COVER PAGE

Project Title:
Assessing the link between aerosol mixing state, structure and composition and their optical properties: Ascension Island as a testbed for the South-East Atlantic aerosol regimes

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ABSTRACT

Forest and savanna fires are a major source of pollution over the globe. Such fire events emit to the atmosphere a considerable amount of "fluffy" fractal black looking particles that are often referred to as black carbon (BC) or soot aerosols. In fact, BC particles (aerosols) emitted from savanna and agricultural fires over the African continent play an important role in the region's and the global climate. These fires occur each year between July and October, which is referred to as the biomass burning (BB) season and are considered among the globe's largest man-made emission sources of BC particles. However, during these fire events, not only BC particles are emitted, but also other types of particles and gases that can interact with each other to create new particles, generating a slew of particles often generally referred to as BB aerosols.

Although the majority of the fire emissions occur inland in the sub-Saharan part of Africa, their effect reaches far beyond the continent due to the prevailing easterly winds, which transport those aerosols over the South-East Atlantic (SEA) ocean, off the west-coast of Africa. The reason why these particles are so important to the regional and global climate is that they absorb sunlight radiation, which overall warms the climate. However, the magnitude of this warming effect is highly uncertain and depends upon a multitude of aspects.

Our overarching goal for this project was to better understand the changes in the aerosol properties as they transport from fire sources downstream toward the ocean and how this can eventually affect the earth's radiative budget in terms of warming or cooling.

Following the above, our work here was focused on the investigation of the African BB aerosol plumes mixing state (mixing of BB aerosols and other aerosol types), composition and size distribution as they transport from the African continent towards the SEA ocean, and their link with some of the commonly measurable bulk optical properties such as mass absorption coefficient (MAC) and single scattering albedo (SSA). We utilized three field missions that were conducted over the SEA ocean between 2016 and 2018. Specifically, we used (1) ground-based measurements from the DOE ARM Mobile Facility (AMF1), which was deployed at Ascension Island (ASI) for the LASIC (Layered Atlantic Smoke Interactions with Clouds) campaign between June 2016 and October 2017, (2) airborne measurements from the UK CLARIFY (Clouds and Aerosol Radiative impacts and Forcing) campaign during Aug-Sep-2017, and (3) airborne measurements from the ORACLES (Observations of Aerosols above Clouds and their interactions) campaign during Aug-2017, and Sep-Oct-2018. The three campaigns cover a relatively large region, from the western African coast on the east towards Ascension Island in the middle of the SEA to the west.

We used the data gathered by these campaigns to find how BB properties and composition change from near emission sources (the ORACLES campaign flights) downstream (the CLARIFY flights and the ground based LASIC measurements). We used particle trajectory following methodologies to connect the measurements from the different campaigns, which allowed us to follow a certain aerosol plume (airmass) from near-source towards Ascension Island. We found out that atmospheric aging processes governed by the UV light from the sun (photochemistry) and cloud processes (aqueous chemistry) govern the changes seen in the particle composition during the transport were more dominant in dictating aerosol composition than specific emission composition or source types. We assessed how aerosol optical properties change during the BB season and what are the main drivers of this change. We found that the enhanced ratio of BC to CO is well correlated with single scattering albedo (SSA) and mass absorption coefficient (MAC_{BC}), providing a simple way to estimate the aerosol optical characteristics in the south-eastern Atlantic Ocean. From the analysis of the location of BB, the primary source fuel, the water content in the fuel, combined with the mean cloud cover and precipitation in the transport areas of the BB plume, we conclude that the increase in BC/CO from June to August is likely to be caused by burning becoming more flaming (hot fires), and the decrease in BC/CO in September and October may be caused by smoldering (colder) fires. We found that aerosol hygroscopicity increases with decreasing altitude below 2km, and that enhanced BB hygroscopicity at lower altitudes is mainly due to a lower organic aerosol (OA) fraction, increased sulphate fraction, and greater hygroscopicity parameter of OA at lower altitudes.

PROJECT ACTIVITIES

Goals and Original Hypotheses:

Our overarching goal for this project was to better understand the changes in the aerosol properties as they transport from fire sources downstream towards the south-east Atlantic (SEA) ocean and how this can eventually affect the earth radiative budget in terms of warming or cooling.

We utilized three field missions that were conducted over the SEA ocean between 2016 and 2018. Specifically, we used (1) ground-based measurements from the DOE ARM Mobile Facility (AMF1), which was deployed at Ascension Island (ASI) for the LASIC (Layered Atlantic Smoke Interactions with Clouds) campaign between June 2016 and October 2017, (2) airborne measurements from the UK CLARIFY (Clouds and Aerosol Radiative impacts and Forcing) campaign during Aug-Sep-2017, and (3) airborne measurements from the ORACLES (Observations of Aerosols above Clouds and their interactions) campaign during Aug-2017, and Sep-Oct-2018. The three campaigns cover a relatively large region, from the western African coast on the east towards Ascension Island in the middle of the SEA to the west.

Our specific objectives were as follows: (1) Explore how differences in bulk aerosol optical properties measured by in-situ instruments are linked with aerosol single particle properties, namely, mixing state, structure, composition and with aerosol sources in the SEA, (2) Assess the differences and trends in aerosol mixing state, structure, composition, water uptake and hygroscopicity during the BB season, and (3) Perform radiative modeling simulations to explore the sensitivity of the results to the assumed refractive indices of black carbon (BC), brown carbon (BrC) and organic matter and particle water uptake.

