloud processing to isolate the effects of clouds alone. Even if you make measurements just after cloud processing, the air mass spent a significant amount of time aging prior to entering the cloud, hence you are wrongly attributing all changes observed between upstream and downstream measurements as being from cloud processing alone, which obviously is not the case.

P6 Figure 1. The decrease in OA attributed to wet scavenging is inconsistent with increases in particle hygroscopicity (indicated by increase in f_{44}). I would assume that the most hygroscopic aerosol would be scavenged and thus lost. Scavenging of OA component should therefore be accompanied by a decrease in κ (and hence f_{44}). But this is not what is observed. Also, why is x-axis on a and b different from c and d? Presumably you are plotting the same data.

P7 L13: The authors hypothesize that the decrease in OA mass during cloud processing is attributed to wet scavenging, but there is no data on precipitation. Are these data available? If so, is there a correlation between the decrease in OA mass and precipitation intensity?

P7 L17: “Two of the dry cases clearly exhibit the increase of OA, indicating the formation of SOA. Although the modified combustion efficiency (MCE) of those two cases are slightly lower than others, they are still higher than 0.98 (Fig. S7), suggesting all BB emissions in our study are from similar flaming fires, consistent with recent studies” I disagree with this. Looking at Figure S7, the MCE from at least the last flight is statistically significantly different than the other flights. Without a statistical test it is difficult to know for sure. Either way, it is therefore not clear to me that differences in $\Delta(\text{OC}/\text{CO})$ cannot be due to differences in combustion conditions.

P7 L35: “However, in comparison to the dry cases, f_{44} in wet cases increases even more at the same ageing time, indicating the contribution of cloud processing”. It would be helpful if the authors plotted the 95% CI of the regression line to assert if cloud processing on f_{44} is statistically significant. Also, I am surprised why the authors have not checked whether cloud processing increases sulfate. Presumably, this effect would be larger than increase in SOA.

P9 L4: It is weird that cloud processing has no impact on the size distribution. If wet scavenging occurred in clouds (as hypothesized earlier to explain decrease in OA/CO ratio), then one would expect that larger and more hygroscopic aerosol (hence more CCN active) to be depleted. The authors offer no explanation on why this is the case.

P9 L17: “Specifically, BrC bleaching and OA photolysis may mostly occur in the small size range, while SOA may more easily condense on large particles, creating the shift in the aerosol distribution.” This doesn’t make sense to me. Why would bleaching and photolysis mostly occur in the small size range? Has this been previously reported?

P9 L21: "Comparing these two cases, it can be seen that the aged aerosol distribution (dash lines) is narrower in the case with cloud processing, as demonstrated by the lower fraction of larger particles (>200 nm). Therefore, the reduction of σ by cloud processing is mainly reflected in the removal of large particles." How can the authors claim this? Even though you are starting with similar distributions doesn't mean that the observed differences are solely attributed to cloud processing. Photochemical aging between the two different days are likely different.

P11 L2: "Thus, the increase in particle size due to ageing is also responsible for the decrease in AAE." I would argue this is the main effect indeed. Mie calculations could validate this assumption

P11 L4: Could the decrease of SSA with increasing cloud processing be the result of higher RH in the line that could interfere with the measurements?

There is an inconsistency between the decrease in AAE with aging (Figure 4a,b which is more pronounced during cloud processing times) meaning the aerosol is less absorbing and the decrease in SSA with increased cloud processing which means the aerosol is more absorptive. Unless changes in SSA and AAE are dominated by size effects. But Mie theory would be needed to make sure the changes have the correct sign.

Cloud processing and weeklong ageing significantly affect the biomass burning aerosols over the south-eastern Atlantic

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Abstract

Southern Africa produces one-third of global biomass burning (BB) emissions by widespread fires, and the BB aerosols it emits are featured with a long lifetime. With the westward transport of BB aerosols over the semi-permanent stratocumulus cloud decks in the south-eastern Atlantic (SEA), ageing and clouds can affect the chemical, physical, and optical properties of BB aerosols, resulting in a significant yet uncertain radiative forcing which may compensate the warming effect from greenhouse gases. Here, we investigated the long-time evolution of BB aerosols in a Lagrangian methodology wherein aircraft observations in the SEA were linked with air mass trajectories. Our results suggest an increase in organic aerosol (OA) over a significantly long time, followed by the decreases of OA before reaching equilibrium. We also find that the aerosol absorption wavelength dependency decreases with ageing as a result of increased particle size and the photochemical bleaching of brown carbon (BrC). Cloud processing highlights the aqueous-phase oxidation of OA, while it significantly reduces large diameter particles and single-scattering albedo (SSA) of BB aerosols, resulting in a less aerosol concentrated yet more absorbing marine boundary layer.

1. Introduction

Southern Africa contributes roughly one-third of the global biomass burning (BB) emissions by widespread fires^{1,2}. These BB aerosols exhibit various physical and chemical properties subject to fuel sources, combustion phase (i.e., flaming, smouldering, pyrolysis), and atmospheric ageing. Despite extensive studies, the radiative forcing by BB aerosols in the SEA region remains uncertain^{3–8}.

The mass, composition, morphology, and size distribution of BB aerosols evolve with ageing^{9–13}, resulting in uncertainties in BB aerosol-radiation-cloud interactions. BB aerosols in the SEA are featured with a long lifetime, suggesting ageing could have a significant yet unclear effect on aerosol properties^{14,15}. With ageing, Organic aerosol (OA) mass can either increase by functionalisation or oligomerisation reactions or decrease by fragmentation^{11,16,17}. Laboratory experiments show a considerable increase in the OA (70% on average) resulting from the formation of secondary organic aerosol (SOA)^{11,18–20}. While field observations have reported conflicting results^{9,21–23}, with the majority suggest negligible changes^{24–28}. For brown carbon (BrC), a particular type of OA that can absorb radiation in the near-UV and visible ranges²⁹, ageing can produce either secondary BrC by multiphase reactions^{30–33}, or it can reduce BrC, known as “BrC bleaching”^{25,29}. Current climate models generally consider OA to be scattering only, leading to significant uncertainties in some regions, where BrC contributes substantially or even dominates the total aerosol absorption^{29,34}.

The number size distribution of BB aerosol evolves with ageing due to collision and coalescence, as well as condensation of SOA on BB particles^{22,24}, affecting the cloud condensation nuclei (CCN) and, in turn, indirect radiative forcing. The evolution of physical and chemical properties of BB aerosol can result in changes in its optical properties. Among them, single-scattering albedo (SSA) and absorption Ångström exponent (AAE) are two critical parameters in calculating the aerosol direct radiative effects. Given that the SSA of BB aerosols is close to the balance points of net absorption and net scattering³⁵, SSA depends on particle size, shape, and chemical composition, the aforementioned changes via ageing can affect direct radiative forcing in the SEA by changing SSA.

Cloud processing, one particular type of ageing, is unique in providing a supersaturated environment and liquid droplets that allow the aqueous-phase reaction to occur³⁶. In addition, it can also modulate aerosol distribution by Brownian capture as well as collision and coalescence. The frequently observed smoke in the marine boundary layer in Ascension Island³⁷ highlights the importance of cloud processing in the SEA. However, as only few studies focus on cloud processing, its effect remains uncertain³⁸. Therefore, cloud processing has been separated from others in this work for a comparative study of its effect.

The lack of understanding of ageing and cloud processing in the SEA also comes from the sparsity of observations. In previous studies, laboratory experiments have focused on examining aerosol ageing within a few hours while the BB aerosol over the SEA undergoes several days of ageing^{14,15}; most field

observations have difficulties in investigating the evolution of BB aerosols. To address these issues, two synergistic aircraft measurement campaigns were performed in the SEA in 2017. By linking aircraft observations from different regions (different transport time of plumes) with air mass trajectories, we are able to investigate the evolution of BB aerosols in the specific air mass in the Lagrangian way. Here we report on the evolution of BB aerosol chemical, optical, and physical properties pertaining to the SEA region.

2. Materials and Methods

2.1 Aircraft measurements.

Aircraft observation campaigns of ORACLES (ObseRvations of Aerosols above CLouds and their intEractionS) and CLARIFY (CLoud–Aerosol–Radiation Interaction and Forcing) were conducted in different regions of SEA. The ORACLES aircraft campaign was conducted from São Tomé in 2017, and flew in the upwind area of the SEA³⁹, while CLARIFY was conducted from Ascension Island, and flew in the downwind regions¹⁴. The fire counts, aircraft tracks, mean aerosol optical depths (AOD), and mean low-cloud fraction during the flight observation can be seen in Fig. S1 (supplement). These two campaigns cover a large area with mean low-cloud fractions ranging from 0.7 to 0.4 and mean AOD from 1.2 to 0.4. A brief description of the data we used is presented in this section, while a more detailed one can be found in campaign overviews^{14,39}. Black carbon (BC) mass concentration was measured by the Single Particle Soot Photometer (SP2), and non-refractory aerosol chemical composition was measured by Aerodyne C-ToF-aerosol mass spectrometer (AMS) in CLARIFY and HR-ToF-AMS in ORACLES⁴⁰. Carbon monoxide (CO) was measured by Los Gatos Research CO/CO₂/H₂O analyser in ORACLES and vacuum ultraviolet fluorescence spectroscopy (AL5002, Aerolaser GmbH) in CLARIFY. The aerosol scattering and absorption coefficients were measured by nephelometers and particle soot absorption photometer (PSAP) in ORACLES, while CLARIFY used the EXSCALABAR instrument (Extinction Scattering and Absorption of Light for Air-Borne Aerosol Research). The absorption, scattering, and extinction coefficients from both campaigns are converted to 450, 550, and 660 nm wavelength for comparison by calculating the Ångström exponent. For the aerosol size distribution, we use the ultra-high-sensitivity aerosol spectrometer (UHSAS) data for particles ranging from 60 to 1000 nm in ORACLES; while for CLARIFY, we use the Passive Cavity Aerosol Spectrometer Probe (PCASP) data for particles from 100 nm to 3 µm, and the Scanning Mobility Particle Size Spectrometer (SMPS) for particles below 100 nm. An undersized issue by UHSAS has been detected, and a correction function is applied for ORACLES data⁴¹. During the campaigns, an intercomparison between ORACLES and CLARIFY aircraft observation has been conducted on 18 August 2017 to ensure measurements from different aircraft are comparable. Although the aerosol concentration is very low during the intercomparison flights, the CO observation shows fairly good agreement. A detailed comparison can be found in Fig. S2 and S3. All variables have been converted under the standard temperature and pressure (STP) for the ensuing analysis.

2.2 Trajectory linking

We use airmass trajectories calculated by the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT)⁴² to link ORACLES and CLARIFY observations. To improve the accuracy, we use hourly high resolution (0.25°×0.25°) ERA5 reanalysis (fifth generation of ECMWF reanalysis data) for the calculation. There are five main procedures to ensure the success of the linking. (1) Identify and limit analysis to only straight-level runs from ORACLES flights. (2) Launch forward trajectory at the coordinate of straight-level runs of each ORACLES aircraft, calculate a trajectory per minute, with a time step of the trajectory of 20 min. (3) Calculate the horizontal and vertical distance between the airmass and aircrafts of CLARIFY and other ORACLES flight at each time step. If the horizontal distance is within 0.5° and the vertical distance is within 300 m, then the case is identified as potentially linked. (4) In those potentially linked cases, the total sampling time is over 2 minutes, and there is not obvious change between the linked trajectory and other trajectories launched at the adjacent times from the upwind ORACLE. Then the airmass is marked as “successfully linked”. (5) For those linked airmass, estimate the initial age of the BB aerosols measured from upwind ORACLES aircraft (detailed in supplement). Only select those with ageing time less than 48 hours (remove already very aged samples) and remove cases with data below detection limit (very low aerosol concentration) for further analysis. The successfully linked cases are illustrated in Fig. S4, along with their airmass trajectories. In total, 26 linked cases have been identified, with 10 ORACLES linked with CLARIFY cases and 16 ORACLES linked with ORACLES itself cases (Table S1). After linking, we can have the samples measured in the exact same airmass but at different times, which ensures the evolution of aerosols can be analysed by Lagrangian methodology.

The cloud processing during the transport of the airmass was calculated by collocating the ERA5 reanalysis cloud liquid water data with the trajectory. Thus, the cloud liquid content at each point of the trajectory is provided, and the mean time of trajectory inside clouds (cloud liquid water content >0.001 g/Kg) is calculated accordingly. To quantify the cloud processing effect, we define a cloud processing intensity term, which is calculated as the mean cloud liquid water content multiplied by the mean in-cloud time within 24 hours before the airmass reaches the downwind linked location. By only considering the cloud processing within the last day of the airmass transportation, the immediate effect of cloud processing on the aerosol can be studied. Fig. S5 shows an example of a linked case with cloud processing along with its trajectory. The airmass travel time is considered here as the further ageing time of BB aerosol.

