Morphological and optical properties of carbonaceous aerosol particles from ship emissions and biomass burning during a summer cruise measurement in the South China Sea

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Abstract. Carbonaceous aerosols constitute a crucial component of atmospheric marine aerosols, among which black carbon (BC) and brown carbon (BrC) are important contributors to light absorption and hence the positive climatic radiative forcing in the marine atmosphere. We conducted a month-long (May 05–June 09, 2021) onboard sample collections and online measurements of carbonaceous aerosols to characterize their morphological and optical properties during a ship cruise in the

20 South China Sea (SCS), covering a marine region of 11.9–24.5 °N and 111.1–118.2 °E. Single particles were collected by a single particle sampler and offline analyses were performed to investigate the mixing state and morphology using a transmission electron microscope (TEM). Online measurements of BC in $PM_{2.5}$ were made by a seven-wavelength aethalometer and organic carbon (OC)/elemental carbon (EC) mass concentrations were measured by a semi-online OC/EC analyzer. Single particle samples were classified into two modes: "stop" when the ship was anchored and "navigation" when

25 the ship sailed at high speed. Feret diameters of the single particles during navigation and stop showed size distributions with the lognormal fitting peaks at 307 and 325 nm, respectively. The fresh (without coating) and aged BC particles (after removal of coating by the electron beams in TEM) showed comparable median fractal dimensions (1.65 vs 1.66), in contrast to their different median lacunarities (0.53 vs 0.59). The aged BC particles showed narrower Feret diameters (298–1980 nm) during navigation than those (304–2982 nm) of freshly-emitted BC from the own ship during stop. Moreover, tar balls, as one

30 important component of single particles from ship emissions and as the tracer of biomass burning, were identified with geometrical diameters of 160–420 nm in the TEM images. The energy dispersive X-ray spectroscopy (EDS) analyses showed those tar balls are mainly mixed with sea salt, organics, BC, and sulfate. We also found a significant fraction of aged BC in various mixing states (core-shell, embedded) with other components of the aerosol particles after long-range transport.

The campaign was further divided into several periods (before monsoon period, BMP; transition monsoon period, TMP;

35 after monsoon period, AMP; and ship pollution period, SPP) according to the wind direction during monsoon and the own ship pollution. The median OC/EC ratios were 8.14, 5.20, 6.35, and 2.63 during BMP, TMP, AMP, and SPP, respectively, showing higher OC/EC ratios for biomass burning emissions than for fossil fuel emissions. Additionally, the median absorption Angström exponent (AAE) values derived from all wavelengths were 1.14, 1.02, 1.08, and 1.06 for BMP, TMP, AMP and SPP, respectively. Particularly, a median AAE value of 1.93 was obtained during two significant biomass burning events. These

40 results showed that biomass burning (BB) and fossil fuel (FF) combustion contributed to 18–22% and 78–82% of all the BC light absorption without the two intense biomass burning events, during which BB and FF accounted for 42% and 58%, respectively. The two BB events originated from the Philippines and Southeast Asia before and after the summer monsoon. Our results demonstrated that BC can serve as the core of aged particles but the fractal dimensions of BC aggerates were subject to little variation; moreover, such BC particles become much more aggerated after aging in the marine atmosphere,

45 which further affects the light absorption of the BC particles in the SCS. This study provides information about the morphology and the optical properties of carbonaceous aerosols which can be used to evaluate their effects on light absorption and hence the climatic radiative forcing in the SCS region.

1 Introduction

50 Carbonaceous aerosols (e.g., organic carbon (OC), elemental carbon (EC)/black carbon (BC), and brown carbon (BrC)) profoundly impact regional and global climate (Corbin et al., 2019; Lu et al., 2020; Rabha and Saikia, 2020). As an important component of carbonaceous aerosols, BC can serve as a tracer of anthropogenic pollution once emitted from the incomplete combustion of fossil fuels and biomass burning. Moreover, BC particles are generally soot-aggerated with onion-like graphite layer microstructures which can be observed under electron microscopy (Adachi et al., 2019). BC and EC are two components

55 of carbonaceous aerosols that are measured differently. BC is typically quantified based on its light-absorbing properties, while EC is measured using thermal-optical methods (Duarte et al., 2021). However, EC can also be referred to as graphitic carbon or soot, with some overlap in their definitions. Another important component of carbonaceous aerosols, BrC, represents a series of light-absorbing organic compounds, contributing significantly to the light absorption of atmospheric aerosols (Wang et al., 2020b). BrC and BC show different light absorption patterns as a wavelength function. BrC typically absorbs more

60 strongly in the visible range (400–700 nm), while BC absorbs more strongly in the ultraviolet (UV) and near-infrared (NIR) ranges (200–400 nm and 700–1000 nm, respectively). Therefore, BrC and BC can be distinguished by measuring the absorption spectra of aerosol particles at different wavelengths (Andreae and Gelencsér, 2006; Bond et al., 2013; Laskin et al., 2015; Li et al., 2020; Yus-Díez et al., 2021). Tar balls are commonly used as typical tracers of biomass and biofuel burning due to their composition of amorphous carbon. These particles also belong to BrC due to their light absorption properties over

65 a broad range of solar spectra, from around 300 nm in the UV range to 2500 nm in the NIR range (Adachi et al., 2019; Hand et al., 2005). Spherical tar balls emitted from biomass burning have been observed in cases of both wild fire burning (Adachi et al., 2019) and laboratory generated tar ball particles (Tóth et al., 2014). In the atmosphere, biomass burning produces a significant amount of tar balls, which are not deliquescent but can absorb water at high relative humidity (RH = ~80%), thereby affecting their ability to scatter and absorb light (Hand et al., 2005).

70   The optical properties of BC and BrC particles are affected by several factors including the emission source, coating component, particle size, morphology, and mixing state of the particles (Wei et al., 2020). The BC configuration in the single particles would influence their radiative effects (Luo et al., 2021). For example, core-shell BC particles show enhanced light

absorption compared to bare BC particles, especially when BC particles are coated with absorptive materials such as BrC (Budhavant et al., 2020; Cappa et al., 2012; Shamjad et al., 2012; You et al., 2016). "Lensing effect" refers to the absorption

75   enhancement if BC is coated with non-absorbing organic or inorganic materials (Luo et al., 2021; Yang et al., 2009). In contrast, if the BC coating materials are highly absorptive, no absorption enhancement may occur at shorter visible and UV wavelengths, a phenomenon known as "shielding effect". When BC is well internally mixed with BrC, its total absorption enhancement becomes smaller than those of not well mixed counterparts due to the absorptive coating that acts as a shield (Feng et al., 2021).

The extent to which BC and BrC contribute to light absorption in atmospheric aerosols can be assessed using the absorption

80   Ångstrom exponent (AAE) (Wang et al., 2020a). AAE is a parameter used to quantify the spectral dependence of aerosol light absorption. It is calculated by fitting a power-law relationship between the aerosol absorption and wavelengths over a given spectral range. The AAE is used to identify sources and types of aerosols and a higher AAE value is associated with sources such as biomass burning or urban pollution, while a lower AAE value suggests absorption by larger particles, such as mineral dust or sea salt (Blanco-Donado, 2022; Duarte et al., 2021). However, many factors such as mixing state, coating, particle size,

85   refractive index, wavelength, and emission source, would affect the AAE values for BC and BrC aerosols, leading to large variations among different studies (Moschos et al., 2021). For example, a previous study showed that the AAE values derived from wavelengths of 405 and 781 nm are very sensitive to refractive index and particle diameter (Chylek et al., 2019). The AAE values of 0.8−1.6 at 470 and 950 nm are attributed to traffic emissions and fuel combustion (Ezani et al., 2021). Comparatively, those AAE values can be as large as 2.0 for ship emissions (Helin et al., 2021). Moreover, the recommended

90   AAE value for fossil fuel (FF) and biomass burning (BB) is 1 and 2 (or higher), respectively (Liu et al., 2023). Other AAE values were also found in previous studies for FF (0.9) and BB (1.68) (Zotter et al., 2017) or FF (1.2) and BB (2.2) as the mostly used optical pair (Milinković et al., 2021). The AAE values of 1.4 and 1.7 for BC and BrC were set to be the lower and upper limits in the modelling study of biomass burning particles mixed with BC and BrC (Chylek et al., 2019). However, the use of constant AAE values for calculating the BC fractions from BB and FF led to large uncertainties without knowledge of

95   the core size or coating thickness of the BC particles (Virkkula, 2021). Currently, the effect of the light absorption is not well known for the carbonaceous particles in the marine atmosphere due to scarce ship-based measurements.

The optical properties of BC and BrC particles can also be investigated through fractal dimension (D_f) analysis based on the

fractal properties of BC aggerates. D_f illustrates how particles aggregate and grow and it can be determined through boxing

counting calculation, ensemble method, or soot parameter method with TEM images (Pang et al., 2022). The D_f values are

100   mainly related to emission sources and aging process of the particles. Previous studies showed that the D_f values of fresh BC

particles tend to be small but become larger after aging because the particles are more compact due to coatings (Luo et al.,

2022; Wang et al., 2017). D_f values of 1.8 and 2.6 were used respectively for fluffy and compact BC particles in a numerical

study to investigate the impact of the BC morphology on light absorption (Luo et al., 2021). Laboratory experiments simulating

wildfires showed that the D_f values of freshly emitted BC were in a range of 1.74−1.92 (Chakrabarty et al., 2006), compared

105   to the range of 1.67−1.83 from a field study of the Las Conchas fire (China et al., 2013). A similar range of the D_f values of

1.67−1.93 were found at a remote site in the southeastern Tibetan Plateau (Wang et al., 2017). The obtained D_f values for the

traffic emissions were as large as 3 (Wei et al., 2020). In addition to the emission sources and aging process, D_f is also dependent

on the particle size. A previous experimental study found that for polystyrene latexes (PSL) particles, the D_f values decreased

with the increase of particle size up to 200 nm (Wu et al., 2013b). Nevertheless, knowledge of the fractal dimension for

110   carbonaceous particles in the marine atmosphere is currently very limited, hindering our ability to understand the aging process

and the optical properties of these particles.