In objective 1 we strived to better understand the processes and composition of the aerosols over the SEA as they age from the source. For this, we needed to link similar airmasses and follow them from emission sources to downwind reception locations. Our hypothesis was that as the BB aerosol age, they will get more oxidized and more scattering.

In objective 2 we assessed how aerosol optical properties, including aerosol water uptake and hygroscopicity properties (which affect the optical properties) change during the BB season and what are the main drivers of this change. For this assessment we investigated: (a) how BB optical properties change over a long period of time using the ground based LASIC measurements, and (b) how aerosol composition and aging change aerosol water uptake and hygroscopicity using composition and water content measurements from the ORACLES campaign along the atmospheric column. The latter gave us the opportunity to investigate the aerosol under different relative humidity conditions, composition, and temperatures to allow us to deduce the main mechanisms that affect aerosol water uptake and hygroscopicity. Our hypotheses for this objective were that initial aerosol composition (based on burning material) would be the main driver for aerosol optical properties after transport and that aerosol hygroscopicity mostly depends on the inorganic species of the internally or externally mixed aerosol.

In objective 3 we investigated the contribution of BrC to the total light absorption of biomass burning aerosols over the South-East Atlantic Ocean with different optical models. We performed closure studies and compared the measurements with Mie scattering simulations based on various optical mixing rules to elucidate the role of aerosol mixing state and composition in their optical properties and especially absorption. Our hypothesis was that BrC, which is prevalent in the BB season, might play a large role in the absorption of BB aerosol over the South-East Atlantic Ocean.

Major Findings:

Objective 1 - Cloud processing and weeklong ageing affect biomass burning aerosol properties over the south-eastern Atlantic Ocean.

The mass, composition, morphology, and size distribution of BB aerosols evolve with ageing, resulting in uncertainties in BB aerosol-radiation-cloud interactions. BB aerosols in the SEA have a long lifetime in the atmosphere, and as such ageing can have an important yet unclear effect on aerosol properties. Aerosol

ageing can cause organic aerosol (OA) mass to either increase by functionalization or oligomerization reactions or decrease by fragmentation. Laboratory experiments show a considerable increase in the OA (70% on average) resulting from the formation of secondary organic aerosol (SOA), while field observations have reported conflicting results, with the majority of field observations suggesting negligible changes. To investigate the changes in OA, size distribution and optical properties as the BB aerosol transport over the SEA Ocean we found cases of linked airmasses between the ORACLES (upwind, near fire sources) and CLARIFY (Downwind, near Ascension Island).

To find linked airmasses we performed a trajectory linking procedure between the ORACLES and CLARIFY flights, by using airmass trajectories calculated by the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT). To improve the accuracy, we use hourly high resolution (0.25° Å~ 0.25°) ERA5 reanalysis (fifth generation of ECMWF reanalysis data) for the calculation. More details about the linking procedure can be found at Che et al. (2022a). The successfully linked cases are illustrated in Figure 1 below. In total, 23 linked cases have been identified, with 11 ORACLES linked with CLARIFY cases and 12 ORACLES cases linked with ORACLES itself. The linking procedure allows the investigation of samples measured in the exact same airmass but at different times, where the evolution of aerosols can be analyzed by the Lagrangian methodology.

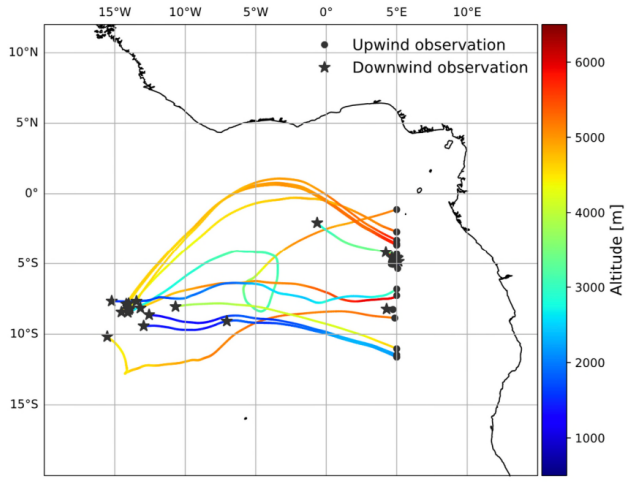

Figure 1: All linked cases. The dots are upwind observations made by ORACLES, while the stars are downwind measurements by ORACLES and CLARIFY. The lines connecting upwind and downwind observations are air mass trajectories, and the colour indicates the altitude.

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

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

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 Δ(OA/CO) indicate an increase in OA mass along with the airmass transport, implying the formation of SOA. A zero value of Δ(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 in OA mass with ageing can be calculated in percentage, as in Eq. (3).

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

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

The OA oxidation level is represented by f44 calculated from AMS 44 m/z data. The difference of f44 between the upwind and downwind observations is calculated as in Eq. (4), and the change of f44 in percentage can be calculated as in Eq. (5)

$$\Delta f44 = f44_{down} - f44_{up} \qquad (4)$$

$$f_{f44} = \frac{\Delta f44}{f44_{up}} * 100\% \qquad (5)$$

Figure 2 (from Che et al. 2022a) shows the BB evolution in terms of OA and oxidation level (presented as changes in the fractionization of m/z 44 measured by AMS). For both no-cloud and cloud-processed cases, the oxidized organic fraction of *f44* increases with ageing in Fig. 2(c, d), despite OA mass decreasing or remaining unchanged (Fig. 2a, b). 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 induced reactions. Both no-cloud and cloud-processed samples have good linear relationships for f44 and daylight time, with R^2 higher than 0.7. *f44* has a higher rate of increase in cloud processed cases rather than no-cloud cases at comparable ageing points, indicating the contribution of cloud processing to *f44*.