2.3 Linked measurement analysis

2.3.1 OA enhancement factor

To determine the evolution of OA mass, we calculated the OA enhancement factor $\Delta(OA/CO)$ as in Eq. (1) to examine the change of OA mass by removing the dilution effect.

$$\Delta \frac{OA}{CO} = \frac{OA_{down}}{CO_{down}} - \frac{OA_{up}}{CO_{up}} \quad (1)$$

The subscripts “down” and “up” indicate the observations in the downwind and upwind, respectively. CO is used as a conservative tracer to account for dilution, as it has a lifetime of about a month. The units of CO have been transformed into the same weight unit of OA; thus, the OA/CO is unitless. Positive values of $\Delta(OA/CO)$ indicate an increase in OA mass along with the airmass transport, implying the formation of SOA. Zero value of $\Delta(OA/CO)$ means there is no net change of OA mass along with the transportation, while negative values indicate a decrease in OA mass. Next, we calculated OA mass concentration at the downwind (OA_{down}^{calc}) by assuming only dilution is affecting the OA mass, as in Eq. (2). Therefore, changes of OA mass with ageing can be calculated in percentage, as in Eq. (3).

$$OA_{down}^{calc} = \frac{OA_{up}}{CO_{up}} * CO_{down} \quad (2)$$

$$f_{OA} = \frac{OA_{down} - OA_{down}^{calc}}{OA_{down}^n} * 100\% \quad (3)$$

The OA oxidation level is represented by f_{44} calculated from AMS 44 m/z data. The difference of f_{44} between the upwind and downwind observations is calculated as in Eq. (4), and the change of f_{44} in percentage can be calculated as in Eq. (5)

$$\Delta f_{44} = f_{44_{down}} - f_{44_{up}} \quad (4)$$

$$f_{f_{44}} = \frac{\Delta f_{44}}{f_{44_{up}}} * 100\% \quad (5)$$

2.3.2 AAE and SSA

The AAE at upwind and downwind locations of airmass trajectories are calculated between 450 and 660 nm wavelengths as in Eq. (6). Then the differences are calculated as in Eq. (7) to study the changes of AAE with ageing.

$$AAE = -\frac{\ln(\sigma_{450}/\sigma_{660})}{\ln(450/660)} \quad (6)$$

$$\Delta AAE = AAE_{down} - AAE_{up} \quad (7)$$

Where the σ_{450} and σ_{660} denote the aerosol absorption coefficient at 450 and 660 nm respectively. SSA is calculated in Eq. (8), and the change of SSA by Eq. (9).

$$SSA = \sigma_{scattering} / \sigma_{extinction} \quad (8)$$

$$\Delta SSA = SSA_{down} - SSA_{up} \quad (9)$$

Where $\sigma_{extinction}$ and $\sigma_{scattering}$ are extinction and scattering coefficients of BB aerosol. The changes of AAE and SSA in percentage can be calculated in Eq. (10-11).

$$f_{AAE} = \frac{\Delta_{AAE}}{AAE_{up}} * 100\% \quad (10)$$

$$f_{SSA} = \frac{\Delta_{SSA}}{SSA_{up}} * 100\% \quad (11)$$

2.3.3 Aerosol size distribution

The aerosol number size distributions measured from CLARIFY and ORACLES are fitted by the normalised lognormal distribution, as in Eq. (12).

$$\frac{dN}{Nd \log D_p} = \frac{1}{\sqrt{2\pi} \log \sigma} \exp \left(-\frac{(\log D_p - \log D_m)^2}{2(\log \sigma)^2} \right) \quad (12)$$

where N is particle number concentration, D_p is the diameter of the particle, D_m is the mode diameter representing the geometric mean, and σ is the standard deviation. All linked cases show mono-modal distributions. The normalized aerosol distribution function enables us to compare changes in the aerosol spectrum without being affected by the decrease in total aerosol concentration due to diffusion.

Uncertainties of the parameters in each linked case are estimated by the Gaussian error propagation with the measured data. Note that only the uncertainty of the data during the observation is considered, the error of the instrument is not included in the calculation.

3. Results

3.1 Oxidation and evolution of organic aerosols

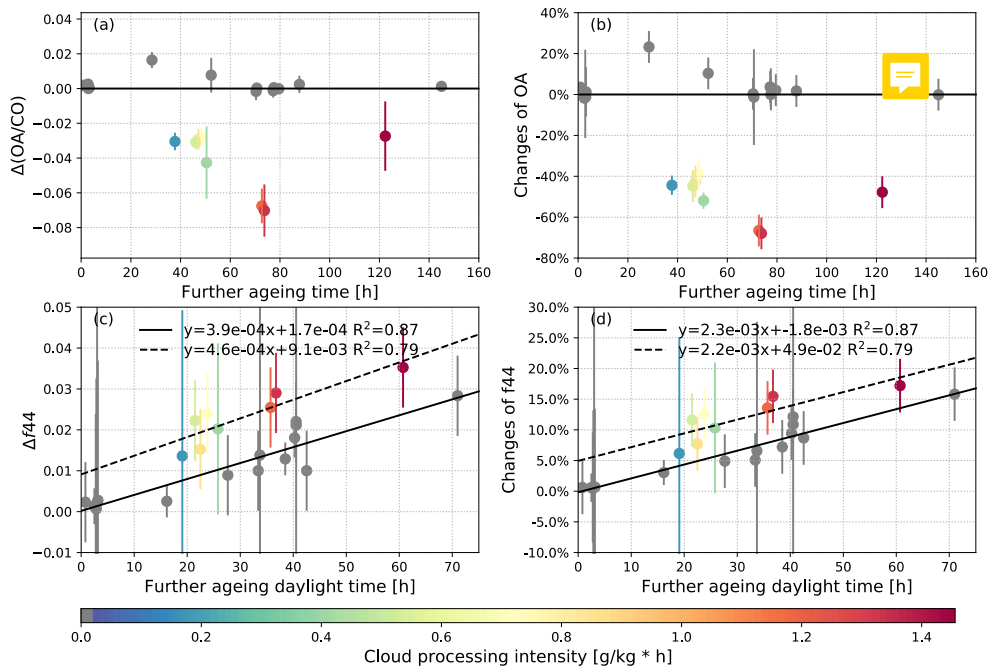


Figure 1. Evolution of (a) OA enhancement factor $\Delta(\text{OA}/\text{CO})$ and (b) changes of OA in percentage with further ageing time, which is the transport time of BB aerosols between two observations; (c) enhanced f_{44} and (d) changes of f_{44} in percentage with further daylight ageing time during the transportation of the BB. The dots are mean values for linked cases, and the error bars are standard errors calculated from Gaussian error propagation. The colourmap indicates the mean cloud processing intensity within the last day of the transport (defined in the method), and grey colour represents samples with no cloud processing. The black horizontal line in (a, b) is the zero line of OA mass changes. The dashed and solid lines in (c, d) are linear regression lines for samples with and without cloud processing, respectively.

From Fig 1(a-b), we find that cloud processing plays a significant role in affecting OA mass. For dry cases, where aerosols that do not undergo cloud processing (grey dots), OA enhancement factors $\Delta(\text{OA}/\text{CO})$ are either slightly above or around zero, indicate OA mass increases lightly or remains unchanged. Whereas for wet cases, where aerosols have subjected to cloud processing (coloured dots), $\Delta(\text{OA}/\text{CO})$ values are negative, showing the decrease of OA mass. The reduced OA can be up to 70%, showing the strong wet removal of BB particles by clouds. The magnitude of wet removal may be related to the cloud processing intensity, as most of the wet cases show the stronger cloud processing (higher of cloud liquid water content, longer of aerosols stay in clouds), the more reduction of OA mass.

Two of the dry cases clearly exhibit the increase of OA, indicating the formation of SOA. Although the modified combustion efficiency (MCE) of those two cases are slightly lower than others, they are still higher than 0.98 (Fig. S7), suggesting all BB emissions in our study are from similar flaming fires, consistent with recent studies^{40,43}. Therefore, the increased OA mass results from the ageing process rather than different burning conditions. From these two cases, we find that $\Delta(\text{OA}/\text{CO})$ decrease with further ageing hour (the transport time of BB aerosols between two observations) increase from ~30 to ~60, indicating that SOA formation peaks before 30 hours of further ageing, after which OA mass starts to decrease. The decrease of OA mass may indicate fragmentation processes such as photolysis, which can cause carbon-carbon bond cleavage and result in smaller and more volatile compounds, becoming dominant after ~ 30 hours of further ageing. This finding is consistent with a filter-based study which found that CLARIFY has more volatile OA⁴⁴. After ~ 60 hours of further ageing, $\Delta(\text{OA}/\text{CO})$ remains around zero for dry cases, indicating that SOA formation and OA volatilisation rates are in equilibrium, resulting in a negligible change in OA mass, and suggesting the remaining OA is more resistant to photolysis.

For both dry cases and wet cases, the oxidized organic fraction f_{44} continues to increase with ageing, despite that OA mass is decreasing or remains unchanged (Fig. 1 (c-d)). The increased amount of f_{44} is linearly correlated with the total hours of daylight for dry and wet cases, indicating that the oxidation of organic aerosol is generally dominated by direct sunlight (photochemical) induced reactions. However, in comparison to the dry cases, f_{44} in wet cases increases even more at the same ageing time, indicating the contribution of cloud processing. There are two potential ways in which cloud processing can result in a higher Δf_{44} , 1) increase in SOA via aqueous-phase reactions, and 2) reduce the mass of less oxidised OA components. Previous studies found that f_{44} correlates strongly with the

OA oxygen-to-carbon (O:C) ratio ⁴⁵, which is also used as a proxy for the hygroscopicity of OA ⁴⁶; thus, OA with higher f_{44} can be assumed to have a higher hygroscopicity and can be more effectively removed by cloud droplets. Therefore, it seems likely that the increase of f_{44} results from SOA formation by cloud processing. This finding highlights the importance of the aqueous-phase reactions, which can increase the highly oxidised OA mass, resulting in more easily activated CCN and further affecting the stratocumulus cloud deck when BB aerosol interacts with the cloud layer. Although observational evidence of SOA aqueous formation is rare, our result is supported by numerous laboratory and modelling studies ^{47,48}.

3.2 Variation of BB aerosol size distribution

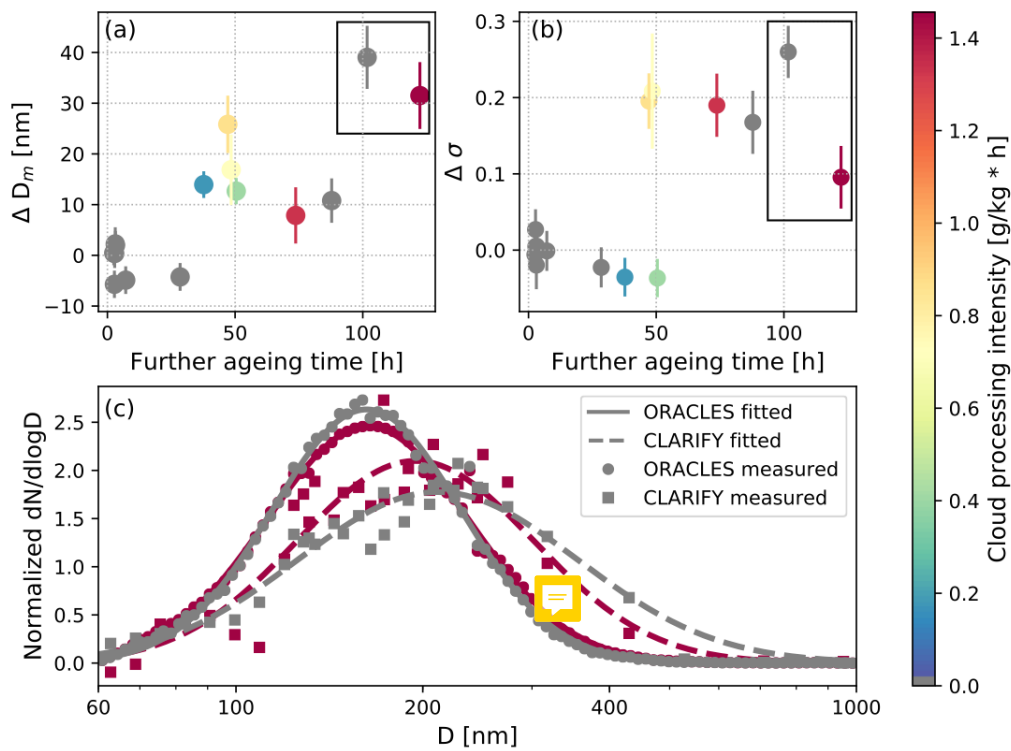


Figure 2. Evolution of (a) aerosol mode diameter D_m and (b) geometric standard deviation σ with further ageing time. (c) Corresponding ORACLES and CLARIFY aerosol size distributions from two cases in the black box of (a) and (b). The dots and error bars in (a-b) are mean values and standard errors from Gaussian error propagation. The dots in (c) are mean particle size distribution data measured by upwind ORACLES, whereas the squares are means from downwind CLARIFY. The solid lines are the fitted size distributions from ORACLES, and dashed lines are fitted size distributions from CLARIFY. The Grey colour represents cases with no cloud processing, and the colourmap indicates the cloud processing intensity.

From Fig. 2 (a), the aerosol mode diameter D_m generally increases with ageing, consistent with Capes et al. (2008). The increased mode diameter can be up to 40 nm, exhibiting considerable changes in BB

aerosol distribution by ageing. The geometric standard deviation σ also generally increases with ageing for cases that show a clear increase in D_m (Fig. 3b). Therefore, the variation in these two parameters indicates that aerosol size distribution broadens and shifts the peak towards larger diameters as it ages. Cloud processing shows no apparent effect on D_m ; however, for cases where the σ is significantly increased, strong cloud processing tends to reduce the σ , suggesting that cloud processing can narrow the aerosol size distribution. To provide a clearer view of the evolution of aerosol size distribution with ageing, two examples have been selected to represent the two most aged cases with and without cloud processing, as in the black box in Fig. 2 (a-b). The changes in the normalized aerosol size distributions for those two cases are illustrated in Fig. 2 (c).