   In the past years, carbonaceous aerosols in the marine atmosphere have been extensively studied on regional and global

scales, focusing on the transport of anthropogenic emissions to the sea areas. The BC background concentrations in Antarctic

and Arctic regions are below 20 ng m^{-3} (Fossum et al., 2022). The BC outflows from Asia to the Pacific Ocean exhibit seasonal

115   variations and originate from anthropogenic and biomass-burning sources in China, Siberia, and Southeast Asia (Matsui et al.,

2013). Ship-based BC and EC measurements reveal significant influence of continental transport on remote oceanic regions,

including the Bay of Bengal (Kedia et al., 2012), Indian Ocean (Kompalli et al., 2021), Southern Indian Ocean and the Southern

Ocean (Ueda et al., 2018), North Sea (Bencs et al., 2020), Antarctic (Chaubey et al., 2013; Schmale et al., 2019), North Pacific

(Taketani et al., 2016; Xing et al., 2014), Arctic (Pankratova et al., 2021; Sharma et al., 2019), Northeast Atlantic (Fossum et

120   al., 2022), the Yellow Sea (Kwak et al., 2022), and Western Pacific (Ma et al., 2022). However, to our knowledge, the BC mass

concentrations have been found to vary significantly across different oceans and seasons, with levels from 3 to 2800 ng m^{-3}

and being influenced by anthropogenic activities and seasonal factors. The online BC measurements in the South China Sea

(SCS) region are limited. An early study reported BC concentrations on Yongxing Island during the rainy season (May 16–June 20, 2008) and the dry season (Dec. 12, 2008–Jan. 8, 2009), with average concentrations of 0.54 and 0.67 µg m^{-3},

125   respectively (Wu et al., 2013a). Recent studies conducted at coastal sites in the SCS found that BC concentrations are strongly impacted by the land anthropogenic emissions (Wang et al., 2022). The time-resolved BC concentration varies with the vertical heights (Sun et al., 2020c) and the carbonaceous materials of OC and EC account for 31–62% in PM$_{2.5}$ (Yan et al., 2018). Nevertheless, quantification of the light absorption potential of BC and BrC aerosols remains challenging due to the limited knowledge regarding the morphology, particle size, and mixing state of carbonaceous particles in the SCS (Kompalli et al.,

130   2021). Furthermore, the atmosphere in the SCS is typically influenced by the southwesterly monsoon from May to August (Wang and Wu, 2020), which affects the air masses from Southeast Asia. In this study, we conducted ship-based measurements of BC, OC/EC, and single particle sampling during summer (May 05–June 09, 2021) in the SCS. The morphology (i.e., the fractal dimension and the size of the single BC particles) and light absorption properties of carbonaceous particles were characterized. The source origins, relationships between the D$_f$ and BC size, as well as the impact of summer monsoon on the

135   light absorption of the BC particles are discussed.

2 Methods

2.1 Cruise route and instrumentation

The cruise measurements were carried out from May 5 to June 9, 2021, covering a marine area of 11.9–24.5 °N and 111.1–118.2 °E in the SCS. Single particles were collected on the TEM grids (3.05 mm I.D., copper meshed and covered with lacey

140   carbon film) located on the front deck during ship navigation and stop using a single particle sampler (DKL-2, Genstar Electronic Technology Co., Ltd., China) which is the same as other studies (Liu et al., 2021; Pang et al., 2022). The sampling flow rate and time were set at 1 L min^{-1} and 10 min, respectively, for each collection. The particles with aerodynamic diameters above 0.2 µm were collected with a collection efficiency of 50%, assuming a particle density of 1.5 kg m^{-3} (Marple and Olson, 2011). More details can be found in the supplementary information (Section 1 of SI). The mixing state and morphology of the

145   single particles were analyzed utilizing a transmission electron microscope (TEM, FEI Tecnai G2 Spirit, Holland) operated at

an accelerating voltage of 120 kV, in conjunction with an energy dispersive spectrometer (EDS, Bruker Nano GmbH Berlin, Esprit 1.9, Germany) for elemental analysis. The thickness of the EDS detector (type XFlash 5060) is 0.45 mm with a Si dead layer of 0.029 mm. Notably, in the EDS spectra, when analyzing particle composition, Cu should be excluded, and a considerable level of C and Si should be observed in the background signals due to the presence of Si in the detector, Cu and

150   C in the TEM grid.

The sampling inlets were installed on the bow of the research vessel with a height of ~ 15 m above sea level. The own ship emissions (e.g., engine, cooking, etc.) were exhausted from the chimney on the stern with a linear distance of ~ 22 m to the inlets. The BC mass concentrations were measured by an aethalometer (Model AE33, Magee Scientific, USA) with a high time resolution of one second or one minute (Drinovec et al., 2015). The sampling air was regulated by a $PM_{2.5}$ cyclone (BGI

155   Inc., Waltham, MA, USA) and subsequently dried by a Nafion dryer (Model MD-700 series, Perma Pure Inc., USA) with a relative humidity below 40% through the filter tape (type 8060) at a flow rate of 5 L min^{-1}. The optical attenuation (ATN) was measured simultaneously from the two spots on the filter. The measured attenuation at seven wavelengths (7 channels) is used to determine the wavelength-dependent absorption coefficient. The mass specific absorption cross-sections (MAC) applied in the BC calculations were 18.47, 14.54, 13.14, 11.58, 10.35, 7.77, and 7.19 m^2 g^{-1} for wavelengths of 370, 470, 520, 590, 660,

160   880, and 950 nm, respectively (Ausmeel et al., 2020). The measured values at 880 nm (channel 6) are for black carbon concentration calculation, at 370 nm (channel 1) for UV particulate matter (UVPM) concentration (Drinovec et al., 2015). The detection limit of AE33 aethalometer is approximately 0.03 µg m^{-3} for 1-min integration period and below 0.005 µg m^{-3} for 1-hour integration period. The instrument was automatically calibrated by zero air every day. Notably, significant spikes were observed during periods when the ship was stationary, when it was traveling at low speeds, and when the wind was blowing

165   from the stern of the vessel.

The OC/EC concentrations were measured by a semi-continuous OC/EC analyzer (Model-4, Sunset Laboratory Inc., USA) based on the optical attenuation and thermo-optical transmittance methods (Geron, 2009) under the NIOSH 5040 thermal-optical protocol (Lappi and Ristimaki, 2017). Similarly, the sampling air passed through a $PM_{2.5}$ cyclone (BGI Inc., Waltham, MA, USA) and was dried by a Nafion dryer (Model MD-700 series, Perma Pure Inc., USA) with a relative humidity below

170   40% at a flow rate of 8 L min^{-1}. The air then passed through a denuder for the removal of volatile organic compounds (VOCs)

and the particles were collected on the quartz filter with 45-min accumulation and 15-min analysis. The instrument was calibrated with the standard sucrose solution as recommended. The manufacturer-claimed detection limits are 0.4 and 0.2 μg m^{-3} for OC and EC, respectively (Brown et al., 2019). However, several previous studies showed that these values may vary substantially in a range of 0.04−2 and 0.001−0.5 μg m^{-3} for OC and EC, respectively, due to the artifact of the quartz filters

175   (Bao et al., 2021; Bauer et al., 2012; Chen et al., 2017; Jung et al., 2011; Karanasiou et al., 2020; Park et al., 2018; Zhang et al., 2021). Here, we estimated the detection limits of 0.15 and 0.012 μg m^{-3} for OC and EC based on 26 effective blank measurements with 3 times standard deviation (3σ) during the campaign.

The measurements of solar radiation (SR), temperature (T), pressure (P), relative humidity (RH), relative wind direction (RWD), and relative wind speed (RWS) were provided by the automatic weather station equipped on the research vessel. The

180   cruise route is from the global positioning system (GPS) onboard the ship.

2.2 Data analyses and processing

2.2.1 Analyses of single particles

A total of 34 samples (15 during navigation and 19 at stop) were analyzed and more than 20 bright-field TEM images were randomly captured for each sample except for those at the center of the grids where particles were easily overlapped. A total

185   of 15624 single particles were statistically analyzed to obtain morphology information (i.e., the Feret diameter, area, perimeter) for each particle using the software Image J (1.53q, National Institute of Health, USA). The D_f values of the BC particles were estimated using the boxing counting method. An example was given in the SI (section 2, Fig. S1) to show how to calculate D_f using the software. A detailed description of the procedure using the boxing counting method and the software ImageJ can be found in the SI. The D_f values are very sensitive to the fill extent and sizes of the particles. A previous study showed low fractal

190   dimensions when the particles contain void volumes (Peyronel et al., 2010).

The own ship emissions can be identified using various measures, for example, high CO, NO$_x$ concentrations (Sun et al., 2020b), high BC concentrations (Alroe et al., 2019; Shank et al., 2012), regular cooking emissions (Cai et al., 2020), and wind speeds/directions between the ship stop and start operation (Ausmeel et al., 2020; Kwak et al., 2022). The contribution of ship

emissions to BC sources on the marine atmosphere depends on engine types, operation modes, fuel types, and loadings (Gagne

195 et al., 2021; Jiang et al., 2018; Karjalainen et al., 2022; Lack and Corbett, 2012; Wu et al., 2021; Zhao et al., 2020). Here, we

classify two sampling modes (navigation vs stop) of single particle analyses according to ship operation, relative wind

direction/speed. The navigation mode is constrained by the relative wind direction of 0−80° or 280−360°, and the relative

wind speed greater than 5 m s^{-1}, averaged for every 10 minutes (consistent with the collection time of TEM samples). The stop

mode is set with the relative wind direction of greater than 80° and less than 280°, or the relative wind speed lower than 5 m

200 s^{-1}. The navigation mode samples are mainly from marine air and air masses of long-range transport while the stop mode

collected air masses which are mixed with the own ship emissions. The temporal profiles of ship heading directions and relative

wind direction/speed are shown in the SI (section 3, Fig. S2). Details of the two sampling modes (navigation vs stop) on a

vector average of 10 minutes are listed in Table S1. Here, we distinguished the own ship emissions (ship pollution) from those

of other ships or long-range transport. In addition, an hourly averaged BC concentration above 2 μg m^{-3} was also considered

205 as ship pollution based on the time series of BC concentration without significant interference of self-emission.