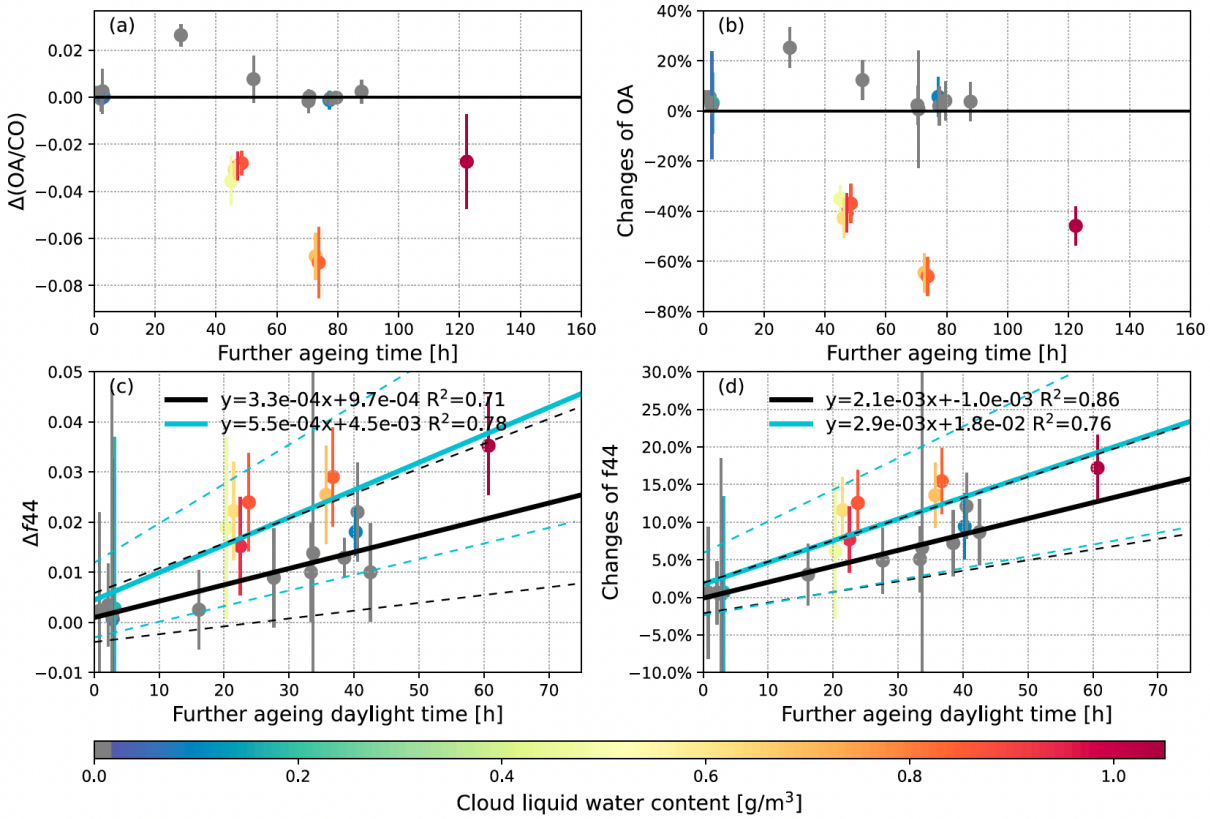

Figure 2 (adapted from Che et al., 2022a, their Fig. 1): Evolution of organic aerosol (OA) with ageing. (a) OA enhancement factor Δ(OA/CO) and (b) changes of OA in percentage as ageing time increases since the upstream observation (further ageing time); (c) enhanced *f44* and (d) changes of *f44* in percentage with further ageing time for daylight hours only, during the transportation of the biomass burning 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, and the grey color 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 colored lines) and without (black colored lines). The fitted equations and R^2 values are shown in each of the plots.

We postulated that there are two potential ways in which cloud processing can result in a higher Δf44, (1) increases the fraction of SOA via aqueous phase reactions, and (2) reduction in the mass of less oxidized OA components. As the air mass enters the cloud layer, the mass of both high and low oxidized OA is reduced by the cloud droplets and supersaturated water vapor. 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 subjected to, resulting in an overall increased *f44* in the observed particles. In addition, OA in BB aerosols that are not removed by cloud droplets may also undergo heterogeneous reactions, forming SOA with high *f44*. ***This finding highlights the importance of cloud processing, as it increases the highly oxidized OA mass, resulting in more easily activated CCN and further affecting the stratocumulus cloud deck when BB aerosol interacts with the cloud layer.***

The Absorption Angstrom Exponent (AAE) at upwind and downwind locations of airmass trajectories were 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.

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

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

Where the σ_{450} and σ_{660} denote the aerosol absorption coefficient at 450 and 660 nm, respectively. Figure 3 shows the changes in AAE during transport (adapted from Che et al. 2022a, Fig. 4).