As can be seen in Fig. 2 (c), for both cases, ageing broadens particle size distributions and shifts it towards larger diameters, resulting in a decrease in aerosols at the small sizes (< 200 nm) and an increase at the large sizes (> 200 nm). The possible cause of these changes is the coagulation of small particles with ageing, as the condensation growth would become very slow or even stops when ageing time has been too long. The strong inversion under the plume layer may have prevented the vertical dilution, thus facilitating coagulation growth. Despite the fact that coagulation should be much obvious in fresher BB aerosols, this result highlights the importance of its role for very aged plumes in the SEA. Another possible explanation is the effects of aerosol chemical evolution with ageing. Specifically, BrC bleaching and OA photolysis may mostly occur in the small size range, while SOA may more easily condense on large particles, creating the shift in the aerosol distribution. Comparing these two cases, it can be seen that the aged aerosol distribution (dash lines) is narrower in the case with cloud processing, as demonstrated by the lower fraction of larger particles (>200 nm). Therefore, the reduction of σ by cloud processing is mainly reflected in the removal of large particles. This is because large particles are good CCN candidates and can be more effectively removed by cloud droplets. However, even in the presence of cloud processing, the aged aerosols still exhibit an increased proportion of large particles. In general, ageing shifts the aerosol distribution towards larger sizes and increases the proportion of large particles. With the increase of the aerosol hygroscopicity resulted from f44 increasing, the ageing process can be an important source of CCN, especially in the intermediate and clean SEA marine boundary layer ⁴⁹.

3.2 Variation of BB aerosol optical properties

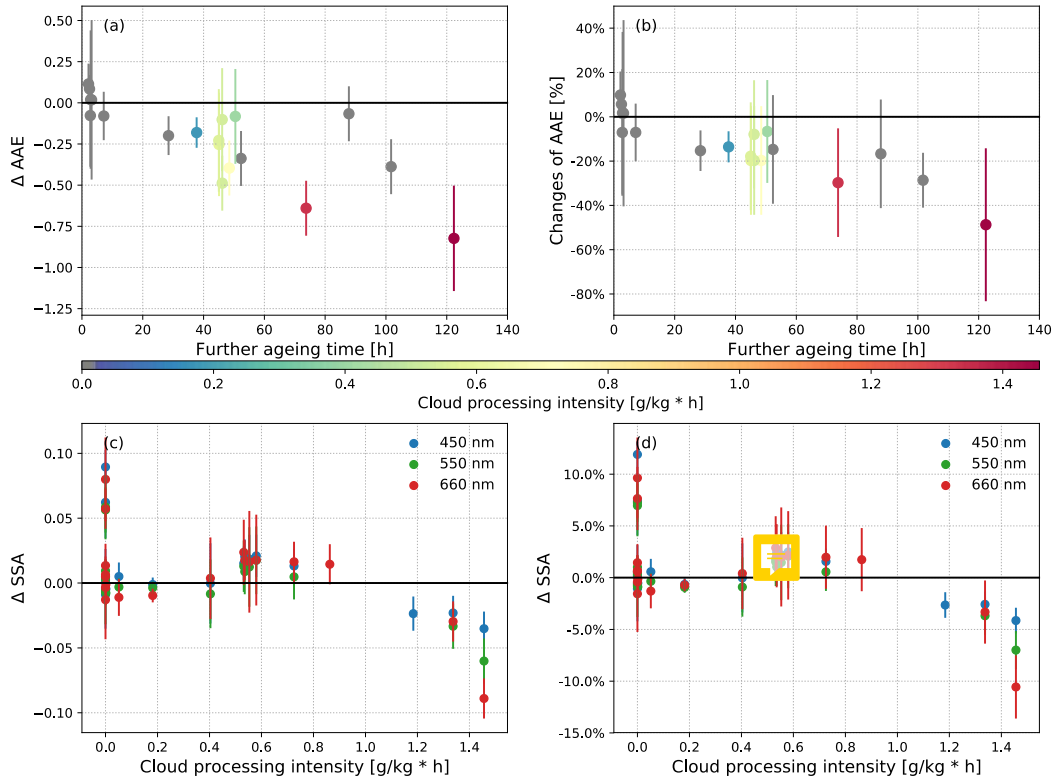


Figure 3. Evolution of (a) AAE and (b) changes of AAE in percentage with further ageing time; (c) the impact of cloud processing on SSA and (d) changes of SSA in percentage. The dots are mean values, and the error bars are standard errors from Gaussian error propagation. The grey colour in (a-b) represents cases with no cloud processing, while the colour map represents the cloud processing intensity. Blue, green, and red dots in (c-d) represent SSA at different wavelengths.

The changes in AAE with ageing and cloud processing are illustrated in Fig. 3 (a-b). Overall, AAE decreases with ageing. The longer it ages, the greater the decrease in AAE, with a maximum reduction of up to 50%. The decrease of AAE indicates the diminishing of the wavelength dependence of the light-absorption coefficient of BB aerosol. For dry cases, the decrease of AAE indicates photochemical degradation of BrC with ageing, as its absorption coefficient has a strong spectral dependence. This finding is consistent with the result of Zhang et al. (in prep.), which suggests upwind ORACLES has more BrC than downwind CLARIFY observations. For wet cases, the aqueous-phase processing and oligomerization of water-soluble organics have been recognized to form light-absorbing BrC, suggesting cloud processing an important source of BrC⁵¹. However, our results find AAE decreases even more for stronger cloud processing cases, suggesting that the contribution of BrC from the aqueous-phase reaction is overridden by wet removal. In general, BrC is considered hygroscopic²⁹, as even tar balls, the most refractive and least hygroscopic BrC, is able to completely dissolve in water droplet under supersaturation⁵². Therefore, its hygroscopic properties lead to the dominance of the wet removal of BrC, resulting in a decrease in AAE. Alongside the above, AAE is highly sensitive to particle size distribution for compact and coated BC, with large particles having a smaller AAE⁵³. As

we have shown in the previous section, ageing increases the mode diameter of aerosol distribution. Thus, the increase in particle size due to ageing is also responsible for the decrease in AAE.

The trend of Δ SSA with ageing is less clear due to the limited data (Fig. S8). However, we find Δ SSA generally decreases with cloud processing intensity (Fig. 3 c-d). For cases with cloud processing intensity smaller than 1 g/kg*h, Δ SSA is approximately equal to or greater than 0, suggesting the possible increase of the SSA for aged BB aerosol. Haywood et al. studied fresh⁵⁴ and 5 hours aged⁵⁵ BB plumes in Southern African during SAFARI-2000 and also found that the aged BB aerosol has a higher SSA. This is likely due to the condensation of scattering material and change in black carbon (BC) morphology from a chain agglomerate to a more spheroidal shape⁵⁶. The BB plume in our study is more aged with mostly compact BC⁴⁴. However, as we illustrated previously, ageing can increase the large particle fraction. Since scattering is highly dependent on diameters, such increase can result in an increase in SSA. For samples with stronger cloud processing, SSA decreases. The higher the cloud processing intensity, the larger the reduction of SSA. The decrease of SSA due to cloud processing can be up to around 10 %, and may result from the wet removal of large particles and thickly coated BC by cloud droplets. Ground-based *in-situ* measurements on Ascension Island showed the lowest SSA values compared to all previously reported observations in the SEA^{37,57}, which can be explained by cloud processing, as the BB plume needs to travel through the extensive stratocumulus cloud deck to reach their sampling location.

4. Conclusion and Discussion

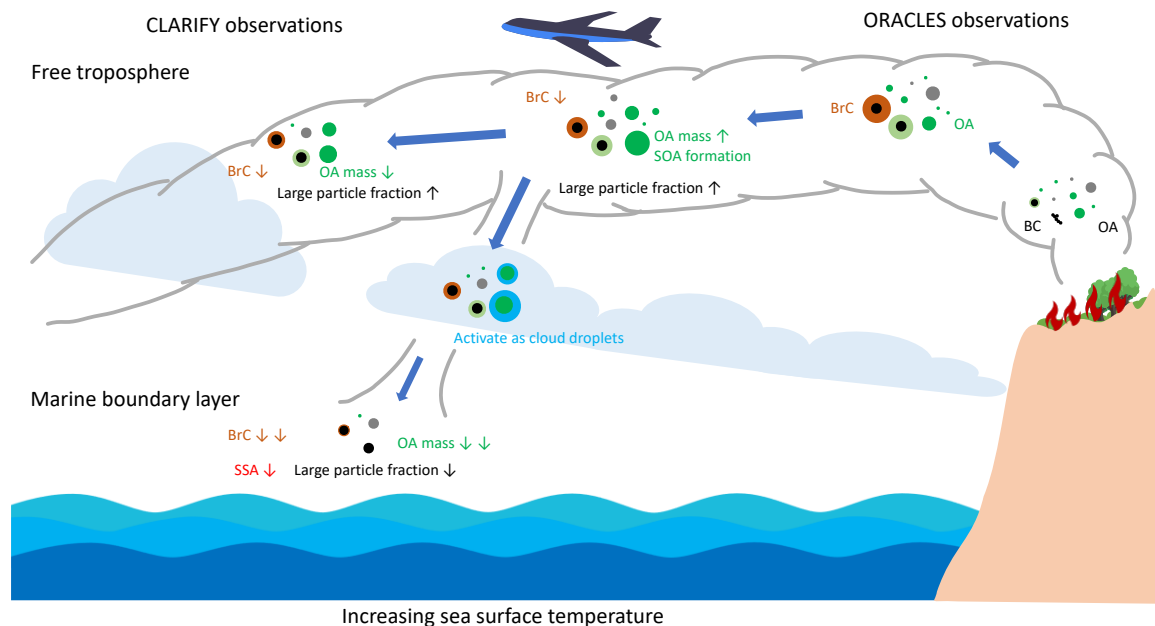


Figure 4. Schematic showing the evolution of BB aerosols with ageing and cloud processing during the westward transport in the SEA. For a clear visualisation of the aerosol changes, most of the aerosols in the figure are externally mixed, which would not match reality, and the actual aerosol mixing is beyond

the scope of this paper. The aerosol changes are illustrated with upward and downward arrows during transport, indicating increases and decreases. Two arrows suggest a significant change. Note those changes are compared to the previous step connected by the big blue arrow.

By linking observations from upwind and downwind areas with trajectories, we investigated the BB aerosol evolution with ageing in the SEA. The main conclusions are presented in Fig 4 schematically. All BB aerosols measured are emitted from flaming fires, with MCE all above 0.98. Our results suggest SOA formation prevails when the further ageing time is less than ~ 30 hours. Taking the average age of BB aerosols measured at the upwind location ~ 40 hours into account (detailed in supplement), it may suggest SOA formation dominate in ~ 70 hours transport of the BB plume after emission. This time scale is significantly longer than previous studies, partly because the strong inversion layer below the plume has prevented vertical diffusion, resulting in relatively high levels of volatile organic compound in the plume. This finding of SOA formation after long time of transport has significant implications on the regional climate, as SOA can modulate BB aerosol direct and semi-direct radiative forcings by affecting BBA optical properties. SOA also can affect the indirect radiative forcing by providing more CCN, as it has a higher hygroscopicity. After ~30 hours of further ageing (~70 hours in total), SOA formation rates may have dropped to a very low level, resulting in the decrease of OA mass, which may be related to the photolysis. At ~ 60 hours of further ageing (~ 100 hours in total), OA mass falls back to the approximate amount measured in the upwind and generally remains constant afterwards, implying that OA is in a dynamic equilibrium between SOA formation and photolysis. However, it is still higher than that freshly emitted, considering the formation of SOA in the first 40 hours after emission. These results can provide key information of the time scales of different effects on the long-lived BB aerosols in the SEA, contributing to a better parameterisation in models. Cloud processing shows a significant reduction in OA mass, showing strong wet removal of OA. The oxidised OA fraction f₄₄ increases steadily with ageing, regardless of the aerosol has undergone cloud processing, and even more markedly if it has, suggesting the continuous oxidation of OA and highlight the aqueous-phase oxidation by clouds.

Besides its effect on BB aerosol chemical composition, ageing also has a significant effect on the physical properties of BB aerosol. With ageing, aerosol size distribution shifts towards larger diameters and the proportion of large particles increases significantly, indicating the important role of coagulation. The increased large particles can result in an increase in CCN, which is very important in the SEA, as the emitted BB aerosol would eventually subside and merge into the gradually deepening marine boundary layer⁵⁸. Comparing aged aerosols that have experienced cloud processing with those not, cloud processing markedly suppresses the increase in the large particles proportion, indicating the effect of clouds on the removal of large particles. As a result of physical and chemical changes of BB aerosol caused by ageing and cloud processing, its optical properties evolve correspondingly. The decrease of AAE may be driven by a combination of causes, one of which is the increase of particle size, as larger particles have a lower AAE. The photochemical bleaching of BrC with ageing may be another reason in reducing AAE. Sedlacek III et al. (submitted) find a decrease in BC coating after a long period of transport of BB plume, which could also be another reason for the decreases in AAE. For those aerosols

that experience cloud processing, one additional reason for the decrease in AAE is the wet removal of BrC, as BrC is generally hygroscopic and can completely dissolve in water droplet under supersaturation. We also find SSA decreases with cloud processing, which may be because the cloud processing can remove large particles and make BC more compact. In addition, thick coated BC particles can also be removed by clouds, as they have a higher hygroscopicity. The reduction of SSA by clouds may suggest the BB aerosol in the SEA boundary layer is more absorbing, as BB aerosols generally need to travel through clouds to reach the marine boundary layer. Those changes in SSA may have a significant effect on the regional radiation balance, as the direct radiative forcing of BB aerosol is sensitive to the SSA⁸. However, as the number of linked samples is relatively scarce, we encourage more multiple aircraft observations to untangle the BB aerosol-cloud-radiation caused by aerosol ageing.