2.2.2 BC, OC, EC and optical EC data

Here, we averaged the BC mass concentrations over one minute and excluded those below the detection limit of 0.03 μg m^{-3}

for minimizing the variations. We also removed the own ship emissions which are characterized by spikes in particle number

concentrations according to the wind directions (Fossum et al., 2022). AAE was calculated according to Eq. (1) using the light

210 absorption at wavelengths of 470 and 950 nm, which are built-in algorithms in the AE33 aethalometer as described elsewhere

(Helin et al., 2021; Kang et al., 2022; Milinković et al., 2021; Zotter et al., 2017). This method serves as a two-composition

source apportionment for BC emitted from fossil fuels and biomass burning (AAE model).

$$\text{AAE} = -\frac{\ln\frac{\sigma_{ap}(\lambda_1)}{\sigma_{ap}(\lambda_2)}}{\ln\frac{\lambda_1}{\lambda_2}} \qquad (1)$$

where σ_{ap} is the aerosol absorption coefficient, σ_{ap} = BC*MAC. λ_1 = 470 nm and λ_2 = 950 nm.

215 Alternatively, AAE can be obtained from the negative slope of linear regression between the log-transformed σ_{ap} and all the

wavelength spectra so that hourly AAE values (all λ) can be obtained following a similar method in Retama et al. (2022). Here,

we define Delta-C as the difference between the concentration derived from the aforementioned UVPM data (at 370 nm) and BC concentration (at 880 nm). This Delta-C parameter was employed as an indicator of smoke from biomass burning in previous wood biomass burning studies (Harrison, 2020; Zhang et al., 2017).

220   The OC and EC (thermal) concentrations lower than the detection limits (0.15 and 0.012 µg m^{-3} for OC and EC, respectively) were excluded. Additional data were removed for those with laser correction factors below 0.88 and calibration peak areas lower than the initial calibration levels (within 10%), and a total of 550 h data were used for further analysis. In comparison, the Sunset optical EC (at 660 nm) is generally consistent with the Magee AE33 aethalometer derived BC (at 880 nm) within 9% (Brown et al., 2019) which is shown in Section 3.3. The EC concentration data from Sunset were considered as ship

225   pollution and were discarded when the BC concentrations from the AE33 aethalometer were higher than 2 µg m^{-3}, in addition to those with relative wind directions of 80–280° regardless of the BC concentrations as mentioned before.

2.2.3 HYSPLIT backward trajectory and MODIS fire data

The backward trajectories were calculated using NOAA HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) (Version 5) at heights of 100, 500 and 1000 m above sea level (AGL). Daily meteorological data with 1.0°×1.0° spatial

230   resolution for trajectory calculation were downloaded from the global data assimilation system (GADS) (ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1/). Here, we calculated the 72-h back trajectories of air masses arriving at the single particle sampling sites along the cruise route.

Moderate Resolution Imaging Spectrometer (MODIS) data are available from the Near real-time MODIS Collection 6 products (https://firms.modaps.eosdis.nasa.gov/download/). Here, we selected a region of 102–127 °E and 0–30 °N fully

235   covering the campaign area. The number of fire hotspots was counted each day during the campaign with a confidence level of higher or equal to 80% as recommended (Giglio et al., 2020). A detailed description of the fire detection algorithms is available online (https://earthdata.nasa.gov/what-is-new-collection-6-modis-active-fire-data).

3 Results and discussion

3.1 Overview

240 Figure 1 shows the time series of ship cruise route and the single particle sampling locations during ship navigation (marked as solid triangles) and stop (marked as open squares) over the SCS during the campaign. The cruise sequences are AB→C→ D→EB→D→A, with AB and EB being non-stop cruise, otherwise the ship stopped occasionally along the arrow routes for other research tasks. Figure 2 shows the time series of the meteorological variables (i.e., solar radiation (SR), temperature, pressure, relative humidity (RH), wind direction (WD), and wind speed (WS)) during the whole campaign (May 05–June 09,

245 2021). The measurements were conducted mostly on sunny days prior to June 02 as shown by the SR data. Subsequently, it became rainy and cloudy due to the summer monsoon in the SCS. One notable meteorological feature during the campaign was the occurrence of the summer monsoon starting from May 27 close to the site E, during which (May 27–June 01), an increase of RH (~9% from campaign-averaged 78.7% to monsoon period-averaged 85.6%) and a slight decrease of pressure (~0.2% from 1007.4 to 1005.4 hPa) were observed. Meanwhile, the wind directions were mainly southerly during this period

250 and later changed to southwest. It should be noted that Typhoon 202103 (CHOI-WAN) traveled across B→D, resulting in a bulge in the middle of the cruise route for avoiding the typhoon during June 03–05, 2021. The typhoon track is available online with the last accessed date Mar. 25, 2023: http://agora.ex.nii.ac.jp/digital-typhoon/summary/wnp/s/202103.html.en.

Figure 3 shows the time series of the mass concentrations of carbonaceous aerosol components in $PM_{2.5}$ (i.e., BC, UVPM, OC, and EC) during the whole campaign. Frequently high spikes of the mass concentrations of carbonaceous aerosol

255 components were observed due to the ship pollution. We notice that ship pollution was significantly pronounced on the first two days after the ship left the harbor and on the last 3–4 days before the ship returned to the harbor, during which the spikes of BC concentrations were measured by the Magee AE33 aethalometer with the relative wind direction of 80–280°.

3.2 Single particle analysis of BC and tar balls

Particle size distribution, composition, and size-dependent BC fractals were investigated based on TEM images. The Feret

260 diameter is commonly used in microscopy for particle size analysis (Zefirov et al., 2018). The size distribution of all the single

particles from the analyzed TEM images is depicted in Fig. 4. The distribution is represented with histograms starting at 50 nm, a width interval of 20 nm, and a bin number of 200. The choice of bin width may vary depending on cases but it is close to the quotient value of the square root of the measured particle number divided by the overall width of the distribution (Pabst and Gregorova, 2007). Moreover, lognormal fitting is used for the peak size identification of particle size distribution (Rice et

265 al., 2013). Figure 4a shows a fitted peak Feret diameter of 307 nm for a total of 6613 particles from 15 samples during navigation, while a fitted peak Feret diameter of 325 nm was obtained for a total of 9011 particles from 19 samples during stop (Fig. 4b). Particles collected during navigation were predominantly aged at high wind speeds, while particles during stop were mixed significantly with freshly emitted particles from the own ship and from other merchant ships or those from long-range transport, possibly leading to the variation of the size distribution. Although the bimodal distribution was observed from

270 particles in the indoor air, which was likely caused by fresh emissions and secondary formation (Pipal et al., 2021), we did not obtain significant bimodal peaks for both navigation and stop particles.

We obtained characteristic values for the particle shape descriptors such as circularity (0.7 ± 0.2) and aspect ratio (1.2 ± 0.3) for all the particles collected during navigation and stop, implying that these particles are not perfectly spherical and may vary in their mixing states. Figure 5 (top images) shows a comparison of the mixing states during navigation (a-c) and stop (d-f)

275 from typical BC TEM images. The BC particles collected during navigation are in the embedded (a), external (b), or core-shell (c) mixing states classified with the methods which are based on single particle analysis of island and mountain samples across East China Sea and Japan (Adachi et al., 2014; Sun et al., 2020a). More TEM images for the heavily coated internal and external BC particles from navigation can be found in the SI (section 4, Fig. S3). The EDS analysis showed that the single particles during navigation were predominantly composed of carbon (C), oxygen (O), sulfur (S), potassium (K), sodium (Na),

280 chloride (Cl), magnesium (Mg), and calcium (Ca) (Fig. S4), indicating that those BC particles were coated with sulfate, sea salt, and organics. Furthermore, small externally mixed BC particles can be transported over the sea and easily coated during long-range transport. Under the TEM electron beam, these coated volatile components were easily vaporized to expose the BC fractal frame (Fig. S3d-f).

Comparatively, much larger BC particles as well as smaller scattered BC particles during stop were found (Fig. 5d-f), among

285 which were apparently emitted from the own ship (e, f). Those BC particles with Feret diameters greater than 2 µm during

stop were fractal aggerates which unlikely survived during long-range transport due to deposition. In addition, heavily coated internal BC particles were found during stop due to the mixing between ship pollution and the marine air (Fig. S5). The bottom panels of Fig. 5 (a-f) show the corresponding images obtained by boxing counting in fractal analysis with the resultant D_f, Feret diameter (D), Lacunarity (L), and sampling number underneath for each TEM sample image. Figure 6 shows D_f and L

290 as a function of D for some representative BC particles during both navigation and stop. These particles were exposed to electron beam and volatile coatings were removed so that the morphology of bare BC was clearly shown regardless of the mixing state of the original BC. The D_f values during navigation were in a range of 1.50–1.77 with a median of 1.65, while the D_f values during stop were 1.48–1.75 with a median of 1.66, indicating no significant differences of D_f (<1%) for the exposed BC particles during navigation and stop. Figure 6 also shows that most of the BC particles during navigation were

295 below 1 μm in Feret diameter, implying that smaller BC particles were more susceptible to be coated and aged during transport. Comparatively, the lacunarities during navigation (0.32–0.90, median: 0.53) and stop (0.35–0.77, median: 0.59) were different, with the former being smaller than the latter, indicating that the lacunarity tended to become smaller (~10%) after coating or aging of the BC particles.