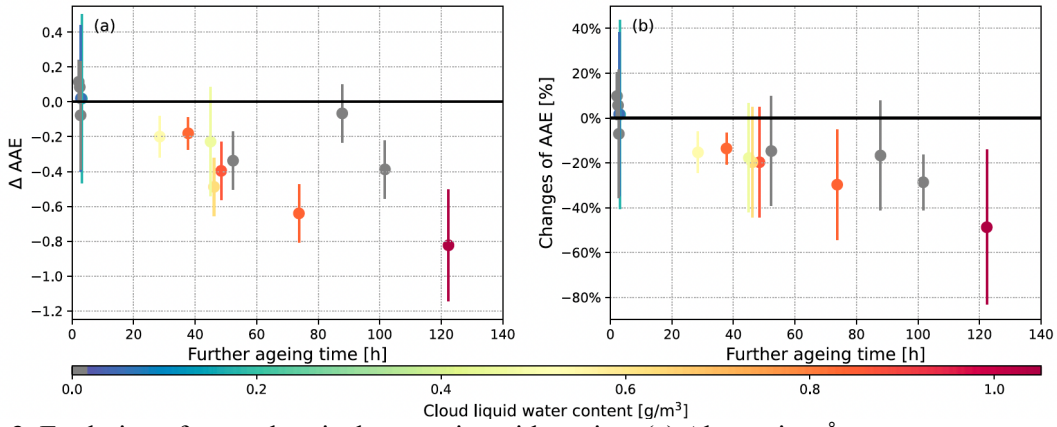

Figure 3: Evolution of aerosol optical properties with ageing. (a) Absorption Ångström exponent (AAE) and (b) the corresponding changes of AAE in percentage with further ageing time. The dots are mean values, and the error bars are standard errors from Gaussian error propagation. The grey color in a, b represents cases with no cloud processing, while the color map represents the cloud liquid water content.

Overall, we see that AAE decreases with ageing. The longer it ages, the greater the decrease, with a 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. As we have also shown (Che et al., 2022a) that ageing increases the mode diameter of aerosol distribution, this mechanism may also be responsible for the AAE reduction, and Mie model simulations suggest the variations in the aerosol number size distribution may be the main reason for the decrease in AAE. However, changes in the size distribution can only account for a partial decrease in AAE, suggesting it is not sufficient to explain the observed reduction in AAE. Therefore, the reduction of BrC might also contribute to the decrease in AAE. 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. This finding is consistent with the result of aerosol optical closure studies in the region, detailed in objective 3 and in our corresponding publication (Zhang et al., 2022), which suggests upwind ORACLES observations have more BrC than downwind CLARIFY observations.

To summarize, by linking observations from upwind and downwind areas with trajectories, we investigated the BB aerosol evolution with ageing in the SEA. Our main conclusions are illustrated schematically by Fig. 4 (adapted from Che et al., 2022a, their Fig. 5), where all BB aerosols measured here are emitted from flaming fires. Our results suggest that SOA formation prevails when the further (beyond 40-48hr) ageing time is less than ~30 h. Taking the average age of BB aerosols measured at the upwind location ~40 h into account, it may suggest SOA formation dominates at high CO concentrations for 70 h of transport of the BB plume after emission. ***This finding of SOA formation after a long transport time has important implications on the regional climate, as SOA can modulate BB aerosol direct and semi-direct radiative forcings by affecting BBA optical properties. SOA can also affect the indirect radiative forcing by providing more CCN, as it has a higher hygroscopicity***, as also depicted in our investigation of objective 2b and in Zhang et al. (2023).

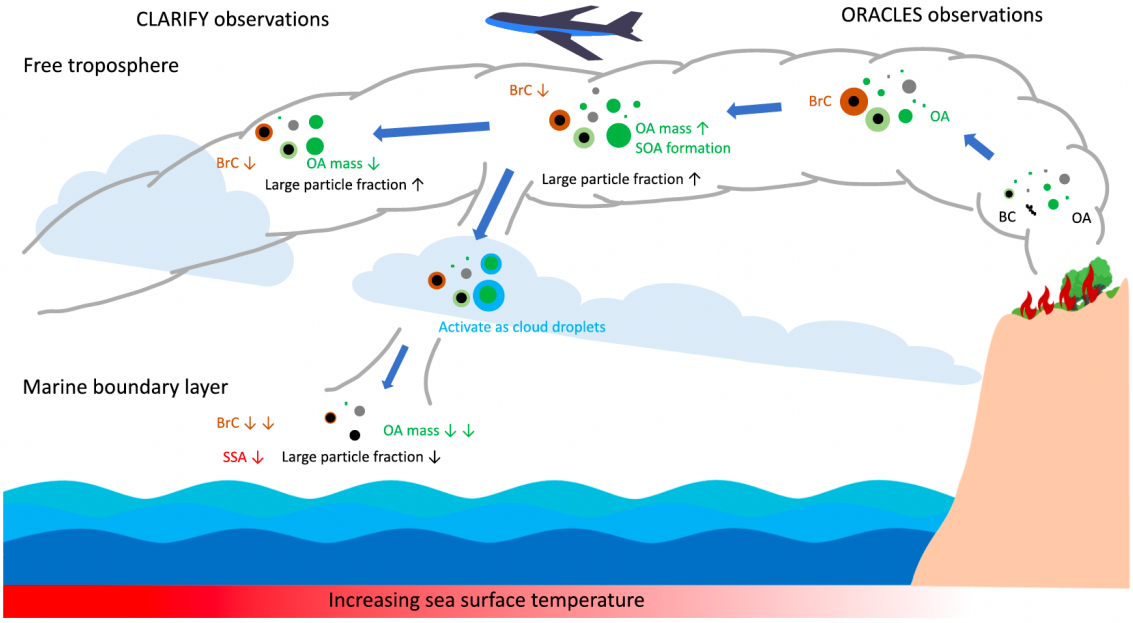

Figure 4: Schematic showing the evolution of biomass burning aerosols with ageing and cloud processing during the westward transport in the southeastern Atlantic. For a clear visualization of the aerosol changes, most of the aerosols in the figure are externally mixed, which would not match reality, and the actual aerosol mixing is beyond the scope of this paper. During transport, changes in aerosols are illustrated by small upward and downward arrows, indicating increases and decreases. Two of such arrows suggest a significant change. Note those changes are compared to the previous step connected by the big blue arrow.