Acknowledgements

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8 Biomass Burn Aerosol Lifecycle into Three Aging Regimes. (submitted).

Review replies to "Cloud processing and weeklong ageing significantly affect the biomass burning aerosols over the southeastern Atlantic" by Haochi Che et al.

We would like to thank all reviewers for their constructive comments and suggestions on the manuscript. The feedback has allowed us to clarify aspects of the paper and to improve our paper.

The reviewer's comments are provided in **blue in the following**, and our responses are in **black**. Changes to the manuscripts made in response to the reviewer are in **green**. In addition, numerous changes in the manuscript are not shown in this response but are highlighted in the revised version.

Reviewer #1:

This study investigates the evolution of BB aerosol as it transports westward over the southeastern Atlantic. They use in situ measurements data from two field campaigns, CLARIFY and ORACLES. They compare the composition, organic fraction, size distribution, and optical properties of the BB aerosol upwind and downwind along the trajectories.

The study provides interesting information on BB aging however, I miss supporting information from satellites. Remote sensing observations of the aerosol properties (AOD, SSA, AE, effective radius, aerosol height (from LIDAR) could all give a better perspective on what is measured and where.

We appreciate the reviewers' suggestions. However, we are not convinced that satellites can provide more accurate data on aerosol scattering, absorption and SSA than aircraft observations. Peers et al. (2019) estimated an uncertainty of 40 % on the above-cloud AOT from the SEVIRI products, indicating a high uncertainty in aerosol satellite data. The persistence of stratocumulus clouds can worsen this situation, especially for retrieving the optical properties of aerosols in the boundary layer and close to clouds. Obtaining SSA from satellites is even more challenging, with large uncertainties in absorption and scattering (Sayer et al., 2020). Pistone et al. (2019) compared SSA from both in-situ and remote-sensing instruments during ORACLES 2016 (see figure below, Fig. 11 in the manuscript; AirMSPI is a remote sensing polarimeter, 4STAR is a remote sensing sunphotometer, and PSAP is an in-situ measurement). Even when using onboard remote-sensing instruments to retrieve SSA, the large error bars and uncertainty do not seem to be able to contribute to better or tighter constraints than in-situ measurements. Also, in this comparison, we see that the in-situ and the remote-sensing instruments agree, overall (given their error bars and general uncertainties). Furthermore, remote-sensing instruments such as 4STAR, AirMSPI and SEVIRI only give the total column quantities, which integrates different plume layers that can add to their overall uncertainty.

Active sensors, although much better in portraying optical properties along the vertical such as the CALIOP/CALIPSO Lidar satellite had experienced many issues during the investigated measurement period, with an overpass once every 16 days over the region. There were Lidar instruments (HSRL in the ORACLES and 355 nm backscatter Lidar in the CLARIFY) on the aircrafts, and these can be used to give some context. Nevertheless, airborne Lidar measurement have a gap below and above the plane, and often will not coincide with the in-situ aerosol layer in most cases.

Indeed, satellites can provide a broader context on the region, which was demonstrated in the overview papers (Redemann et al., 2021, Haywood et al., 2021), as well as in the regional examinations of aerosol above and below cloud (e.g. LeBlanc et al., 2020, Chang et al., 2021). Nevertheless, as the focus of the investigation here is the Lagrangian changes along an aged trajectory, we feel that daily or even hourly total column observations are not as adequate enough to support our analysis. Therefore, in this work we have focused on in-situ measurements along the trajectory path. We did incorporate cloud properties from satellites along the trajectory, as suggested by the reviewer, and detailed below.

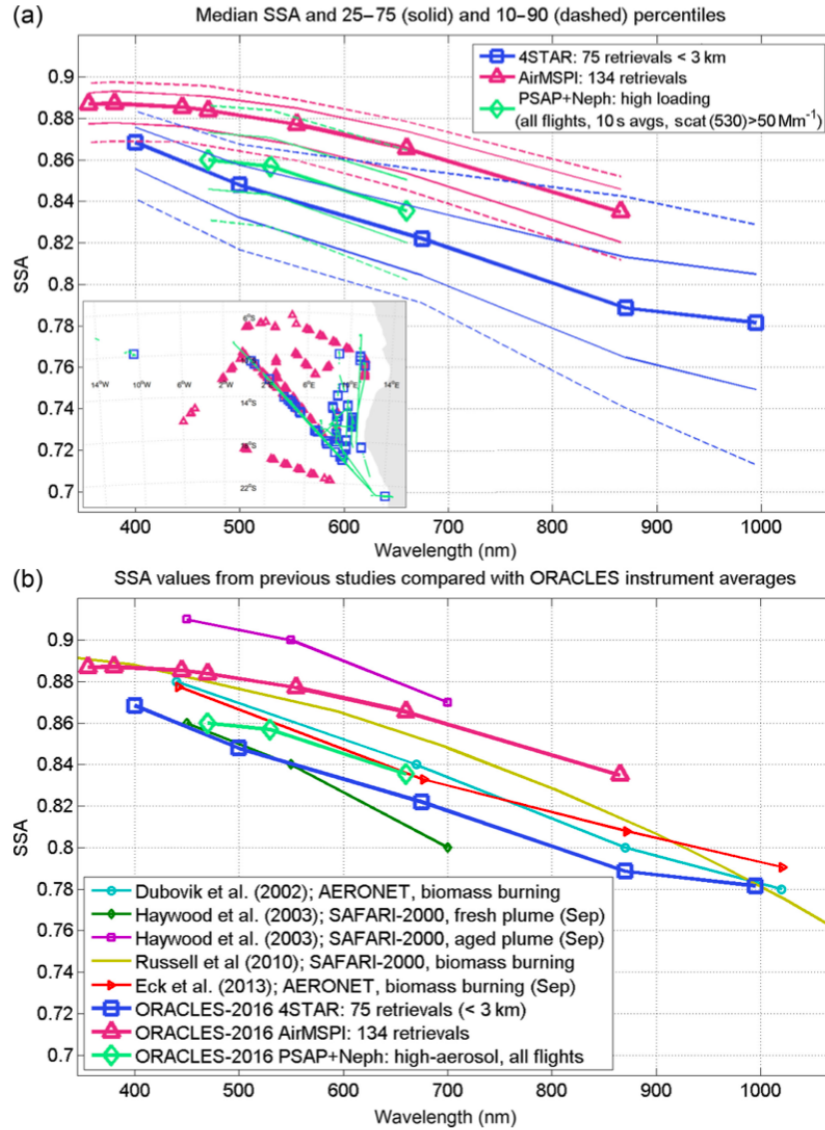


Figure. (a) SSA from all measurements/retrievals over ORACLES-2016, from 4STAR, AirMSPI, and the nephelometer and PSAP in situ data. The campaign-wide median is indicated by the thick solid line, 25th–75th percentiles are indicated by thin solid lines, and 10th–90th percentiles are indicated by the dashed lines. Note that the medians of the different instruments are not strictly comparable, as the campaign-wide averages are calculated using more data than just the coincident cases. The inset shows the spatial distribution (latitude/longitude) of measurements by the three instruments. (b) The median SSA by the instrument, as shown in panel (a) compared with SSA from previous studies in this same region.

On the same note, their results suggest that cloud processing is one of the main factors controlling changes in BB. Therefore I would recommend explaining the cloud processing estimations in more detail. Using reanalysis information for estimating the cloud properties along the trajectories is a good first approximation but I am not sure how reliable it is on the scales needed for this analysis. What if the cloud fraction is not uniform? Then the liquid water content values will be different than the mean. Geostationary satellites could be used to follow cloud properties along the trajectories and polar-orbiting (that usually provides more detailed microphysical information) could be used to have a better perspective on the type of clouds and expected LWC.

This is a very good suggestion. The resolution of the ERA5 data is 0.25, and the geostationary satellites can indeed provide much higher resolution data (3km), allowing us to better assess the cloud processes. High-spatial resolution geostationary data (3 km at the subsatellite point with a repeat cycle of 15 min) from SEVIRI on the Meteosat Second Generation satellite are used to retrieve cloud properties (using an algorithm similar to MODIS) from the NASA Langley cloud retrieval for the ORACLES campaign. An air mass that experiences cloud processing is defined as one that has clouds on its transport trajectory, and the height of the air mass is below the cloud top height and above the cloud base height. Then the cloud liquid water content is calculated for those air masses with cloud processing. The SEVIRI indeed have a much higher temporal and spatial resolution than ERA5, enabling us to estimate the cloud processing. However, this method highly depends on the vertical cloud location. A comparative study of cloud top height (CTH) retrievals found that on average, the CTHs detected by the SEVIRI algorithms are 1.0 to 2.5 km lower than CALIOP observations (Hamann et al., 2014). For optically thick clouds, the correlation coefficients between the SEVIRI and CALIOP are usually above 0.95, while for multi-layer clouds, the correlation coefficients are between 0.6 and 0.8. Clouds over the Southeast Atlantic are mainly single-layer stratocumulus, while studies have also found that mid-layer clouds are also frequent in this region (Adebiyi et al., 2020). Therefore, these results suggest that the use of SEVIRI data to estimate the contribution of clouds to aerosols is influenced by cloud top height retrieval and thus has some uncertainties.

Besides the clouds, the GPM (Global Precipitation Measurement) IMERG (Integrated Multi-satellite Retrievals for GPM) precipitation V06 final run data (Huffman et al., 2019) is also used to identify the precipitation in the studied area. IMERG is an algorithm of GPM which aims to combine multiple types of satellite data, including microwave satellite data and infrared satellite data, station gauge data, and others. The data has a high spatial resolution of 0.1 degrees and is available every half hour. During the transport of the air mass, if the height of the trajectory is lower than the height of the cloud base and precipitation occurs at the location of the air mass, the air mass is determined to be influenced by precipitation. Only one sample was found to be slightly influenced by precipitation, with the accumulated precipitation of around 0.003 mm. Therefore, we removed this sample to avoid the influence of precipitation on the aerosol fuming transport. The cloud base height is from the SEVIRI cloud product.

The cloud processing in the draft is then represented by the liquid water content derived from the SEVIRI, and the sample with precipitation has also been removed. All relevant figures have been updated accordingly, and the related discussion also has been revised and highlighted in the draft. Here we show Fig. 1 as an example of the updated figure. It is worth noting, however, that although the values of the cloud processing are different, it do not affect the main conclusions and is generally consistent with the results obtained using ERA5 reanalysis data.

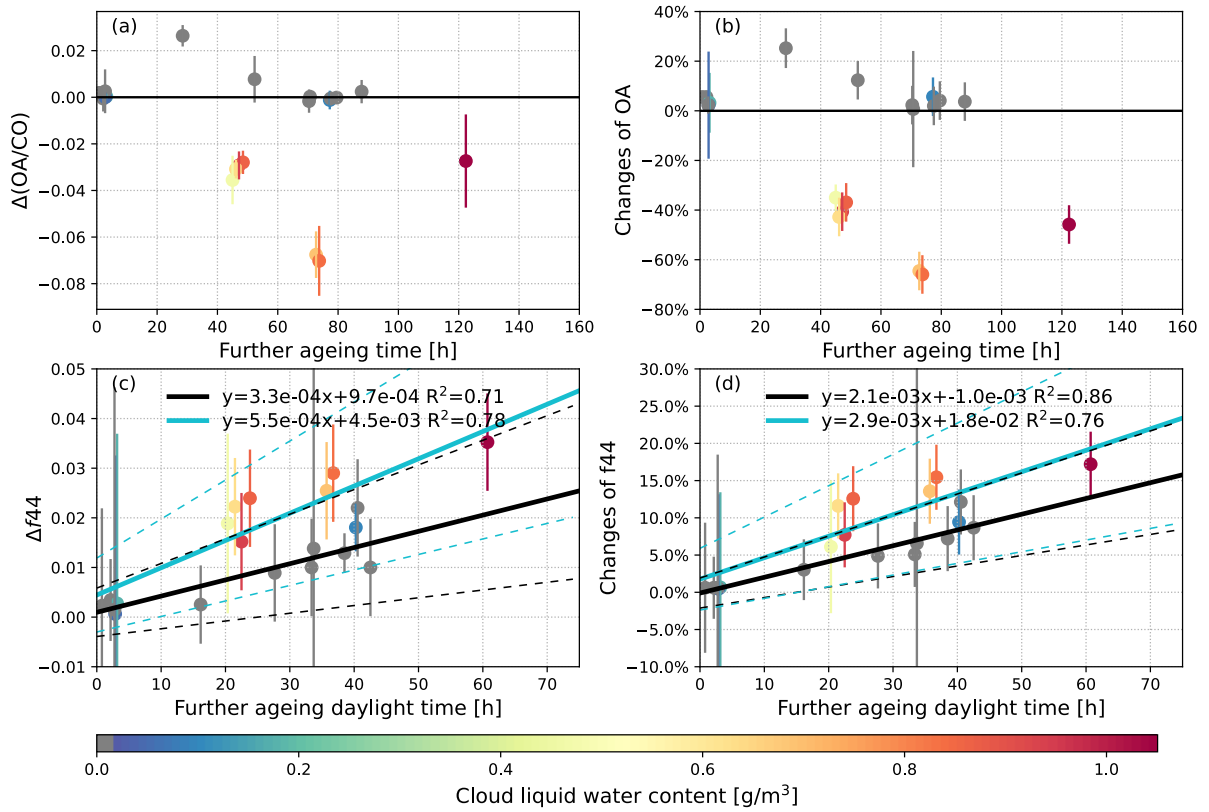


Figure 1. Evolution of (a) OA enhancement factor $\Delta(\text{OA}/\text{CO})$ and (b) changes of OA in percentage with further ageing time, which is the transport time of BB aerosols between upstream and downstream observations; (c) enhanced f_{44} and (d) changes of f_{44} in percentage with further daylight ageing time during the transportation of the BB. The dots are mean values for linked cases, and the error bars are standard errors calculated from Gaussian error propagation. The colourmap indicates the mean cloud liquid water content within the last day of the transport derived from the SEVIRI satellite data (detailed in the method), and the grey colour represents samples with no cloud processing. The black horizontal line in (a, b) is the zero line of OA mass changes. The dash and solid lines in (c, d) are linear regressions and 95% confidence intervals for samples with cloud processing (cyan coloured lines) and without (black coloured lines). The fitted equations and R^2 values are shown in each of the plots.