Tar balls were frequently observed during the campaign. The spherical tar ball particles in the marine atmosphere were mixed

300 with sea salt (Fig. 7a and d for TEM image and EDS spectrum, respectively), organic carbon and sulfate (Fig. 6b and e) from the samples collected on May 27 during navigation. In contrast, the particles collected on June 01 were found to be amorphous carbon agglomerates which were mixed with sulfate (Fig. 6c and f). During these days, the wind directions were from southwest, with air masses originating from both the Philippines and Southeast Asia. The difference between tar ball spheres and amorphous carbon agglomerates may be related to biomass burning type or source origin. Similar particle morphologies

305 were found in other studies on brown carbon during aircraft measurements over the Yellow Sea in 2001 (Zhu et al., 2013). Tar balls mixed with BC during stop were also observed (Fig. S6), with geometrical diameters of 160–420 nm, much larger than nano-soot spheres (40–50 nm) (Fig. S7). In comparison, the laboratory-generated tar balls were measured to have AAE values of 2.7–3.4, with an average of 2.9 at 467–652 nm (Hoffer et al., 2016).

3.3 Air mass trajectories and mass concentrations of carbonaceous aerosols

310 Figure 8 shows the time series of fire spots distribution and the 72-h backward trajectories at three AGLs (100, 500 and 1000

m) over the SCS during the campaign. Only several backward trajectories are shown to avoid massive overlapping. Several

fire spots located in the sea were attributed to oil or natural gas drilling processes which generate thermal energy, combustion,

and exhaust. Such processes included the prevalent hydrocarbon exploration and production activities in this region. A

comprehensive cartographic representation of these endeavors within the SCS can be accessed via the online platforms

315 (https://amti.csis.org/south-china-sea-energy-exploration-and-development/). Note that since the ship moved along the cruise

route, the air mass backward trajectories also changed with the movement of the ship. For example, significant biomass burning

was detected in Laos, northern Vietnam, and the Philippines during May 15–24, as indicated by the corresponding fire spots.

However, the back trajectories to the sampling route (C→D) during this period were mainly from the Philippines.

Here, we classified the campaign period into several groups based on the cruise route, change of wind direction during

320 monsoon, backward trajectories, and ship pollution, as listed in Table 1: (1) BMP-1 (before monsoon period 1), AB route

mainly with northeast wind direction during May 05–09; (2) BMP-2, B→C→D route close to the Philippines primarily with

southeast wind direction during May 10–22; (3) BMP-3, D→E close to mainland China with the same wind direction as BMP-

2 during May 23–26; (4) TMP (transition monsoon period), EB route with south wind direction during May 27–Jun 01; (5)

AMP (after monsoon period), B→D→A route with southwest wind direction during June 02–09; (6) SPP (ship pollution

325 period), ~35% of the online measurement data could be attributed to this category in this study due to the interference of the

research vessel self-emission.

The BC concentrations measured by the Magee AE33 aethalometer agree excellently with the optical EC concentrations

obtained from the Sunset OC/EC analyzer, as evidenced by a linear regression coefficient of 0.97. However, the BC

concentrations were considerably higher than the thermal EC concentrations, exhibiting linear regression coefficients of 1.66

330 and 1.55, respectively. These findings, presented in Fig. S8 of Section 5 in the SI, are in line with previous research conducted

by Brown et al. (2019). The OC/EC ratios can be used as an indicator for the source origins of the air masses. Figure 9 shows

the median OC/EC ratios (8.14, 5.20, 6.35 and 2.63) for the classified periods (BMP, TMP, AMP, and SPP, respectively).

Notably, EC median mass concentrations (0.24, 0.25 and 0.17 µg m^{-3}) for the marine air masses during BMP (0.013–0.69 µg m^{-3}), TMP (0.015–0.60 µg m^{-3}), AMP (0.014–0.74 µg m^{-3}) were lower than the median concentration (1.70 µg m^{-3}) during SPP.

335 In addition, this study revealed a significant variation in EC concentrations during SPP, ranging from 0.15 to 22.8 µg m^{-3}. Previous studies showed that OC/EC ratio could be characterized by various sources, ranging from 1.37–1.71 for residential cookstoves, 1.63–2.23 for rural emissions, 1.05–1.24 for diesel exhaust, and 0.80–1.12 for urban environments (Khan et al., 2012). A low OC/EC ratio (<3) corresponded to the predominant contribution of the primary OC in submicron particles reported in a previous study in the Southern Indian Ocean, Northern Indian Ocean and Bay of Bengal (Neusüß, 2002). Here,

340 the median OC/EC ratio of 2.63 during SPP is much higher than the characteristic values of diesel combustion, most likely because the sample air during SPP is composed of marine air and the own ship exhaust. Our results are consistent with a recent study which showed that the diesel combustion from ships accounted for 15% of BrC in the total light absorption at a coastal site in Shanghai during June–July, 2021 (Kang et al., 2022). In contrast, the OC/EC ratios during other periods (i.e., BMP, TMP and AMP) were even much higher (5.20–8.13), indicating that the aerosols were highly aged during the long-range

345 transport of biomass burning aerosols. This is also consistent with our recent study in the SCS which showed that during monsoon periods in the summer of 2019. The biomass burning organic aerosols became aged through atmospheric processes during transport (Sun et al., 2023).

3.5 Light absorption of carbonaceous aerosols

The long-range biomass burning transport affects the air mass in the SCS. Figure 10 illustrates the wavelength-dependent mass

350 concentration measured by the AE33 aethalometer during the campaign, showing (a) an example of a ship plume, and (b, c) two significant biomass burning events during BMP (BB-1: 6:00–7:00 on May 15 and 15:00–22:00 on May 16) and during TMP (BB-2: 15:00 on May 30–00:00 on May 31). The ship plumes, predominantly emitted from fossil fuel combustion, showed similar absorption at all seven wavelengths. In contrast, significant absorption at low wavelengths was detected during the biomass burning events, a phenomenon also observed in other field measurements in urban cities and towns where air

355 masses were susceptible to biomass burning (Zhang et al., 2017). A comparison of the two methods for AAE calculation is presented in the SI (Section 6, Fig. S9). The fitting results demonstrate that the AAE calculated for all wavelengths was lower

than the AAE calculated for only 470 and 950 nm wavelengths. The fitting slope is 0.78, and the determination coefficient (R^2) is 0.98, indicating a strong correlation between the two methods.

Figure 11 shows the hourly averaged AAE derived from all wavelengths as a function of the BC concentrations by AE33 aethalometer with the median (range) AAE values of 1.14 (0.57−1.48), 1.02 (0.51−1.36), 1.08 (0.54−1.42), and 1.06 (0.65−1.37), respectively, for the classified periods (BMP, TMP, AMP, and SPP), and the corresponding BC median (range) mass concentrations of 0.28 (0.033−1.17), 0.14 (0.042−2.86), 0.17 (0.055−1.08), and 3.01 (0.21−36.5) μg m^{-3}, respectively. Like EC, ship pollution led to emissions of high BC concentrations, reaching as high as 36.5 μg m^{-3}. The median BC concentrations decreased significantly during TMP and AMP, likely due to the increase of the RH which further increased the scavenging of the BC particles during navigation as reported previously (Girach et al., 2014). Note that the biomass burning events were excluded from the above calculations and are further discussed below.

During the biomass burning events, the correlations of AAE with AE33 BC and Delta-C concentrations are respectively shown in Figs. 11 and 12, characterized by very high median AAE values (1.85 and 1.86, respectively for BB-1 and BB-2) and BC concentrations (1.93 and 1.67 μg m^{-3}). Notably, high BC (1.45−3.62 μg m^{-3}) mass concentrations at 370–660 nm were observed during the biomass burning events due to more efficient light absorption of BrC in the range than at higher wavelengths, while no significant wavelength-dependent BC concentrations were found during ship pollution (Fig. 10a). The higher AAE values imply much stronger absorption of non-BC light-absorbing particles (BrC) at shorter (UV-vis) wavelengths, which mainly originated from the biomass burning emissions (Ponczek et al., 2022). Moreover, the median OC/EC ratios were 5.03 and 5.29 respectively for the two biomass burning events, even much higher than those for SPP (Fig. 9). The 72-h backward trajectories also showed that the BB-1 air masses mainly originated from the Philippines while the BB-2 air masses were from the mainland Vietnam, both with high densities of fire spots (Fig. 8). The AAE values were also highly correlated with the Delta-C values with a determination coefficient (R^2) of 0.92 (Fig. 12), further demonstrating a significant contribution of BrC to the AAE enhancement. In addition, we further correlated the observed high AAE values with the Delta-C values for the two biomass burning events and confirmed that these high AAE values (1.45–3.62) were indeed attributed to biomass burning rather than ship emitted tar balls which covered an AAE range of 2.7–3.7 at 405 and 781 nm wavelengths in a previous wood burning study (Chylek et al., 2019).

Our study found that the AAE values from all wavelengths for the marine atmosphere and ship pollution were 1.02–1.14 and 1.06, respectively, except for a higher AAE value (1.93) during the two biomass burning events. The AAE values for ship pollution are dependent on the fuel types and loading conditions (Laskin et al., 2015). For example, heavy fuel oil operated at

385   high loads can result in AAE values (at 470/950 nm, and hereafter unless specified) of 2.0, while the intermediate fuel oil has an AAE value of 1.3 at high loads (Helin et al., 2021). In addition, the presence of tar balls may contribute to the enhancement of BrC absorption as mentioned in Section 3.2, as tar balls from ship emission have higher AAE values (2.5–6 depending on the wavelengths) (Corbin et al., 2019). The occurrence of tar balls in this study was about 12% in the analyzed single samples. These tar balls were likely aged during long-range transport from biomass burning and hence affected the light absorption of

390   BrC in the SCS.

3.6 BC sources from fossil fuel vs biomass burning

The source origins of BC particles can be investigated using the AAE model. In the model, we employed respectively the characteristic AAE values of 1 and 2 for FF and BB to calculate their corresponding BC concentrations, namely BC(FF) and BC(BB). Figure 13 shows the time series of BC(FF) and BC(BB) for different classified periods. The BC(FF) and BC(BB)

395   values were much higher before the monsoon than during/after the monsoon, except for the periods during BB-1 and BB-2 with significantly high BC(FF) and BC(BB) values (peaks > 1 μg m^{-3}), while high BC(FF) values were seen during SPP. Table 2 summarizes the average concentrations and the ranges of BC(FF) and BC(BB), along with their corresponding fractions. In general, both the average BC(FF) and BC(BB) values were low during BMP, TMP, and AMP, compared to those during the biomass burning events and SPP. BC(FF) contributed over 80% of ship pollution during SPP, whilst the BC(BB) could

400   contribute to more than 40% of the total black carbon during the two BB events. We hence conclude that fossil fuel combustion is the major contributor to the light absorption of BC except during the seasonal biomass burning events and biomass burning can have a profound contribution to the BC light absorption in the SCS.