Objective 2(a) - Seasonal variations in fire conditions are important drivers in the trend of aerosol optical properties over the south-eastern Atlantic.

BB aerosol absorbing capacity is a fundamental input in climate models. For fresh BC, the mass absorption coefficient (MAC_{BC}) falls within a narrow range of 7.5±1.2 m^2 g^{-1} at 550 nm, while with ageing and internal mixing, MAC_{BC} can increase by approximately 50%. The increased absorption results from coatings on BC particles through the so-called lensing effect and is often represented by an absorption

enhancement (E_{abs}). Observations in different global regions have reported varying E_{abs}, depending on the coating thickness and mixing states of BC particles.

During the BB season in Africa (June to October), the physical and chemical properties of BB aerosols change with variations in combustion conditions, source fuel and meteorological conditions, resulting in variations in the optical characteristics of BB aerosols. Although satellite and surface-based sun photometer observations are able to estimate long-term SSA variation, the presence of the extensive clouds makes it difficult to retrieve SSA in the marine boundary layer in the SEA. Therefore, aircraft observations such as ORACLES and CLARIFY, and especially the ground based LASIC campaign at Ascension Island (ASI), which we will focus on here, allows, for the first time, the opportunity to observe long-term changes in BB optical property changes over this climatically important region. With 17 months of continuous observations, LASIC enables a detailed study of the variation of the optical properties of BB aerosols and the factors influencing them. Therefore, here we examined the monthly variations of SSA, MAC_{BC}, and E_{abs} measured on ASI during the 2-year BB seasons and explore the factors responsible for these variations. Figure 5 (adapted from Che et al., 2022b, Fig. 2) shows the seasonal variations of E_{abs} within the two-year LASIC campaign.

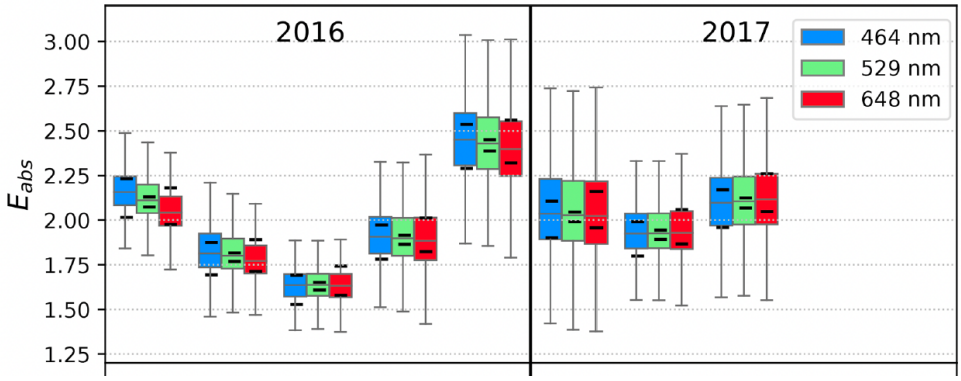

Figure 5: Monthly percentiles (10 %, 25 %, 50 %, 75 %, and 90 %) of absorption enhancement E_{abs}. E_{abs} is calculated by assuming an AAE of 1 for the fresh BC. The solid black lines in the upper panel indicate the upper and lower boundary of the calculated median E_{abs} when the AAE is in the range of 0.8– 1.4.

The high value of MAC_{BC} (~15-20 at 530 nm, as in Che et al., 2022b) and E_{abs} (Fig. 5) observed on ASI may be attributed to two factors: the high concentration of other absorbing aerosols, such as BrC and dust, or thickly coated BC particles. We found that contribution from BrC on total absorption at 464 nm is generally around 1 %–2 %, suggesting BrC has a minimal influence on the aerosol absorption measured on ASI. Zhang et al. (2022) found about 10% of BrC at 470 nm near the African continent, while others from CLARIFY found even lower values of about 10% BrC at a much lower wavelength (405 nm) in the free troposphere near ASI. As the observed BB plumes at ASI are generally considered to have experienced cloud processing (Che et al., 2022a), this could further reduce the BrC content. In addition to considering the contribution to absorption from BrC, we showed (Che et al. 2022b, Fig. 3 and Dang et al. 2022) the plausible existence of dust particles (Fe bearing) as a contributor to the observed absorption, based on single-particle filter analysis by TEM-EDX sampled close to ASI. Fe-bearing particles are suspected of contributing to this large E_{abs}, since Fe oxides, such as magnetite, have strong and uniform absorption at visible wavelengths, which could lead to a high MAC_{BC} and an AAE around 1, consistent with our measured AAE (Che et al., 2022b). However, as limited amount of filter samples containing BB were collected near ASI in the BL, it makes it difficult to estimate the proportion of Fe-bearing aerosols and whether they contribute significantly to the absorption enhancement in ASI.

To further understand the trend in ASI aerosol absorption optical properties, we investigated the monthly variations of the enhanced ratio of BC to CO (BC/ΔCO). This ratio increases from June to August and decreases in the following 2 months in both 2016 and 2017, showing an opposite trend to that of SSA,

MAC_{BC}, and even AAE and E_{abs}. As BC/ΔCO can indicate the emission conditions near the fire source, this finding may suggest that the seasonal variation of aerosol properties observed on ASI may be driven by the burning conditions of African fires. We found (Che et al., 2022b) that BC/ΔCO shows a good linear relationship with the optical properties of aerosols observed on ASI, and therefore, further investigated the potential drivers of the variations of aerosol optical properties during the BB seasons as they relate to this ratio.