Finally, I may miss information but It is not clear why only the last 24 h are considered for cloud processing. What if the aerosols passed through clouds before that.

During aerosol transport, clouds can effectively remove some aerosols and affect their chemical composition; however, if cloud removal occurs long before the observation (e.g., more than one day before), the aerosols will again undergo mixing and ageing during the subsequent transport after leaving the cloud region, resulting in further changes in their chemical composition and mixing state. In this case, the effect of clouds on aerosols is mixed with the aerosol ageing and it is difficult to separate the two processes effectively. In fact, we have analyzed the effect of the cloud processing on the longer period, and found that the mass of aerosol did not change significantly throughout the transport. We suspect that the BB aerosols were mixed with others (e.g. sea salt) within the boundary layer after it left the clouds. Therefore, it is difficult to determine the actual contribution of the cloud to aerosols by taking a longer period of cloud processing into account.

To examine the effect of cloud processing on aerosols, the ideal situation is to measure the aerosol before and immediately after they pass through clouds. However, it is difficult to achieve this practically with aircraft observations. By considering the cloud processing as aerosol goes through clouds in the last day of the transport, we assume that aerosols do not receive significant mixing and other ageing effects within 24 hours after being subject to cloud processing. Although also subject to uncertainties, this assumption allows us to distinguish and assess the role of clouds on aerosols. To avoid confusion for readers, the identification of cloud processing is discussed further in the manuscript, as shown below.

The Spinning Enhanced Visible and InfraRed Imager (SEVIRI) on the Meteosat Second Generation satellite was utilized here, using cloud properties generated by NASA Langley (Minnis et al., 2011). The SEVIRI cloud data has a high resolution (3 km at the subsatellite point with a repeat cycle of 15 min) and was used to provide cloud processing information by collocating with the linked trajectories. An air mass that experiences cloud processing was defined as one with cloud liquid water content above 0.01 g/m^3 on its trajectory, and an air mass height above cloud base and below cloud top. The accumulated cloud liquid water content within 24 hours before the air mass reached the downwind linked location was calculated and used in our analysis. By considering the aerosol cloud processing in the last day of transport, we assume that aerosols are not subject to significant mixing and other ageing effects in the 24 hours after being in-cloud. As the cloud processing estimate requires the vertical height of the cloud, the uncertainty in SEVIRI cloud height can therefore lead to uncertainties in the cloud processing (Hamann et al., 2014). Fig. S5 shows an example of a linked case with cloud processing along with its trajectory.

The GPM (Global Precipitation Measurement) IMERG (Integrated Multi-satellitE Retrievals for GPM) precipitation V06 final run data (Huffman et al., 2019) was used to identify precipitation. The data has a high spatial resolution of 0.1 degrees and is available every half hour. During the transport of the air mass, if the height of the trajectory was lower than the height of the cloud base, and precipitation was present at the location of the air mass, the air mass was determined to be influenced by precipitation. Only one sample showed a slight influence due to precipitation, with an accumulated precipitation of around 0.003 mm. We removed this sample to remove the effects of precipitation from our linked cases.

Reviewer #2:

In their paper, Hoachi Che and colleagues link through lagrangian trajectories aerosol and BB emission tracers measured on flights during a campaign over the southeastern Atlantic, in order to derive aging characteristics of organic aerosol mass, and its oxidative, size distribution and optical properties. They present interesting results which I think merit publication in Nature Communications Earth and Environment. The results are somewhat explorative due to relatively small number of cases, but observations over this area are scarce. However, several major questions need to be answered before publication. We are particularly grateful to the second reviewer who revised the manuscript in great detail and made very helpful comments.

1) How to make sure that the encountered air parcels during the linked flights are indeed affected by biomass burning emissions. The only criterion given is that a back trajectory passes over fire pixels, but is this sufficient? This requires that fire emissions are transported up to the trajectory height (often in the mid-troposphere). To make sure this point, absolute BB emission tracer concentrations, here CO, should be given and compared to background unaffected by fire emissions. The main paper and also the SI only show tracer ratios or differences required for the aging analysis, but no absolute concentrations.

are transported in the free troposphere due to the high altitude of the continent and the low marine boundary layers (Che et al., 2022; Gordon et al., 2018). The background concentration of CO is around 60 ppb (Wu et al., 2020a); therefore we excluded samples with CO concentrations less than 100 ppb to ensure that the aerosols we sampled were influenced by biomass burning. Four samples with CO concentrations less than 100 ppb, all of which have been removed. In addition, we also removed one sample which was affected by

precipitation. The new linked samples are illustrated in the following table, and can be found in the supplement.

Table S1. The summary of linked cases. There are 11 ORACLES linked with CLARIFY cases and 12 ORACLES linked with ORACLES cases.

ID	Linked with	Upwind Altitude (m)	Downwind Altitude (m)	Upwind CO (ppbv)	Age of fire at upwind (h)	Transport time (h)	Trajectory distance (km)	Cloud processing *
20170815_1c	CLARIFY	2077	1346	311	46	72.7	2019.7	Y
20170815_2c	CLARIFY	2078	1421	310	44	73.7	2057.8	Y
20170817_1c	CLARIFY	1673	1698	215	48	48.2	909.6	Y
20170817_2c	CLARIFY	1672	1644	211	48	48.5	894.9	Y
20170817_3c	CLARIFY	1670	1669	267	40	45.0	899.9	Y
20170821c	CLARIFY	5791	4572	211	39	87.8	2083.6	N
20170824c	CLARIFY	3314	2247	362	41	122.0	2091.9	Y
20170826_1c	CLARIFY	5322	4499	119	36	77.5	2465.8	N
20170826_2c	CLARIFY	5318	4254	121	32	70.7	2600.1	N
20170826_3c	CLARIFY	5799	4565	114	35	77.5	2596.2	N
20170830c	CLARIFY	4469	3889	489	39	52.3	1788.8	Y
20170813_2o	ORACLES	1524	1598	294	45	2.5	49.0	N
20170815_1o	ORACLES	2078	1683	387	47	47.7	1377.5	Y
20170826_2o	ORACLES	5798	5759	126	38	3.0	98.1	N
20170826_3o	ORACLES	1124	1102	155	38	3.2	56.0	N
20170826_4o	ORACLES	1071	1066	154	40	2.9	51.1	N
20170826_5o	ORACLES	1020	1245	191	39	2.8	59.6	N
20170826_6o	ORACLES	1624	1582	155	38	35	62.7	N
20170826_7o	ORACLES	1020	943	196	38	3.1	67.3	N
20170828_1o	ORACLES	5815	4492	119	39	124.7	2718.0	N
20170828_2o	ORACLES	5800	4554	132	41	118.4	2565.5	Y
20170830o	ORACLES	3560	2818	333	36	28.5	680.1	N
20170831o	ORACLES	3362	2950	362	34	7.2	108.1	N

Note we have also recalculated the linked samples by relaxing the linking conditions. There are now a total of 23 linked samples. However, not all linked samples include AMS, SP2, aerosol scattering /absorption and size distribution observations. Some of the ORACLES linked with ORACLES samples only have few observations available.

2) The organic aerosol aging analysis differentiates dry and wet trajectories, with cloud processing for the

latter ones. It should be noted that the dry cases usually occur at much higher mid-tropospheric altitudes, while the wet ones are located at lower altitudes where they meet the lower atmospheric stratocumulus cloud. Thus the discussion of results should recognize that there are correlated discerning factors, including height and temperature in addition to cloud processing. How would this affect the discussion? For instance, lower temperatures at higher altitudes affect the phase distribution for SVOC species.

Many thanks to the reviewer's suggestion. We calculated the change in temperature along with the transport of the BB aerosols in this revision and included it in the manuscript in Section 3.1. Indeed, as the reviewer suggested, the change in temperature is also closely related to the change in OA mass. As shown in the figure below, the samples where we found a significant decrease in OA were all those where the temperature had increased with transport.

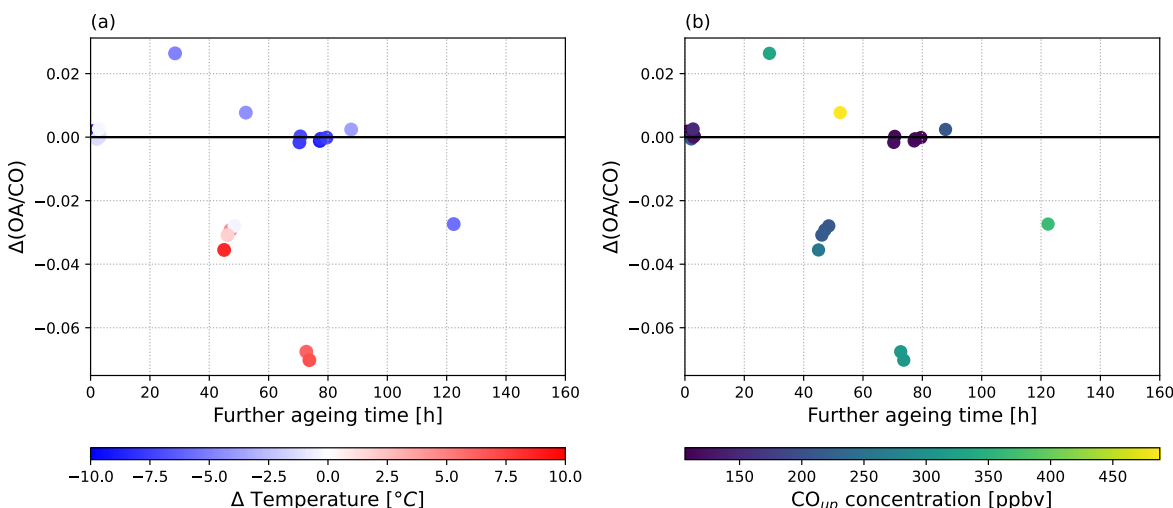


Figure 2. Evolution of OA enhancement factor $\Delta(\text{OA}/\text{CO})$ with further ageing time (ageing hours since the upstream observation) coloured by (a) variation in temperature and (b) upstream CO concentrations (CO_{up}) during transport of the linked BB samples.

In Fig. 2(b), BB aerosols that experience an increase in temperature during transport also show a decrease in organic matter. It is, however, worth noting that it is difficult to distinguish whether the decrease in organic matter is mainly due to the clouds or to temperature changes. For aerosols that experience cloud processing, the temperature increases during transport due to subsidence from the free troposphere to the marine boundary layer. Therefore, the cloud processing is often accompanied by an increase in temperature. Dang et al. (2021) found BB aerosols to have low volatility from the ORACLES campaign based on an analysis of filter samples. This may indicate that the change in temperature does not significantly affect organic matter. In addition, the sample represented by the rightmost point in Fig 2(b) shows a decrease in the OA mass with transport, and also a slight decrease in temperature (probably because the aerosol was in or close to the inversion layer initially). This inconsistency may indicate that temperature changes did not significantly affect the organic matter; the change in organic matter in this sample was mainly due to the strong cloud processing. However, the role of temperature on organics is challenging to determine due to the lack of direct observations of the volatility of organics, so we included a discussion of the temperature in the revised manuscript in section 3.1 and highlighted all modifications.

In addition to clouds, temperature is another important factor influencing OA matter and ageing. Fig. 2 (b) illustrates the temperature variations during the transport of the linked BB aerosols, where the temperature increases for those samples with significantly decreased OA mass. This result suggests that the increase in temperature may also contribute to reducing OA mass, likely resulting from the evaporation of high volatile OA. However, as the aerosol spends more time in the atmosphere it subsides, reaching a warmer temperature, suggesting the reduction in OA and the increase in temperature may be independent. Dang et al. (2021) found that OA measured in ORACLES has lower volatility than CLARIFY OA; therefore, the change in OA mass due to temperature is likely to be minor, suggesting that cloud processing may be the dominant factor behind the reduction in OA mass.