Active biomass burning pollution during January–May in Southeast Asia occurs routinely because of crop residue and sugar cane burning. A previous study showed that during dry and wet seasons, the annual contribution of BC(BB) was 11% and 30%

405   respectively in the Peninsular India (Soyam, 2021) based on the two-component AAE model (Drinovec et al., 2015; Yus-Díez

et al., 2021). Table 3 summarizes the BC concentrations, AAE values, and the corresponding fraction of biomass burning (or fossil fuel) in previous and present studies for the marine atmosphere conducted at coastal sites or ship-based cruise measurements using the AE series instrument. The BC(FF) and BC(BB) fractions of 58% and 42% were obtained respectively during the two BB events, while they accounted for 78–83% and 18–22% during other periods, similar to those found at the

410   coastal site in Central Adriatic (79% and 21%), and significantly different from those reported at a coastal site in the East China Sea (Yu et al., 2018). However, observation data are still lacking on the contribution of BC from fossil fuel vs biomass burning in the sea regions which warrants more future studies during different seasons.

3.7 Limitation of this study

This cruise campaign for carbonaceous aerosols has several limitations which might need to be aware of due to the time and

415   area coverage constraints. The presence of other light-absorption aerosol components, polluted dusts, oil and gas drilling emissions, as well as fishery policy may contribute to the uncertainties in the AAE model used for the BC source apportionment in this study. Firstly, the composition of aerosols and refractive index may strongly affect the AAE calculation. The source apportionment of BC for biomass burning and foil fuel is based on the AAE two-component model which only considered BC(BB) and BC(FF) as the light absorption materials. An AAE range of 0.9–1.4 is used for pure BC from foil fuel

420   emissions, while it is 1.68–2.2 for biomass burning as mentioned earlier. The current AAE two-component model does not include other potential light-absorbing materials, such as mineral dust and biological particles (Pileci et al., 2021). Interestingly, two types of possible biological particles were observed during the campaign (Fig. S10, in the SI, section 7). A similar type of biological particles was observed and identified as brocosomes in another campaign near the East China Sea (Fu et al., 2012). However, more future studies are needed to identify the types and species of biological particles and to evaluate their

425   contributions to the light-absorption.

Secondly, based on the Cloud-Aerosol Lidar & Infrared Satellite Observation (CALIPSO) data on May 15 and June 07 when the orbit just passed over the SCS region and the Southeast Asia (Fig. S11 and S12, in the SI, section 8), we found the presence of polluted dust in the vertical profile over the Philippines, Indonesia, Thailand and Malaysia. Long-range transport of dust may affect our measured AAE data. Thirdly, oil and natural gas drilling (Liu and Li, 2021) is active in the SCS region and the

430   distribution map is available online (https://www.oilmap.xyz/). These activities potentially contribute to the BC emissions

(Cordes et al., 2016), and these BC are similar to those of continental emitted BC from incomplete burning of oil or natural

gas.

Lastly, Chinese fishery policy enacts fishing prohibition for about three and a half months every year in the SCS during

summer which correspond to May 01–Aug 16 in the year of 2021 in 12°N within our campaign region. Therefore, the cruise

435   measurements mainly captured ship emissions from the commercial ships in the SCS whose routes are available online

(https://www.marinetraffic.com/en/ais/home/centerx:116.6/centery:20.5/zoom:4). The average BC mass concentrations (~0.2

μg m^{-3} for BC(FF) and 0.05–0.08 μg m^{-3}for BC(BB) are only limited to data of about a month and the coverage area. Hence,

more future measurements covering more seasons and wider areas are needed to better understand the morphology and optical

properties of the carbonaceous aerosols in the SCS.

440   **5. Conclusions**

As important components of carbonaceous aerosols, BC and BrC in the marine atmosphere may exert significantly positive

climatic radiative forcing through light absorption on the regional and global scales. However, quantification of their absorption

potential is tremendously challenging due to little knowledge on the microphysical properties, such as morphology, particle

size, and mixing state of BC or BrC in the marine region such as SCS. This ship-based study was intended to investigate the

445   morphological and optical properties of the BC particles in the SCS during summer using combined online aethalometer, semi-

online OC/EC analyzer, and offline TEM/EDS analyses. The results showed that the lognormal fitted Feret diameter

distribution of the single particles peaks at 325 nm when the ship stopped, while it peaks at 307 nm when the ship navigated.

This minor difference in the size distribution could be attributed to the distinguishable air mass origins of the own ship

emissions for the former and the mixed other ship emissions and long-range transport for the latter. Furthermore, the Feret

450   diameters of the single particles spread much more narrowly during navigation (298–1980 nm) than those of the freshly emitted

particles during stop (304–2982 nm). In addition, the two types of single particles have similar median fractal dimension values

(1.65 vs 1.66) but different lacunarity values (0.53 vs 0.59), indicating their different aging degrees. The aged BC particles

were present in various mixing states (core-shell, embedded, external) with other aerosol components after long-range transport.

Interestingly, a fraction of single particles were identified as tar balls with geometrical diameters of 160–420 nm which were
primarily mixed with sea salt, organics, BC, and sulfate, and those tar balls were found to originate from either ship emissions
or long-range transport of biomass burning.

Since the marine atmosphere is mainly subject to the influence of biomass burning and fossil fuel combustion, a two-
component (BB and FF) AAE model was employed to evaluate the source contributions to the light absorption of the BC
particles. The modeling results indicated that BB and FF contributed respectively to 18–22% and 78–82% of all the BC light
absorption except for a substantial percentage of 42% for BB (hence 58% for FF) during the two observed significant biomass
burning events. The results from trajectory calculations showed that biomass burning was predominantly from the Philippines
and South East Asia before and after the summer monsoon during the cruise campaign. However, this highly simplified two-
component AAE model may have substantial uncertainties on the evaluation of the source contributions when other sources
of BC particles were present and those included dust, biological materials, oil and gas drilling emissions during the
measurements. Nevertheless, this study demonstrates that emissions from commercial ships and biomass burning from
Southeast Asia contribute to the enhanced light absorption of the BC particles in the SCS, especially during the crop harvest
seasons before monsoon, and the aged BC particles became more aggerated after long-range transport of air masses containing
biomass burning emissions.

Author contributions

JZ, CZS, and SZZ planned the cruise campaign. CZS, YYZ, BLL, MG, and XS performed the measurements. CZS performed
the data analysis and wrote the original draft. CZS and DXC performed funding acquisition. JZ and SZZ performed funding
acquisition and supervision. All authors reviewed and edited the manuscript.

Declaration of competing interest

The authors declare no conflict of interest.

475 **Data availability**

Data for figures and tables, along with raw data from online measurements and offline analyses of this study are available from JZ via zhaojun23@mail.sysu.edu.cn upon request. The supplementary data are available online at xxx.

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Table 1. Classification of the campaign period during May 05–June 09, 2021.

Name	Date	Cruise route	Monsoon	Wind direction
BMP-1	May 05–09	AB	before	0–90°, northeast
BMP-2	May 10–22	B→C→D	before	90–180°, southeast
BMP-3	May 23–26	D→E	before	around 180°, southeast
TMP	May 27–Jun 01	EB	transition	around 180°, south
AMP	June 02–09	B→D→A	after	180–270°, southwest
SPP*	Screened	Screened	N/A	Screened

775   * Ship pollution period is screened based on BC concentration and relative wind direction as mentioned in the method section.

Table 2. Source apportionment of BC based on the two-component AAE model.

Period	a.BC(FF)[*]	a.BC(BB)[*]	r.BC(BB)[*]	r.BC(FF)[*]	f.BC(FF)[*]	f.BC(BB)[*]
	(μg m^{-3})	(μg m^{-3})	(μg m^{-3})	(μg m^{-3})	(%)	(%)
BMP	0.2 ± 0.1	0.08 ± 0.06	0–0.9	0–0.3	77.9 ± 5.8	22.1 ± 5.8
TMP	0.2 ± 0.3	0.06 ± 0.1	0.02–1.8	0–1.1	82.2 ± 6.2	17.8 ± 6.2
AMP	0.2 ± 0.1	0.05 ± 0.05	0.01–0.9	0–0.3	80.8 ± 4.0	19.2 ± 4.0
SPP	4.4 ± 5.7	0.7 ± 0.9	0.2–32.8	0.04–10.3	83.0 ± 6.7	17.0 ± 6.7
Bio. [**]	0.8 ± 0.3	0.8 ± 0.4	0.05–1.2	0–1.5	58.1 ± 16.7	41.9 ± 16.7

[*] a represents average, r for range, f for fraction;

[**] Bio. stands for the two biomass burning events as noted in the main text.

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Table 3. Summary of AAE values, mass concentrations, and the relevant fractions for the BC particles in PM$_{2.5}$ from coast site

and cruise measurements using the AE series aethalometer.