The magnitude of BC/ΔCO depends primarily on two factors, one being the condition of the combustion, and the other being the scavenging of aerosols during the transport of the plume. We first fitted the available observational data for BC/ΔCO values with modified combustion efficiency (MCE). This resulted in a reasonable linear relationship between MCE and BC/ΔCO, with the R^2 value of 0.44. Therefore, it suggests that with the increasing fraction of flaming combustion, BC/ΔCO also increases, and that one of the major factors contributing to the variation in the observed BC/ΔCO ratio is the change in combustion state from the BB region. Based on our fitted line, we estimate that BC/ΔCO is around 0.004 when MCE is 0.9. This means for fresh plumes with BC/ΔCO >0.004, the burning is dominated by flaming combustion, while when BC/ΔCO <0.004, the burning is mainly smoldering.

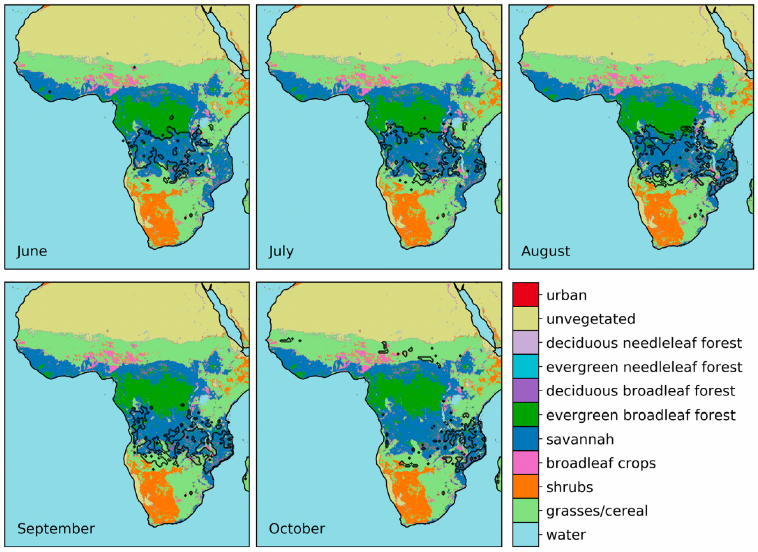

Figure 6: Major burning locations and land covers during the BB season in 2016. The different colors on the land indicate different land types. Areas with an accumulated fire count greater than 500 are illustrated in the black contour each month. The land cover data are from the MODIS collection 6 product MCD12Q1

To understand the drivers in changes of the BB burning conditions, we first compared the changes in fuel sources in the different months. As shown in Fig. 6, we found that the main burning areas shifted eastwards from June to October (Che et al., 2022b). From June to August, the main burning areas gradually expanded. By contrast, the smallest burning areas are found in September and October, mainly in south-eastern Africa. For the fuel source, our analysis indicated that savannah burning is predominant in each month, while the proportion of burning in grasses and/or cereal is higher in September and October. The increased burning in grasses/cereal areas may suggest a source of fuel dependence on the observed decrease in BC/ΔCO in September and October, in addition to higher relative humidity, increased precipitation, and lower winds, which altogether may contribute to the more smoldering fire conditions. We then compared the monthly mean water stress level in major burning fuels by using NDMI (normalized difference moisture index) from Landsat 8 satellite. The results (Figure 10 in Che et al. 2022b) show that the fuel becomes increasingly drier from June to August, which could be the reason for the more flaming combustion.

To summarize, the reduction in the water content of fuels may be responsible for the change in the burning conditions from June to August. The decrease in BC/ΔCO in September and October may be caused by two factors, one being a lower proportion of flaming conditions, possibly associated with a decrease in mean surface wind speed in the burning area, and the other being an increase in precipitation in the BB transport pathway, leading to enhanced aerosol scavenging, which ultimately results in an increase in SSA and MAC_{BC}.

Objective 2(b) - Aerosol hygroscopicity over the South-East Atlantic Ocean during the biomass burning season depends on sulphate and OA properties.

As aerosol hygroscopicity plays a vital role in aerosol radiative forcing and its ability to act as cloud nuclei, it is important to be able to accurately model BB aerosol hygroscopicity as they age during transport. Specifically, the hygroscopicity of organic aerosol (OA), the dominant component of aerosols in most cases, is poorly characterized due to its chemical complexity. The ORACLES campaign provides a comprehensive observation of aerosols above the SEA Ocean with 4-12 days of transport from African fires, making it a valuable opportunity to investigate the hygroscopicity of aged BB aerosol and the OA within the BB aerosol at different stages and environmental conditions. We utilized the scattering enhancement factor $f(80\%)$ from ORACLES 2016 and 2018 airborne measurements to investigate the hygroscopicity (Zhang et al., 2023) and water uptake of BB aerosols, its vertical distribution, its relationship with chemical composition, and its sensitivity to organic aerosol (OA) hygroscopicity over the South-East Atlantic (SEA) Ocean during the biomass burning (BB) season.

Figure 7 (adapted from Zhang et al., 2023), shows the distribution of aerosol hygroscopicity during ORACLES 2016 and 2018, including their variation along the atmospheric column.