3) The quasi linear increase of the oxidation status (f_{44}) with respect to photochemical processing time is an interesting result and puts confidence on the method. However, the discussion of the larger Δf_{44} values is unclear (« thus, OA with higher f_{44} can be assumed to have a higher hygroscopicity and can be more effectively removed by cloud droplets. Therefore, it seems likely that the increase of f_{44} results from SOA formation by cloud processing »). The second statement can not be concluded from the first one, as the first one talks about removal processes and not formation. Please clarify.

Thank the reviewer for this comment. We have re-analysed the variation of f_{44} and revised the manuscript. The above sentence has been removed, and the new analysis is shown below.

For both no-cloud and cloud-processed cases, the oxidised organic fraction of f_{44} increases with ageing in Fig. 1(c-d), despite OA mass decreasing or remaining unchanged (Fig. 1 c-d). Comparing the further ageing time, the increased amount of f_{44} is better linearly correlated with the hours of daylight time of further ageing, indicating that the oxidation of organic aerosol is generally dominated by photochemical or OH (also related to sunlight) induced reactions. Both no-cloud and cloud-processed samples have good linear relationships for f_{44} and daylight time, with R^2 higher than 0.7, and all samples are within the 95% confidence intervals. f_{44} has a higher rate of increase in cloud-processed cases rather than no-cloud cases at comparable aging points, indicating the contribution of cloud processing to f_{44} . There are two potential ways in which cloud processing can result in a higher Δf_{44} , 1) increases the fraction of SOA via aqueous-phase reactions, and 2) reduction in the mass of less oxidised OA components. As the air mass enters the cloud layer, the mass of both high and low oxidised OA is reduced by the cloud droplets and supersaturated water vapour. However, when the air mass exits the clouds, it may carry aerosols which formed from the evaporation of cloud droplets. The OA of those cloud residual particles is highly hygroscopic and has a high oxidized fraction due to the aqueous phase oxidation they have been subject to (Aiken et al., 2008; Frosch et al., 2011), resulting in an overall increased f_{44} in the observed particles. As well, OA in BB aerosols that are not removed by cloud droplets may also undergo heterogeneous reactions, forming SOA with high f_{44} . This finding highlights the importance of cloud processing, as it increases the highly oxidised OA mass, resulting in more easily activated CCN and further affecting the stratocumulus cloud deck when BB aerosol interacts with the cloud layer. Although observational evidence of SOA aqueous formation is rare, our result is supported by numerous laboratory and modelling studies (Ervens et al., 2011; Lim et al., 2010).

4) The increase in size distribution during aging is attributed to coagulation. Are the authors sure that this is a relevant process ? At my knowledge this process more affects very small particles. For illustrating my purpose authors can look at figure 2.7, p48 of the thesis of Hilel Dergaoui (2012) that can be downloaded at <http://www.theses.fr>. It shows that particles larger than 100 nm diameter are not affected by coagulation.

Many thanks to the reviewer for this comment. We agree with the reviewer that indeed coagulation mainly affects small particles (usually < 100 nm). This is also consistent with Capes et al. (2008), who used a coagulation box model to simulate the variation in the number size distributions of their observed African biomass aerosols (shown below), and found that the changes in the aerosol number size distribution due to

coagulation were mainly below 100 nm, and that coagulation could not account for the observed increase in larger particles. They also performed the simulation with a few days of ageing, which is relatively close to the ageing times of our observed BB aerosols. They found that longer simulations yield no significant changes to distribution shape in this case. Therefore, they concluded that coagulation alone could not simulate the growth of the observed size distribution between 100 and 200 nm over the timescale of several days. However, the entrainment of multiple plumes into the same air parcel could affect the size distribution in this way. Size-dependent condensation and re-evaporation processes may also have played a role in the size distribution evolution and these were not represented in the model.

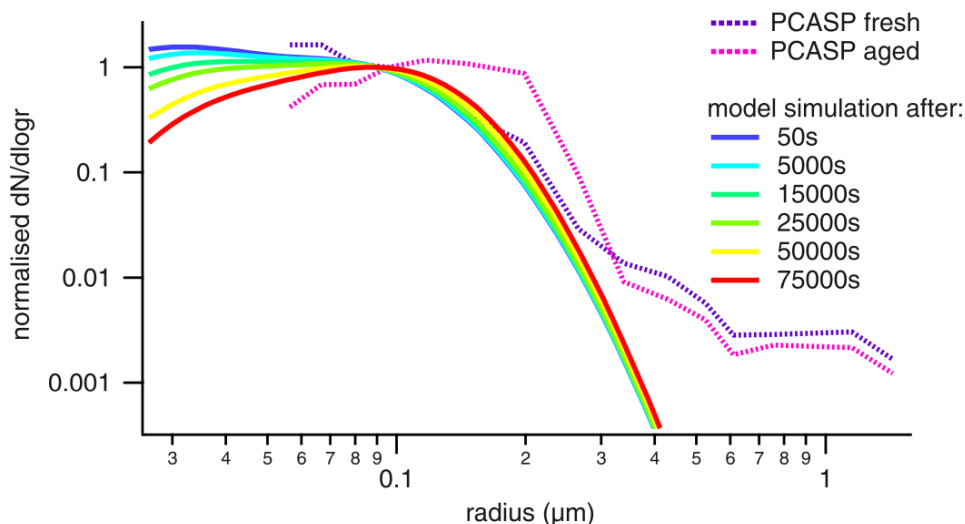


Figure 7 in Capes et al. (2008). Number size distributions from the model simulation and PCASP measurements.

Therefore, we revised the manuscript as the following. Also, note that the figure has been updated, as we re-calculated the cloud processing with the satellite data, and removed samples affected by precipitation and low CO concentrations.

Compared to the dry sample, the particle concentration of the wet sample decreases significantly after ageing, demonstrating the considerable effect of cloud processing in removing aerosols. For both cases, ageing broadens particle size distributions and shifts them towards larger diameters (ΔD_m and $\Delta \sigma > 0$), resulting in a decrease in aerosols at the small sizes (< 200 nm), and an increase in large particles (> 200 nm) for the dry sample. The possible reason for the decrease in small-sized particles for the dry sample is coagulation, since the condensation growth would become very slow or even stops with sufficient ageing, while coagulation can still occur. The strong inversion under the plume layer may have prevented the vertical dilution of the plume, thus facilitating coagulation growth. Although coagulation should be much more obvious in fresher BB aerosols, this result highlights the importance of its role for very aged plumes in the SEA. For the wet sample, particles below 400 nm decrease significantly with ageing and cloud processing, while above that, the changes are less pronounced. This may be due to the inherently low concentration of particles above 400 nm in diameter that may mix with cloud residuals, which have a large size, as they exit the clouds. For the dry sample, particles above 200 nm increase after ageing. This result is consistent with the findings of Capes et al. (2008), who used a coagulation box model to simulate the changes in the particle size distribution with ageing for African BB aerosols, and found that coagulation mainly affects particles below 100 nm. Therefore, coagulation alone is unable to explain the observed increase in large particles, which may be more likely due to the entrainment of multiple plumes into the same air parcel and size-dependent condensation and re-evaporation processes. Compare these two cases;

it can be seen that the aged aerosol distribution (from CLARIFY) is narrower in the case with cloud processing, as demonstrated by the lower fraction of larger particles (>200 nm). Therefore, the reduction of σ by cloud processing is mainly reflected in the removal of large particles. In general, ageing shifts the aerosol distribution towards larger sizes and increases the proportion of large particles. With the increase of the aerosol hygroscopicity resulting from f_{44} increasing, the ageing process can be an important source of CCN, especially in the intermediate and clean SEA marine boundary layer (Kacarab et al., 2020).

5) At several occasions (for example page 10, from line 13 on), authors indicate removal by clouds as an important process. This would imply that clouds are present at the arrival points, otherwise cloud evaporation would reconstitute processed aerosol. In one example shown, clouds are present at the end of the trajectory, so removal is certainly an important process. But is this true for the other « wet » flights also. Rain would lead to irreversible removal. Did rain events happen, were they included in the analysis?

Yes, this is true for all wet samples, as we limited cloud processing to those aerosols that encountered clouds within 24 hours of the second observation. Therefore, all wet samples were subjected to cloud processing at or near the end of the trajectory before observation, and this is also the reason that we only considered cloud processing within the last 24 hours of the transport of the air mass.

We have used the GPM (Global Precipitation Measurement) IMERG (Integrated Multi-satellite Retrievals for GPM) precipitation V06 final run data (Huffman et al., 2019) to identify the precipitation in the studied area. Only one sample slightly influences precipitation, with the accumulated precipitation of around 0.003 mm. Therefore, we removed this sample to avoid the influence of precipitation on the aerosol. Therefore, all samples analysed in the manuscript are free from the effects of precipitation.

6) The paper lacks a finalizing step. There are numerous typos or English grammar errors, sometimes formulations are awkward, figure legends unclear. The paper needs a thorough rereading. There should be no problem with many native English speakers among the co-authors, and which are hopefully ready to reread the paper. I annotated typing and some minor or technical remarks directly in the paper.

We are grateful to the reviewer for all the important and constructive comments! We have revised the manuscript substantially and perused the full text. All corrections have been highlighted in the revised manuscript.

Reviewer #3 (Remarks to the Author):

Che et al. report measurements of biomass burning emissions off the coast of Africa using upstream and downstream aircraft measurements to compare organic aerosol mass changes as well as changes in the optical properties (SSA and AAE) of the transported aerosol. Upstream and downstream measurements are linked via HYSPLIT analysis. The authors also try to estimate the effects of cloud processing on SOA formation and on changes in optical properties of the aerosol. The presented measurements are valuable, and the analysis technique used to probe the effects of aerosol aging by linking trajectory is valid. However, I found that there are major inconsistencies in the reported measurements that are not fully addressed in the manuscript.

For instance, the authors hypothesize that the decrease in OA mass (using the OA/CO ratio) for air mass that spent some time inside a cloud is due to wet scavenging. Yet, the higher the cloud processing intensity the higher was the measured aerosol hygroscopic (as approximated by increasing f_{44} with increasing cloud processing intensity). This is inconsistent since the more hygroscopic aerosol would likely be scavenged first.

Yes, clouds can remove highly hygroscopic aerosols, but this does not mean that the only aerosols that leave clouds are those with low hygroscopicities, such as uncoated BC. When aerosols leave clouds, they

tend to also contain particles of cloud residue, which are aerosols released by the evaporation of cloud droplets. These aerosols have a large particle size, high hygroscopicity, and a high f_{44} . Cloud processing can reduce OA such as mz_{43} , mz_{60} , mz_{44} . However, when the aerosols come out of the clouds, mz_{44} is resupplied, thus leading to a rise in f_{44} . We have modified the main text to include the discussion of the cloud residuals.

There are two potential ways in which cloud processing can result in a higher Δf_{44} , 1) increases the fraction of SOA via aqueous-phase reactions, and 2) reduction in the mass of less oxidised OA components. As the air mass enters the cloud layer, the mass of both high and low oxidised OA is reduced by the cloud droplets and supersaturated water vapour. However, when the air mass exits the clouds, it may carry aerosols resulting from the evaporation of cloud droplets. The OA of those cloud residual particles is highly hygroscopic and has a high oxidized fraction due to the aqueous phase oxidation they have been subject to (Aiken et al., 2008; Frosch et al., 2011), resulting in an overall increased f_{44} in the observed particles. As well, OA in BB aerosols that are not removed by cloud droplets may also undergo heterogeneous reactions, forming SOA with high f_{44} .

Also, the authors present conflicting results regarding the role of cloud processing on changes in aerosol optical properties. For instance, the authors reported that photochemical aging decreases AAE, and the decrease is more pronounced when the air mass spent some time inside clouds. This means that cloud processing made the aerosol less absorbing. Yet, the authors also show a negative correlation between cloud processing intensity and SSA, meaning that cloud processing made the aerosol "look" more absorbing (the authors attribute this to potential wet removal of thickly coated BC particles). Obviously, changes in particle size impacts both SSA and AAE, as rightly pointed by the authors, which could explain the apparent contradiction. However, the effect of size is only briefly discussed and not fully explored in the manuscript leaving the reader to guess what the actual role of the size distribution on optical properties is. Mie theory predictions could yield insight into the role of the size distribution to changes in SSA and AAE. Unfortunately, this is also not explored in the manuscript. More detailed comment can be found below.

We thank the reviewer for the comment. However, we disagree that the decrease in AAE means the particle is becoming "less absorbing". Liu et al. (2018) analysed the AAE of BC particles from numerical aspects and found that for coated BC particles, the larger the particle diameter, the lower the AAE, as illustrated in the figure below. They also found that for BC with geometric mean diameters larger than $0.12\ \mu\text{m}$, BC AAE becomes smaller when BC particles are aged (compact structures or coated by other non-absorptive materials). However, aged BC particles also have a stronger absorption due to the 'lensing effect' from the coating. Therefore, AAE can only represent the dependence of BC absorption at different wavelengths and does not indicate the strength of BC absorption.