Region	Time	AAE values (at wavelengths, nm)	BC avg. conc. ($\mu g\ m^{-3}$)	Fraction (%)	Reference
East China Sea[c]	May, 2017	0.9–1.3 (370–950)	0.8–3.6	2.5–11 or 45–60 for BrC	(Yu et al., 2018)
Central Adriatic[c]	Feb.–Jul., 2019	1.25–1.49 (470/950)	0.57 ± 0.64	79 for BC(FF) 21 for BC(BB)	(Milinković et al., 2021)
Bay of Bengal[c, n]	Dec., 2008–Jan., 2009	1.81–1.98 (370–950)	5.1 ± 3.0[c]; 2.5 ± 1.4[n]	<10 for BC(FF) >85 for BC(BB)	(Kedia et al., 2012)
South China Sea[n]	Sep.–Oct. 2019	-	1.9 ± 0.4	-	(Wang et al., 2022)
South China Sea[c]	Dec. 2017	1.2–1.5 (375/880)	6.6–4.9	-	(Sun et al., 2020c)
South China Sea[n]	May–Jun. 2021	1.02–1.14 or 1.93 (370–950)	0.33 ± 0.38	78–82 for BC(FF) 18–22 for BC(BB) BB events: 58 for BC(FF) 42 for BC(BB)	This study

[c] coastal site measurement;

[n] cruise (remote) measurement.

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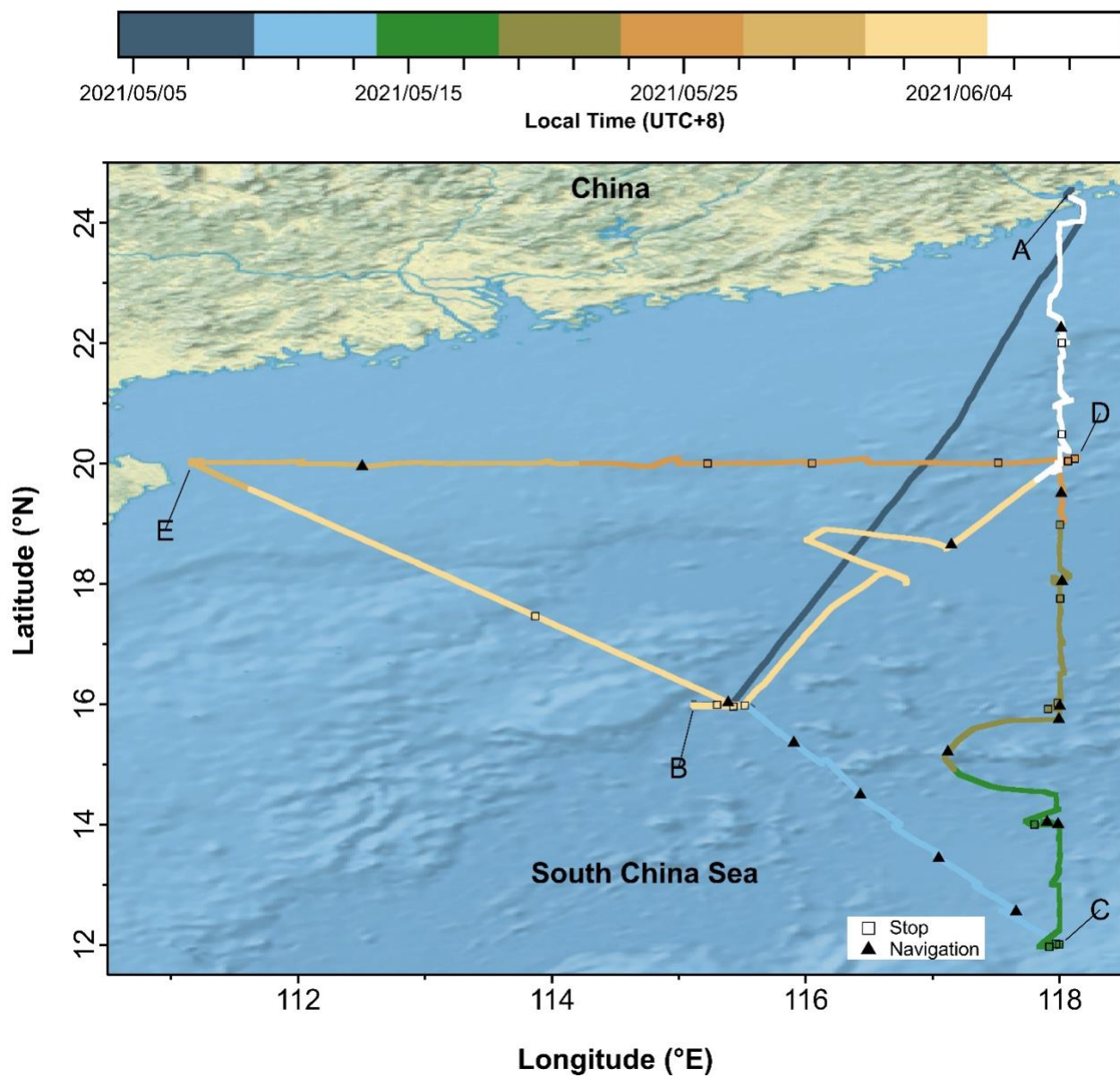
Figure 1. Map of the cruise route for the campaign in the South China Sea during May 05–Jun 9, 2021. The ship route is dated by the intensity bar at the top. The open squares and solid triangles indicate the single particle sampling location, collected during stop and navigation, respectively.

790
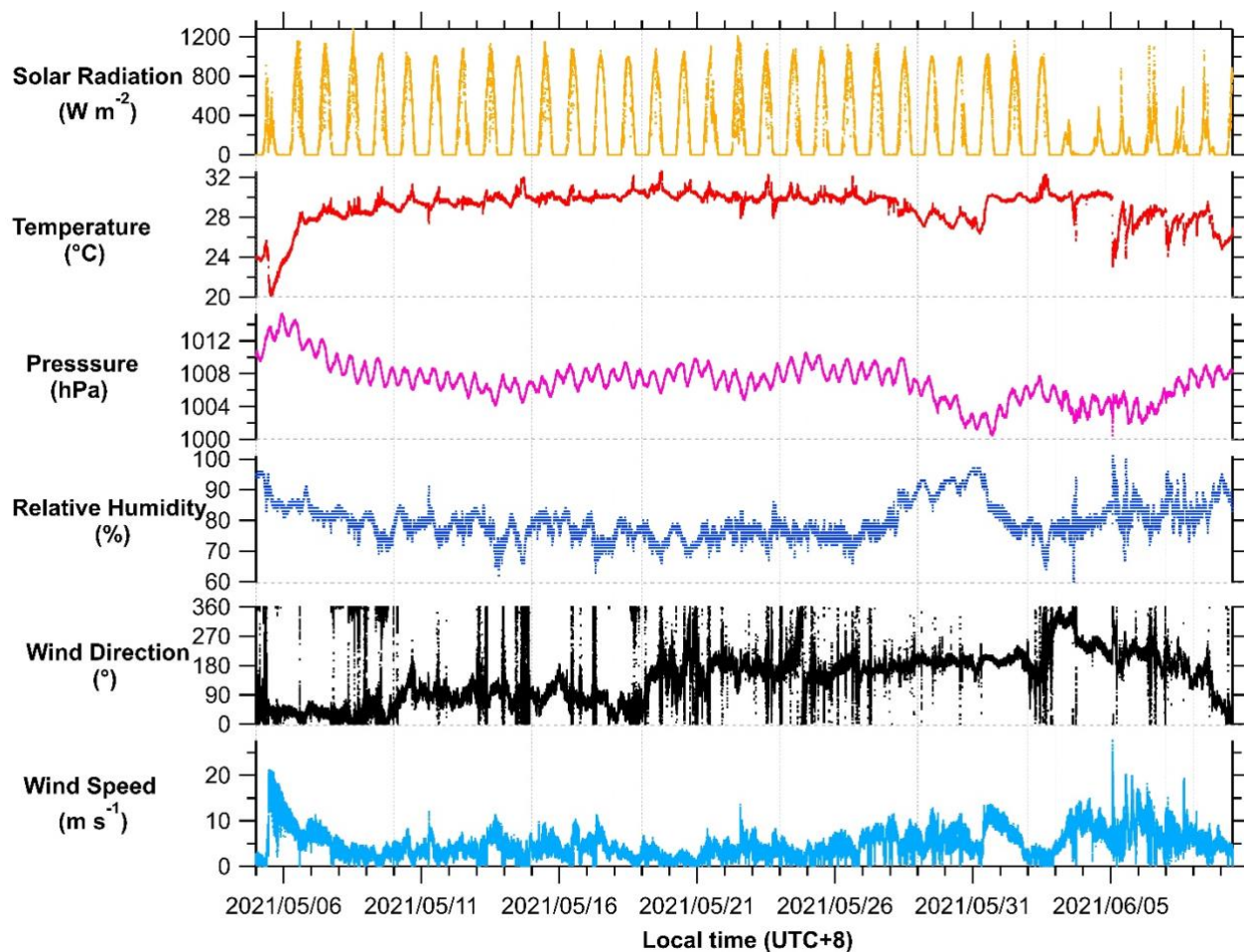
Figure 2. Time series of meteorological variables of solar radiation (SR), temperature, pressure, relative humidity (RH), wind direction (WD), and wind speed (WS) during the campaign. The time resolution is 1 min for all the data except for WS and WD (3 sec). All data points are shown in dots style.
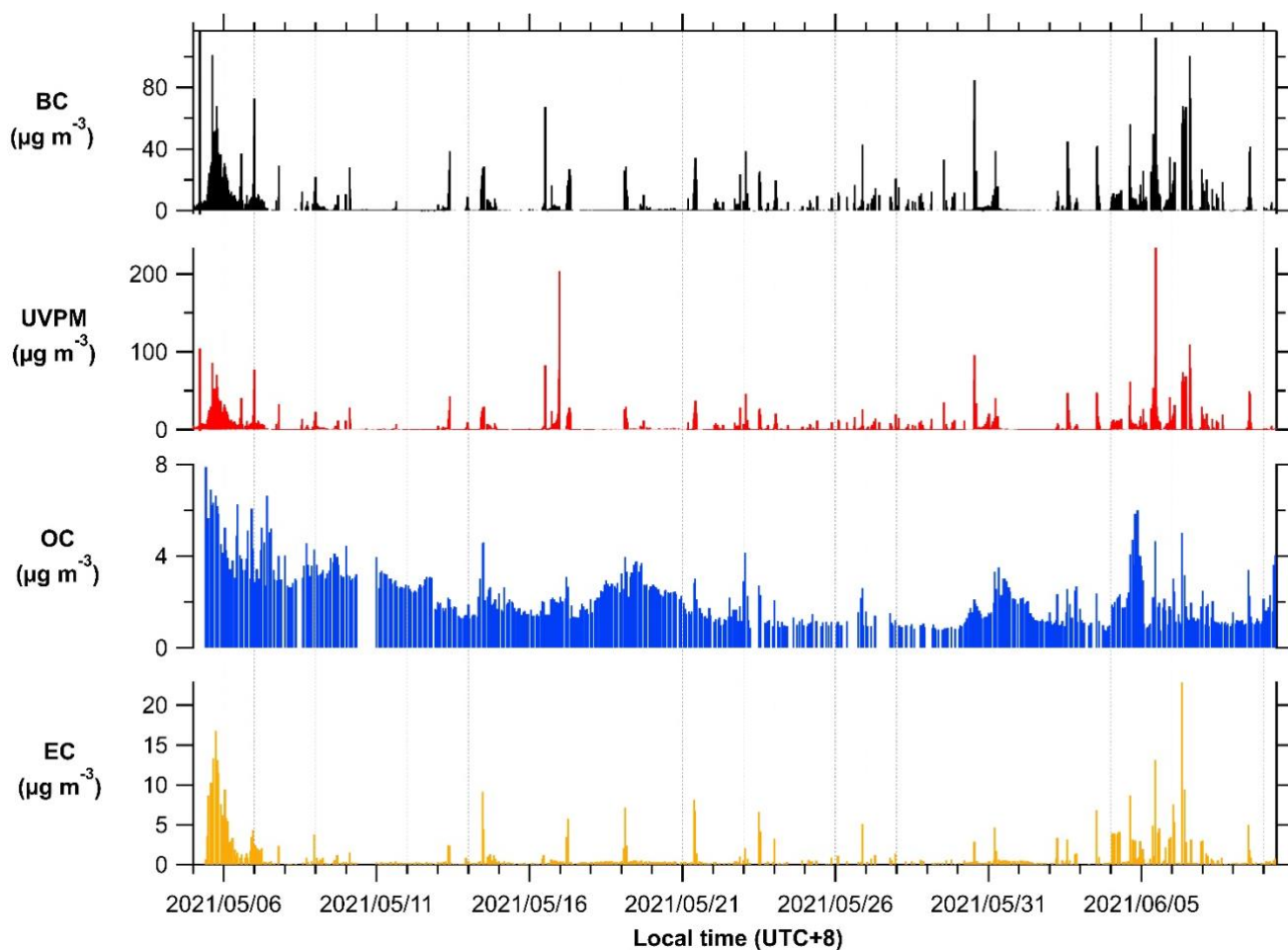
Figure 3. Time series of the mass concentration of black carbon (BC), ultraviolet particle matter (UVPM), organic carbon (OC) and elemental carbon (EC) in PM$_{2.5}$ during the campaign. The time resolution is 1 min for all the data except for OC and EC (1 h). All data points are shown in stick-to-zero style.