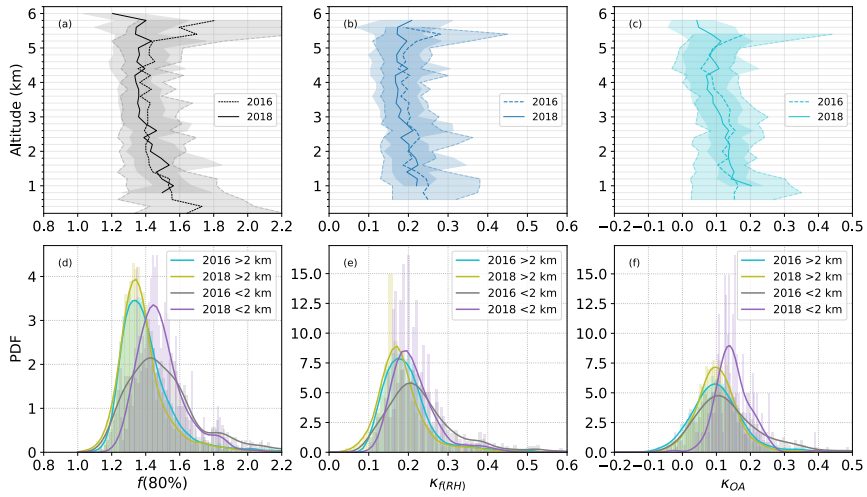

Figure 7: Vertical profiles and PDF of $f(80\%)$ (a, d), $\kappa_{f(\mathrm{RH})}$ (b, e), and κ_{OA} (c, f) for aerosols in the 2016 (dotted line) and 2018 (solid line) ORACLES campaign. Dashed lines in a, b, and c represent the 10$^{\mathrm{th}}$ percentile, mean, and 90$^{\mathrm{th}}$ percentile, respectively.

We found that (Zhang et al., 2023), in general, the aerosol hygroscopicity stays stable above 2 km in both years' campaigns; while below 2 km, aerosols become more hygroscopic at lower altitudes (Fig. 7). This is consistent with the vertical variation of sulphate and OA mass fraction, i.e. more sulphate and less OA at lower altitudes. The probability density function (PDF) distributions of $f(80\%)$ and $\kappa_{f(\mathrm{RH})}$ are similar in the 2016 and 2018 campaigns, with larger variations and higher values of the aerosol hygroscopicity PDF under 2 km (Fig. 7d and 7e). For $f(80\%)$ below 2 km, a primary mode with a diameter around 1.45 is evident, but there is also a second mode with a diameter around 1.81 for aerosols in both years. While the second mode is subtle, it can be identified in the PDF of $\kappa_{f(\mathrm{RH})}$, (Fig. 7e). This suggests the presence of highly hygroscopic substances and could indicate marine influence, as most aerosols below 2 km are within the MBL. For aerosols above 2 km, the mean and standard deviation of $f(80\%)$ and $\kappa_{f(\mathrm{RH})}$ are 1.38±0.12 and 0.19±0.08, respectively, belonging to less hygroscopic particles. These values are generally lower than those for marine aerosols, higher than dust and polluted dust particles, and consistent with the median level of the hygroscopicity for smoke-dominated aerosols found in the literature.

We retrieved the hygroscopicity parameter κ_{OA} using Mie simulations (Zhang et al., 2023). It shows a large variation, with the mean and standard deviation being 0.11±0.08 and the 25th and 75th percentiles of 0.06 and 0.16, respectively. No clear relationship was found between κ_{OA} and OA oxidation level; while a slight increase in κ_{OA} with volatility is shown in 2016, which may be related to the fragmentation during

OA oxidation, where the highly aged and low volatile OA may dissociate into more volatile fragments that are still highly functionalized and hygroscopic. In all, OA hygroscopicity under sub-saturated conditions can be largely influenced by solubility, molecular weight, molecular functional groups, and carbon number; to better understand the variation of κ_{OA}, more molecular investigations are needed. In comparison with other campaigns, we find the variation of aerosol hygroscopicity in the SEA is mainly due to changes in chemical composition, particularly sulphate and OA, as well as variations in OA hygroscopicity during transport. Sensitivity study indicates that solely due to the increase in OA hygroscopicity observed in our study, the aerosol scattering coefficients at 80 % RH can be amplified by 80 %. Relying on the campaign's mean κ_{OA} value leads to a poor prediction of f(80%). The dependence of f(RH) on κ_{OA} suggests that using a constant κ_{OA} can be acceptable when the OA fraction is low and κ_{OA} demonstrates limited variations. ***However, in situations where these two conditions are not met, κ_{OA} can significantly influence the scattering coefficients and thus aerosol radiative effect. Therefore, accommodating the variability of κ_{OA} is advisable***.

Objective 3 - Light absorption over the South-East Atlantic Ocean is dominated by BC, and affected by BrC and other possible absorbers.

Black carbon (BC) and brown carbon (BrC) are the two main light-absorbing carbonaceous aerosols that play a significant role in Earth's radiative forcing and climate. In objective 3 we investigated the contribution of BrC to the total light absorption of biomass burning aerosols over the South-East Atlantic Ocean with different mixing assumptions.