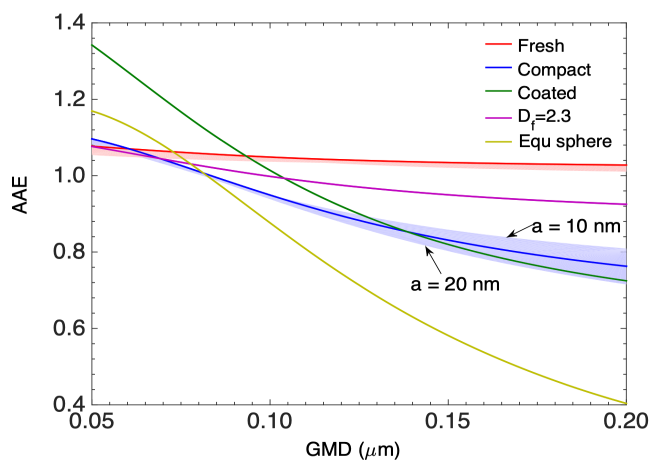


Figure 6 in Liu et al. (2018). AAEs of fresh, compact and coated BC as a function of volume equivalent GME of BC particles (or BC core for coated BC)

We performed a Mie model simulation according to the suggestion. However, using the Mie model requires knowledge of the refractive index of the aerosol, which depends on the chemical composition and mixing state. Unfortunately, we do not have the data for the coating distribution of BC particles; thus, we have to assume that BC aerosols are homogeneously mixed, i.e. that all particles of different sizes contain the same volume ratio of BC. However, such an assumption can introduce a great uncertainty because not all particles contain BC, and also coating thickness is supposed to decrease with the increase of the core diameter. Therefore, given the large uncertainties in the Mie model, we have included the results from the Mie model in the supplement rather than in the main text. The Mie simulations confirm the changes we observed in AAE and SSA, so this is not a conflict.

Minor comments:

P4 L11: "Launched" and not "lunched"

Thanks to the reviewer, we have corrected it in the manuscript.

P4 L26: "By only considering the cloud processing within the last day of the air mass transportation, the immediate effect of cloud processing on the aerosol can be studied." This doesn't make sense to me. You are not making measurements just before cloud processing to isolate the effects of clouds alone. Even if you make measurements just after cloud processing, the air mass spent a significant amount of time aging prior to entering the cloud, hence you are wrongly attributing all changes observed between upstream and downstream measurements as being from cloud processing alone, which obviously is not the case.

This comment is the same as the last comment from the first reviewer, which we have answered there.

P6 Figure 1. The decrease in OA attributed to wet scavenging is inconsistent with increases in particle hygroscopicity (indicated by increase in f_{44}). I would assume that the most hygroscopic aerosol would be scavenged and thus lost. Scavenging of OA component should therefore be accompanied by a decrease in κ (and hence f_{44}). But this is not what is observed. Also, why is x-axis on a and b different from c and d? Presumably you are plotting the same data.

We thank the reviewer for these comments. We have re-analysed the variation in f_{44} and revised the manuscript. The new analysis with f_{44} is shown in the following paragraph. The x-axis is different for f_{44} , and it is daylight time, not the total ageing time, since daylight time has a better correlation with f_{44} and makes more sense from the photochemical point of view.

For both no-cloud and cloud-processed cases, the oxidised organic fraction of f_{44} increases with ageing in Fig. 1(c-d), despite OA mass decreasing or remaining unchanged (Fig. 1 c-d). Comparing the further ageing time, the increased amount of f_{44} is better linearly correlated with the hours of daylight time of further ageing, indicating that the oxidation of organic aerosol is generally dominated by photochemical or OH (also related to sunlight) induced reactions. Both no-cloud and cloud-processed samples have good linear relationships for f_{44} and daylight time, with R^2 higher than 0.7, and all samples are within the 95% confidence intervals. f_{44} has a higher rate of increase in cloud-processed cases rather than no-cloud cases at comparable aging points, indicating the contribution of cloud processing to f_{44} . There are two potential ways in which cloud processing can result in a higher Δf_{44} , 1) increases the fraction of SOA via aqueous-phase reactions, and 2) reduction in the mass of less oxidised OA components. As the air mass enters the cloud layer, the mass of both high and low oxidised OA is reduced by the cloud droplets and supersaturated water vapour. However, when the air mass exits the clouds, it may carry aerosols which formed from the evaporation of cloud droplets. The OA of those cloud residual particles is highly hygroscopic and has a

high oxidized fraction due to the aqueous phase oxidation they have been subject to (Aiken et al., 2008; Frosch et al., 2011), resulting in an overall increased f_{44} in the observed particles. As well, OA in BB aerosols that are not removed by cloud droplets may also undergo heterogeneous reactions, forming SOA with high f_{44} . This finding highlights the importance of cloud processing, as it increases the highly oxidised OA mass, resulting in more easily activated CCN and further affecting the stratocumulus cloud deck when BB aerosol interacts with the cloud layer. Although observational evidence of SOA aqueous formation is rare, our result is supported by numerous laboratory and modelling studies (Ervens et al., 2011; Lim et al., 2010).

P7 L13: The authors hypothesize that the decrease in OA mass during cloud processing is attributed to wet scavenging, but there is no data on precipitation. Are these data available? If so, is there a correlation between the decrease in OA mass and precipitation intensity?

Only one sample is affected by the precipitation. We have removed this sample from the analysis. The precipitation is calculated with the GPM (Global Precipitation Measurement) IMERG (Integrated Multi-satellite Retrievals for GPM) precipitation V06 final run data.

P7 L17: "Two of the dry cases clearly exhibit the increase of OA, indicating the formation of SOA. Although the modified combustion efficiency (MCE) of those two cases are slightly lower than others, they are still higher than 0.98 (Fig. S7), suggesting all BB emissions in our study are from similar flaming fires, consisting with recent studies" I disagree with this. Looking at Figure S7, the MCE from at least the last flight is statistically significantly different that the other flights. Without a statistical test it is difficult to know for sure. Either way, it is therefore not clear to me that differences in $\Delta(OA/CO)$ cannot be due to differences in combustion conditions.

Thanks for the reviewer's suggestion. We have added the statistical test. When testing the effect of MCE on $\Delta(OA/CO)$, we removed the wet samples and only analysed the dry ones to avoid the effect of clouds. A Spearman's rank correlation was performed to give a p-value of 0.08. As this p-value is higher than 0.05, we consider that the two variables are independent and do not have a significant correlation. This means changes in MCE does not drive the variation of $\Delta(OA/CO)$. However, this result is caveated due to only having 13 samples, with a small sample size possibly having a large error.

Following the suggestion of the second reviewer, we analysed the CO upstream concentrations. The results show that high CO concentrations accompany samples with increased OA. In contrast, the samples with a substantially unchanged OA in dry environments have low CO concentrations. Therefore, this may indicate that the increase in OA may be related to the high concentration of plume still observed after ~ 40 hours of ageing, as it may preserve high concentrations of volatile organic gases.

The manuscript has been revised as follows:

Two of the dry cases clearly exhibit the increase of OA, indicating the formation of SOA. Although the modified combustion efficiency (MCE) of those two cases are slightly lower than others, they are still higher than 0.98 (Fig. S7), suggesting all BB emissions in our study are from similar flaming fires, consisting of recent studies (Wu et al., 2020b). Statistical significance tests for MCE and $\Delta(OA/CO)$ find that the two variables are not significantly correlated (p-value>0.05), although the small sample number may have led to large uncertainties in such tests. Therefore, the increased OA mass results from the ageing process rather than different burning conditions. As seen in Fig. 2(a), the two samples with increased $\Delta(OA/CO)$ are accompanied by high upstream CO concentrations, while the samples with substantially unchanged $\Delta(OA/CO)$ in the dry environment have low CO concentrations. Therefore, this may indicate that the increase in OA may be related to the high concentration of the plume still observed after ~ 40 hours of ageing, as it may preserve high concentrations of volatile organic gases.

P7 L35: "However, in comparison to the dry cases, f44 in wet cases increases even more at the same ageing time, indicating the contribution of cloud processing". It would be helpful if the authors plotted the 95% CI of the regression line to assert if cloud processing on f44 is statistically significant. Also, I am surprised why the authors have not checked whether cloud processing increases sulfate. Presumably, this effect would be larger than increase in SOA.

According to the reviewer's suggestion, we have added the 95 % confidence interval. The revised figure is illustrated below. Still, given our small sample size, such statistical estimates may be subject to large errors.

Yes, we agree that sulphate aerosol would be increased by cloud processing. However, the aerosols that undergo cloud processing are also generally within the marine boundary layer, which implies that the ocean is a source of sulphate aerosols in addition to biomass burning. Under another modelling study (in prep.) that we have performed in this region we found that marine sulphate production via oxidation of DMS is one of the most important sources of CCN in the boundary layer, demonstrating the vital contribution of the ocean to sulphate aerosols (Che et al., 2022). It is therefore difficult to distinguish whether these increases in sulphate are due to cloud processing or to the contribution of marine emissions. We are, however, investigating sulphate aerosols in another study, in preparation, where we are trying to quantify the contribution of different sources to sulphate aerosols in the marine boundary layer through filter samples collected from ORACLES and CLARIFY. However, this is the subject of our following study and is beyond the scope of this manuscript.

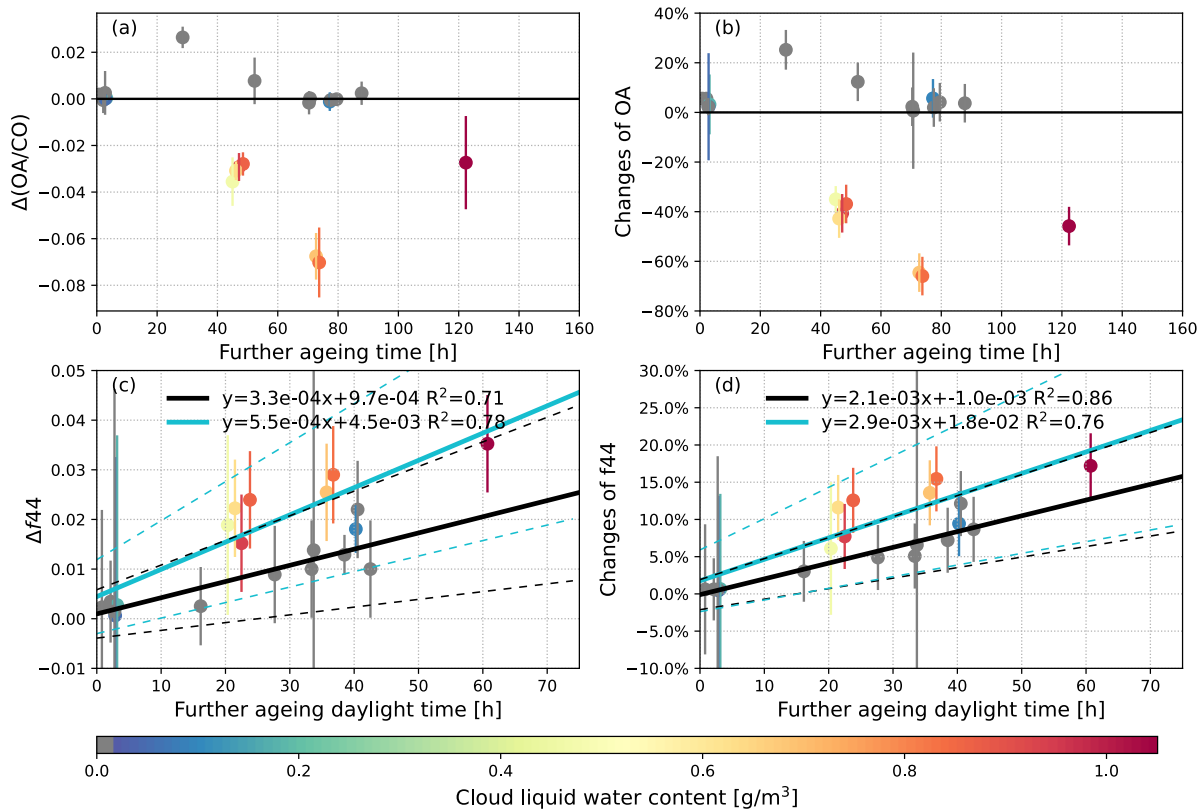


Figure 1. Evolution of (a) OA enhancement factor $\Delta(OA/CO)$ and (b) changes of OA in percentage as ageing time increases since the upstream observation (further ageing time); (c) enhanced f44 and (d) changes of f44 in percentage with further ageing time for daylight hours only, during the transportation of

the BB aerosols between upstream and downstream observations. The dots are mean values for linked cases, and the error bars are standard errors calculated from Gaussian error propagation. The colourmap indicates the mean cloud liquid water content within the last day of transport as derived from the SEVIRI satellite data (as detailed in the method section), and the grey colour represents samples with no cloud processing. The black horizontal lines in (a, b) are the zero lines of OA mass changes. The dashed and solid lines in (c, d) are linear regressions and 95% confidence intervals for samples with cloud processing (cyan coloured lines) and without (black coloured lines). The fitted equations and R^2 values are shown in each of the plots.

P9 L4: It is weird that cloud processing has no impact on the size distribution. If wet scavenging occurred in clouds (as hypothesized earlier to explain decrease in OA/CO ratio), then one would expect that larger and more hygroscopic aerosol (hence more CCN active) to be depleted. The authors offer no explanation on why this is the case.