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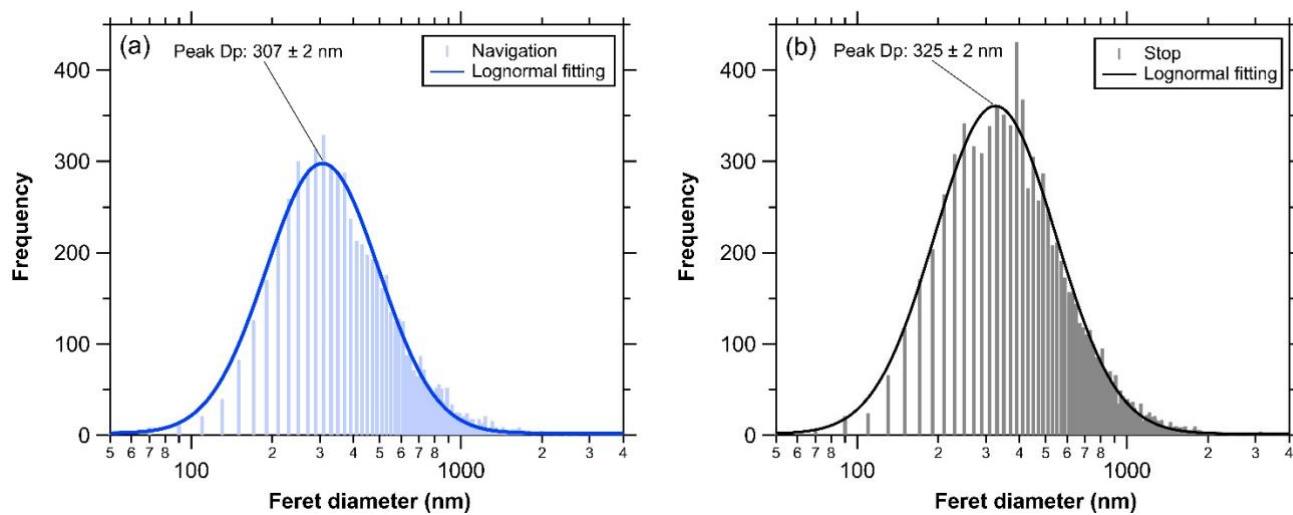


Figure 4. **Lognormal fitting of particle size distribution using Feret diameter determined from the TEM images with the ImageJ analysis during navigation (a) and stop (b). The histograms are set with a bin starting at 50 nm, a bin width of 20 nm, and a total bin number of 200.**

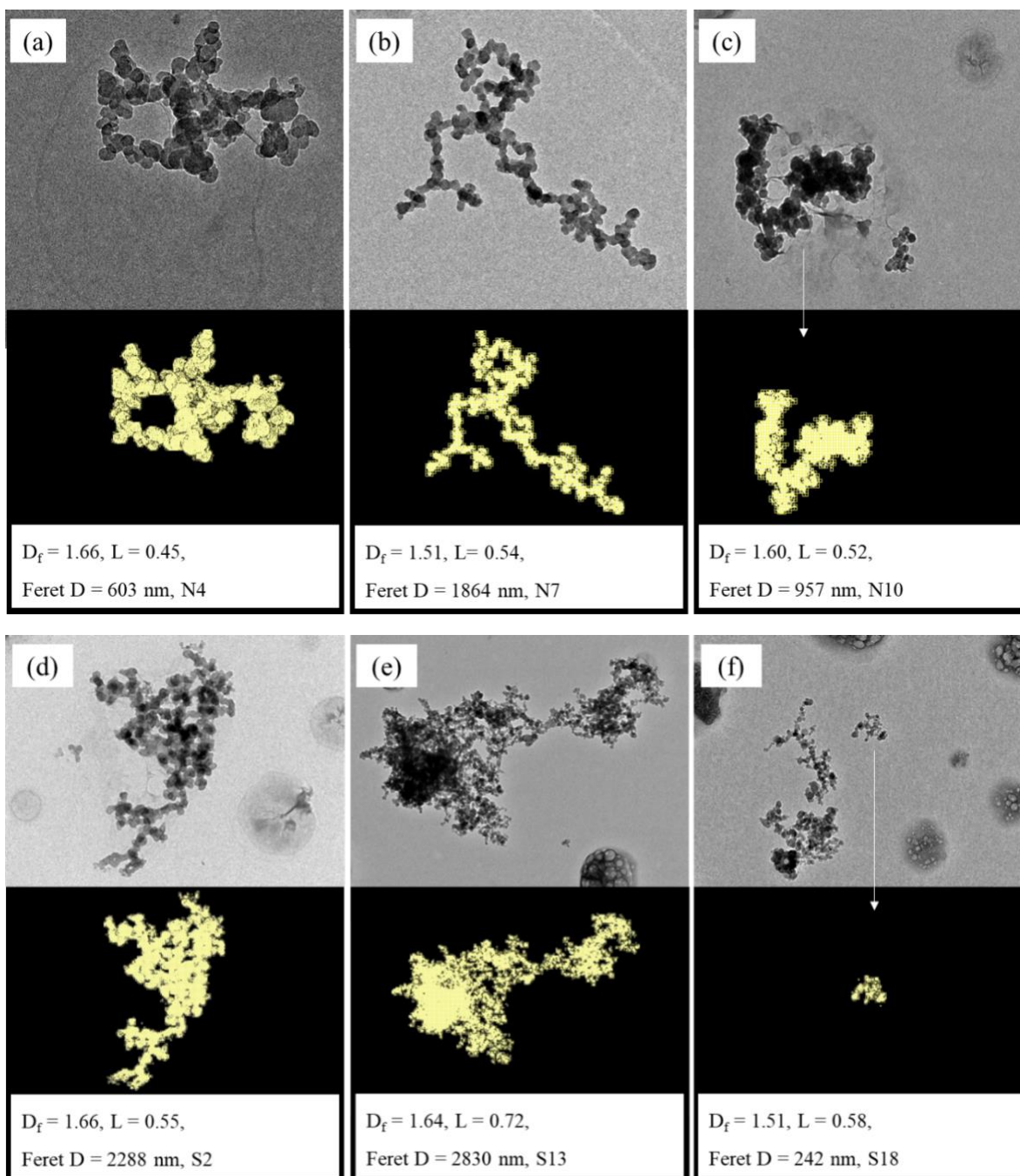



Figure 5. Examples of the BC TEM images and their corresponding Feret diameter (D), fractal dimension (D_f) and Lacunarity (L) based on the boxing counting method from the fractal analysis: (a-c) BC particles collected during navigation and (d-f) during stop. More sampling information can be found in Table S1 of SI (serial numbers N4, N7, N10, S2, S13, S18, etc.).