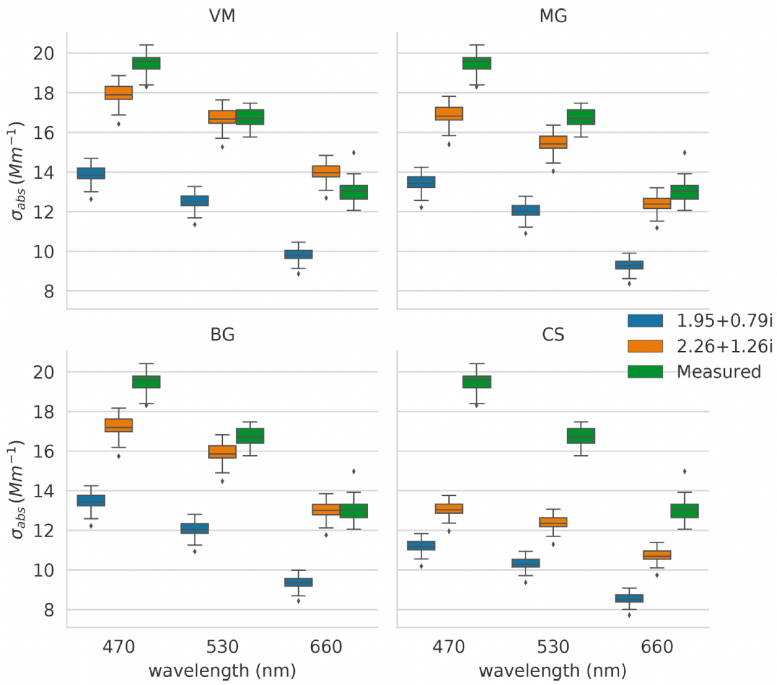

Figure 8: Modelled (blue and orange markers) and measured (green markers) absorption coefficients for research flight 06. Variables are modelled with two mBC values (shown in the legend) using the CS-core-shell, MG-Maxwell-Garnett, BG-Bruggemann, and VM-volume Mixing optical models. OA is assumed to be non-absorbing with refractive index mOA of 1.55. The horizontal lines in the boxes represent the median value, the boxes represent the 25th to 75th percentile, the whiskers represent 1.5 times the interquartile range, and the diamonds represent outliers.

Our closure studies (comparison between observations and various optical models) suggested contributions from absorbers besides BC and BrC at 660 nm. In Figure 8 (adapted from Zhang et al., 2022), we show an example of closure comparing different optical mixing rule models with measurements.

Detailed methodology can be found at Zhang et al., 2022. In short, we performed Mie simulation to reproduce the scattering and absorption coefficients measured by the airborne nephelometer and PSAP instruments on-board the P-3 aircraft during ORACLES 2018. ***We found that the contribution of BrC to the total absorption at 470 nm ranges from 8 %–22 %. Nevertheless, different aerosol mixing rule optical models resulted in different estimations compared to observations, underscoring the importance of model treatment in future absorption assessments.***

To further elucidate the reasons for the relatively high absorbance at long wavelengths, we compared the specific flight segments analyzed to aerosol sampled by filters during those flights and analyzed for single-particle elemental composition by an electron transmission microscopy (as detailed in Dang et al., 2022). ***This analysis further suggested that these long-wavelength absorbers might include iron oxides from dust particles.***

PROJECT PUBLICATIONS AND CONFERENCE PRESENTATIONS

Zhang, L., Segal-Rozenhaimer, M., Che, H., Dang, C., Sun, J., Kuang, Y., Formenti, P., and Howell, S.: Aerosol hygroscopicity over the South-East Atlantic Ocean during the biomass burning season: Part I – From the perspective of scattering enhancement, EGUsphere [preprint], https://doi.org/10.5194/egusphere-2023-2199, 2023.

Che, H., Segal-Rozenhaimer, M., Zhang, L., Dang, C. et al. Cloud processing and weeklong ageing affect biomass burning aerosol properties over the south-eastern Atlantic. Commun. Earth Environ 3, 182 (2022a). https://doi.org/10.1038/s43247-022-00517-3

Che, H., Segal-Rozenhaimer, M**.,** Zhang, L., Dang, C., Zuidema, P., Sedlacek III, A.J., Zhang, X. and Flynn, C., 2022. Seasonal variations in fire conditions are important drivers to the trend of aerosol optical properties over the south-eastern Atlantic, Atmos. Chem. Phys., 22, 8767–8785, 2022, https://doi.org/10.5194/acp-22-8767-2022, (2022b).

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Haochi Che, M. Segal Rozenhaimer, Lu Zhang, Caroline Dang, Paquita Zuidema, Amie Dobracki, Arthur J. Sedlacek III, Hugh Coe, Huihui Wu, Jonathan Taylor, Jens Redemann, Jim Haywood, Biomass burning aerosol ageing and seasonal variation in the south-eastern Atlantic, DOE-ASR PI annual meeting (virtual), June 23, 2021, (Poster)

M. Segal Rozenhaimer, Caroline Dang, Haochi Che, Lu Zhang, Steve Howell, Mary Karacab, Sara Purdue, Pui-Shan Wong, Thanos Nenes, Amie Dobracki, Art Sedlacek, Hugh Coe, Paola Formenti, Jens Redemann, Paquita Zuidema, James Haywood, Assessing the link between Aerosol mixing state, structure and composition and their optical properties: Ascension Island as a testbed for the South-East Atlantic Aerosol, DOE-ASR PI meeting, June, 2020 (Invited talk)

M. Segal-Rozenhaimer, Caroline Dang, Haochi Che, Lu Zhang, Steve Howell, Mary Karacab, Sara Purdue, Pui-Shan Wong, Thanos Nenes, Amie Dobracki, Art Sedlacek, Hugh Coe, Paola Formenti, Jens Redemann, Paquita Zuidema, James Haywood, Chemical properties of biomass-burning aerosols derived from filter analysis from ORACLES and CLARIFY, ORACLES Science Team Meeting, May 2020, (Invited talk)