Cloud processing has an impact on the size distribution. We have recalculated the data and replotted the figure based on the comment from reviewer 2. The new figure shows D_m (mode diameter) increases for samples subject to cloud processing. The main text has been updated as follows.

Compared to the dry sample, the particle concentration of the wet sample decreases significantly after ageing, demonstrating the considerable effect of cloud processing in removing aerosols. For both cases, ageing broadens particle size distributions and shifts them towards larger diameters (ΔD_m and $\Delta \sigma > 0$), resulting in a decrease in aerosols at the small sizes (< 200 nm), and an increase in large particles (> 200 nm) for the dry sample. The possible reason for the decrease in small-sized particles for the dry sample is coagulation, since the condensation growth would become very slow or even stops with sufficient ageing, while coagulation can still occur. The strong inversion under the plume layer may have prevented the vertical dilution of the plume, thus facilitating coagulation growth. Although coagulation should be much more obvious in fresher BB aerosols, this result highlights the importance of its role for very aged plumes in the SEA. For the wet sample, particles below 400 nm decrease significantly with ageing and cloud processing, while above that, the changes are less pronounced. This may be due to the inherently low concentration of particles above 400 nm in diameter that may mix with cloud residuals, which have a large size, as they exit the clouds. For the dry sample, particles above 200 nm increase after ageing. This result is consistent with the findings of Capes et al. (2008), who used a coagulation box model to simulate the changes in the particle size distribution with ageing for African BB aerosols, and found that coagulation mainly affects particles below 100 nm. Therefore, coagulation alone is unable to explain the observed increase in large particles, which may be more likely due to the entrainment of multiple plumes into the same air parcel and size-dependent condensation and re-evaporation processes.

P9 L17: "Specifically, BrC bleaching and OA photolysis may mostly occur in the small size range, while SOA may more easily condense on large particles, creating the shift in the aerosol distribution." This doesn't make sense to me. Why would bleaching and photolysis mostly occur in the small size range? Has this been previously reported?

This sentence has been deleted.

P9 L21: "Comparing these two cases, it can be seen that the aged aerosol distribution (dash lines) is narrower in the case with cloud processing, as demonstrated by the lower fraction of larger particles (> 200 nm). Therefore, the reduction of σ by cloud processing is mainly reflected in the removal of large particles." How can the authors claim this? Even though you are starting with similar distributions doesn't mean that the observed differences are solely attributed to cloud processing. Photochemical aging between the two different days are likely different.

In order to make them comparable, we specifically selected two samples with approximate ageing times, rather than samples with large differences in ageing times. In addition, this figure has been updated based on the comments of the second reviewer, the corresponding analysis has also been revised.

P11 L2: "Thus, the increase in particle size due to ageing is also responsible for the decrease in AAE." I would argue this is the main effect indeed. Mie calculations could validate this assumption

We thank the reviewer for these comments. Mie calculations do help to explain the variation in these aerosol optical parameters. However, using the Mie model requires knowledge of the refractive index of the aerosol, which depends on the chemical composition and mixing state. Unfortunately, we do not have the data for the coating distribution of BC particles. Thus we have to assume that BC aerosols are homogeneously mixed, i.e. that all particles of different sizes contain the same volume ratio of BC. However, such an assumption can introduce a great uncertainty because not all particles contain BC, and also coating thickness is supposed to decrease with the increase of the core diameter. Therefore, given the large uncertainties in the Mie model, we have included the results from the Mie model in the supplement rather than in the main text.

In order to be able to identify, by using the Mie model, whether the observed changes in the optical properties of the aerosol are mainly driven by the variations in the aerosol number size distribution, we used the average refractive index ($1.62 + 0.04j$) from the ORACLES campaign (Zhang et al., 2022), assuming that the BC is internally mixed, and fixed this refractive index but change the number size distribution of the aerosol for the calculation. The figure below shows the results from the Mie calculation.

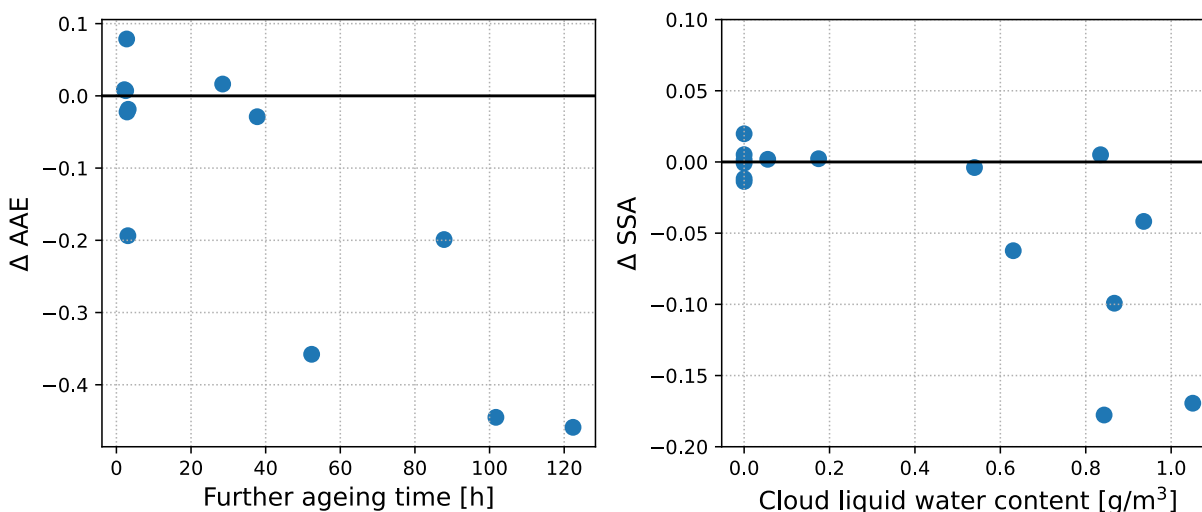


Figure S8. Mie model simulated variations of (a) AAE with further ageing time and (b) SSA with cloud processing.

Overall, AAE decreases due to changes in the number size distribution of BB aerosols (Fig. S8, a), suggesting that changes in the aerosol number size distribution are indeed an important factor in the decrease in AAE. However, there is an increase in AAE in the figure at an ageing time of approximately 30 hours, which is not consistent with what is observed. In addition, the maximum decrease in AAE due to the variation in aerosol number size distribution is 0.45, which is smaller than the actual observed value (0.8). Therefore, the number size distribution changes are not sufficient to explain the reduction in AAE, suggesting that in addition to the variations in the number size distribution, the bleaching of BrC also

contributes to the decrease in AAE. However, we agree with the reviewers that the variations in the number size distribution may be the main reason for the decrease in AAE according to the results from the Mie model.

Accordingly, the following changes have been made to the main text.

The changes in AAE with ageing and cloud processing are illustrated in Fig. 4 (a-b). Overall, AAE decreases with ageing. The longer it ages, the greater the decrease, with the maximum reduction of AAE up to 50%. The decrease of AAE indicates the diminishing of the wavelength dependence of the light-absorption coefficient of BB aerosol, which may be caused by the photochemical degradation of BrC and variations in the aerosols size distribution. In general, AAE is highly sensitive to particle size distribution for compact and coated BC, with large particles having a smaller AAE (Liu et al., 2018). As we have shown in the previous section, ageing increases the mode diameter of aerosol distribution, which may be responsible for the AAE reduction. Mie model simulations suggest the variations in the aerosol number size distribution may be the main reason for the decrease in AAE (Fig. S8). However, changes in the size distribution can only account for a partial decrease in AAE (more than 50 %), suggesting it is not sufficient to explain the observed reduction in AAE. Therefore, the reduction of BrC also contributes to the decrease in AAE. As the absorption coefficient of BrC has a strong spectral dependence, photobleaching of BrC leads to a decrease in AAE, which can be used along with the variation in aerosol size distribution to explain the reduction in AAE in dry samples. This finding is consistent with the result of Zhang et al. (2022), which suggests upwind ORACLES have more BrC than downwind CLARIFY observations. For wet cases, the mode diameters of aerosol size distributions increase with ageing, resulting in a decrease in AAE. In addition to that, the removal of BrC also contributed to the decrease in AAE in the wet samples. The aqueous-phase processing and oligomerisation of water-soluble organics have been recognised to form light-absorbing BrC, suggesting cloud processing is an important source of BrC (Graber and Rudich, 2006). However, our results find AAE decreases even more for stronger cloud processing cases, suggesting that the contribution of BrC from the aqueous-phase reaction is overridden by wet removal. This is because BrC is generally considered to be hygroscopic (Laskin et al., 2015), as even tarballs, the most refractive and least hygroscopic BrC, is able to completely dissolve in water droplet under supersaturation (Hand et al., 2005). Therefore, its hygroscopic properties lead to the dominance of the wet removal of BrC, resulting in a decrease in AAE.

P11 L4: Could the decrease of SSA with increasing cloud processing be the result of higher RH in the line that could interfere with the measurements?

No. Both absorption and scattering were observed in the dry environment, where the aerosol was dried after passing through the inlet pipe. Therefore, RH should not be interfering with the observations.

There is an inconsistency between the decrease in AAE with aging (Figure 4a,b which is more pronounced during cloud processing times) meaning the aerosol is less absorbing and the decrease in SSA with increased cloud processing which means the aerosol is more absorptive. Unless changes in SSA and AAE are dominated by size effects. But Mie theory would be needed to make sure the changes have the correct sign.

Thanks for the comment. We have performed the Mie simulation for the variation in SSA (Fig. S8, b). Mie model simulations confirm that variations in aerosol number size distribution are the main factor contributing to the decrease in SSA. We, therefore, have added this sentence to the main text.

The higher the cloud processing intensity, the larger the reduction of SSA. The decrease of SSA due to cloud processing can be up to approximately 10 %, and may result from the wet removal of large particles and thickly coated BC by cloud droplets. Mie model simulations confirm that variations in aerosol number size distribution are the main factor contributing to the decrease in SSA.

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16th Jun 22

Dear Dr Che,

Your manuscript titled "Cloud processing and weeklong ageing significantly affect the biomass burning aerosols over the south-eastern Atlantic" has now been seen by our reviewers, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment under the open access CC BY license (Creative Commons Attribution v4.0 International License).

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Clare Davis, PhD
Senior Editor
Communications Earth & Environment

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REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

The authors have addressed all of my comments. I have no further requests.

Reviewer #2 (Remarks to the Author):

I think the authors have well responded to my and other referees suggestions and significantly increased the paper's quality. The paper's writing has also significantly improved.

There are a few technical corrections, which do not need further review from my side.

Page 8 « the increased amount of f44 is better linearly correlated ... »
Better than what ?

Page 15 « for very ages plumes in the SEA. » -> aged

Page 15 : « Therefore, the reduction of BrC might also contribute to the decrease in AAE. » -> contribute

Page 15 :
As the absorption coefficient of BrC has a strong spectral dependence, photobleaching of BrC leads

to a decrease in AAE, which can be used along with the variation in aerosol size distribution to explain the reduction in AAE in dry samples.

Please replace by :

As the absorption coefficient of BrC has a stronger spectral dependence than that of BC, photobleaching of BrC leads to a decrease in AAE, which can be used along with the variation in aerosol size distribution to explain the reduction in AAE in dry samples.

Reviewer #3 (Remarks to the Author):

The authors have satisfactorily answered all of my comments. I recommend publication

Review replies to "Cloud processing and weeklong ageing significantly affect the biomass burning aerosols over the southeastern Atlantic" by Haochi Che et al.

We would like to thank all reviewers for their constructive comments and suggestions on the manuscript. The feedback has allowed us to clarify aspects of the paper and to improve our paper.

The reviewer's comments are provided in **blue in the following**, and our responses are in **black**. Changes to the manuscripts made in response to the reviewer are in **green**. In addition, numerous changes in the manuscript are not shown in this response but are highlighted in the revised version.

Reviewer #2 (Remarks to the Author):

I think the authors have well responded to my and other referees suggestions and significantly increased the paper's quality. The paper's writing has also significantly improved.

There are a few technical corrections, which do not need further review from my side.

Page 8 « the increased amount of f44 is better linearly correlated ... »
Better than what ?

We have removed the 'better', and revised the sentence as follows:

The increased amount of f44 is linearly correlated with the hours of daylight time, indicating that the oxidation of organic aerosol is generally dominated by photochemical or OH (also related to sunlight) induced reactions

Page 15 « for very aged plumes in the SEA. » -> aged

We corrected this in the manuscript.

This result highlights the importance of its role for very aged plumes in the SEA.

Page 15 : « Therefore, the reduction of BrC might also contribute to the decrease in AAE. » -> contribute

We corrected this in the manuscript.

Therefore, the reduction of BrC might also contribute to the decrease in AAE.

Page 15 : As the absorption coefficient of BrC has a strong spectral dependence, photobleaching of BrC leads to a decrease in AAE, which can be used along with the variation in aerosol size distribution to explain the reduction in AAE in dry samples.

Please replace by :

As the absorption coefficient of BrC has a stronger spectral dependence than that of BC, photobleaching of BrC leads to a decrease in AAE, which can be used along with the variation in aerosol size distribution to explain the reduction in AAE in dry samples.

Thanks for the suggestion! We have replaced it in the manuscript.

As the absorption coefficient of BrC has a strong spectral dependence than that of BC, photobleaching of BrC leads to a decrease in AAE, which can be used along with the variation in aerosol size distribution to explain the reduction in AAE in dry samples