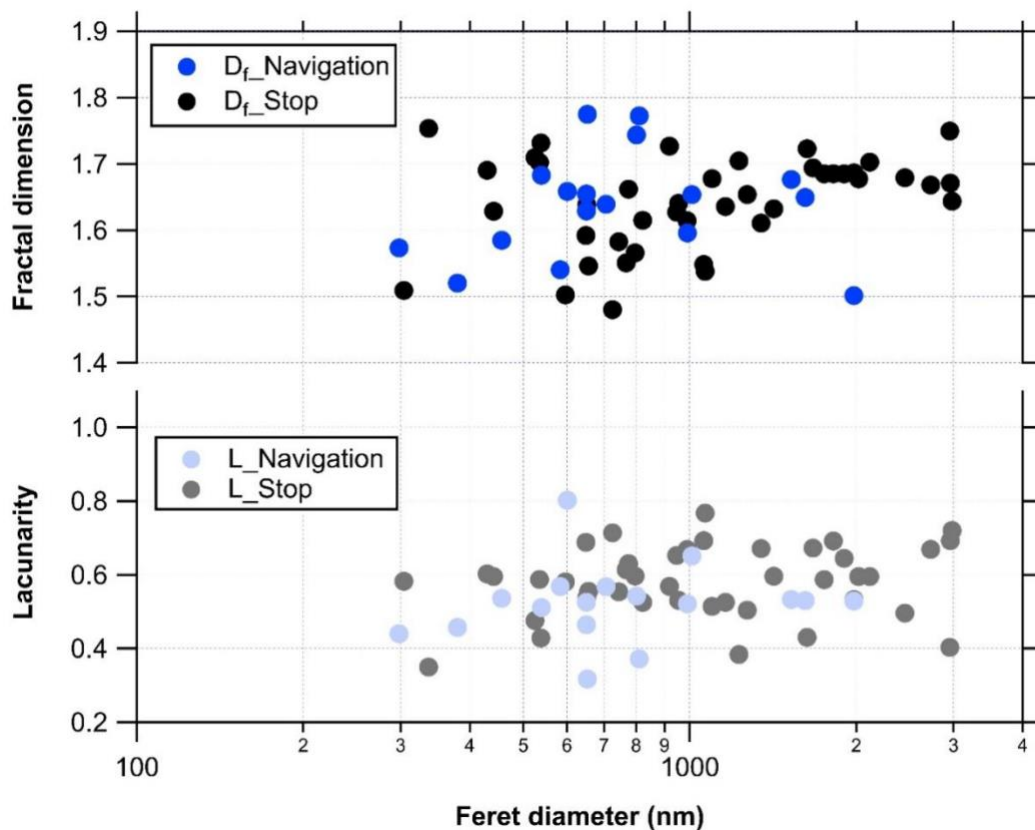



Figure 6. The size-dependent fractal dimension (D_f) and lacunarity (L) for each BC particle during navigation and stop.

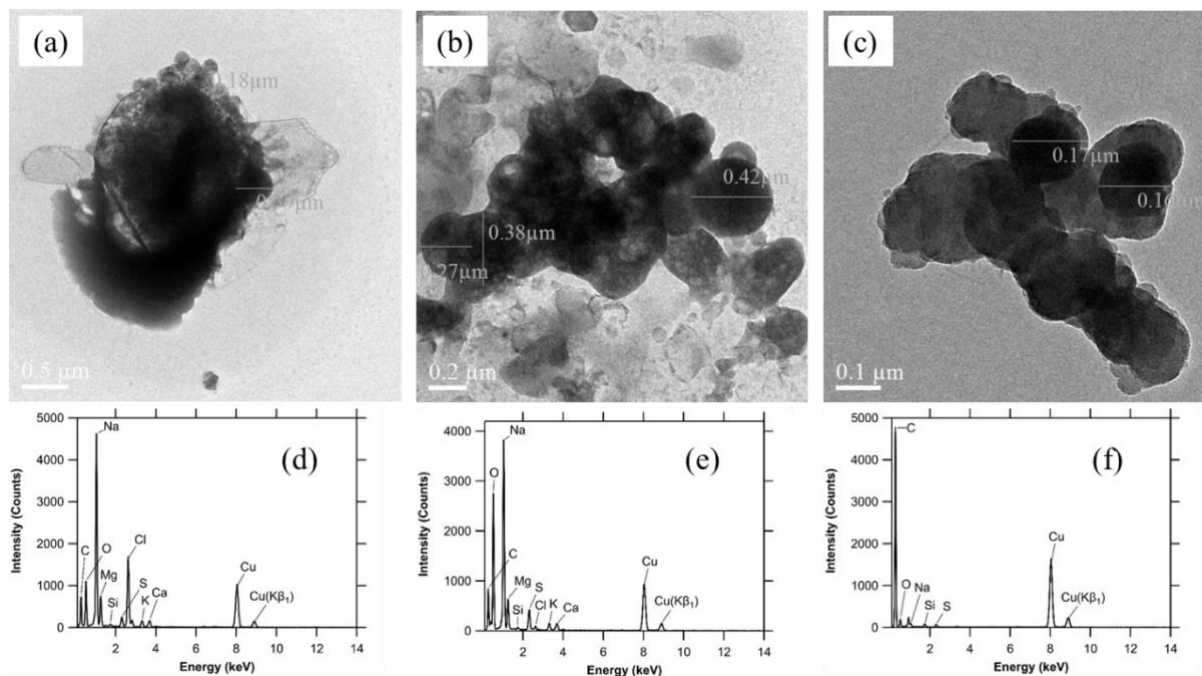



Figure 7. The example TEM images and their corresponding EDS spectra of tar ball particles collected during navigation: tar balls mixed with sea salt (a, d) at 8:55 on May 27, tar balls mixed with OC, sulfate (b, e), and tar balls mixed with sulfate (c, f) at 18:07 on Jun 01. The EDS spectra were collected by focusing the electron beam in the TEM and the illuminated area covers the particle for elemental analysis.

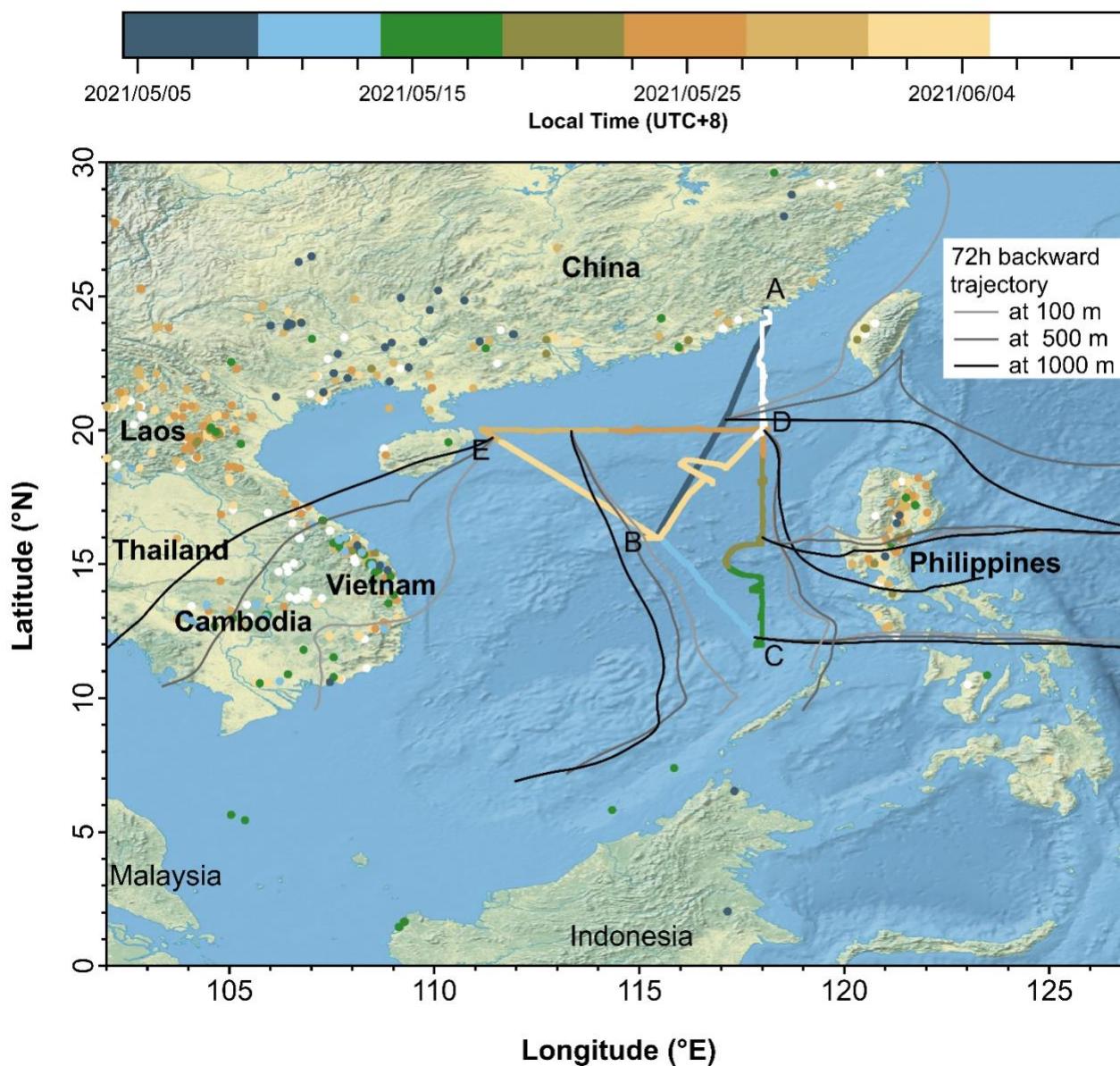



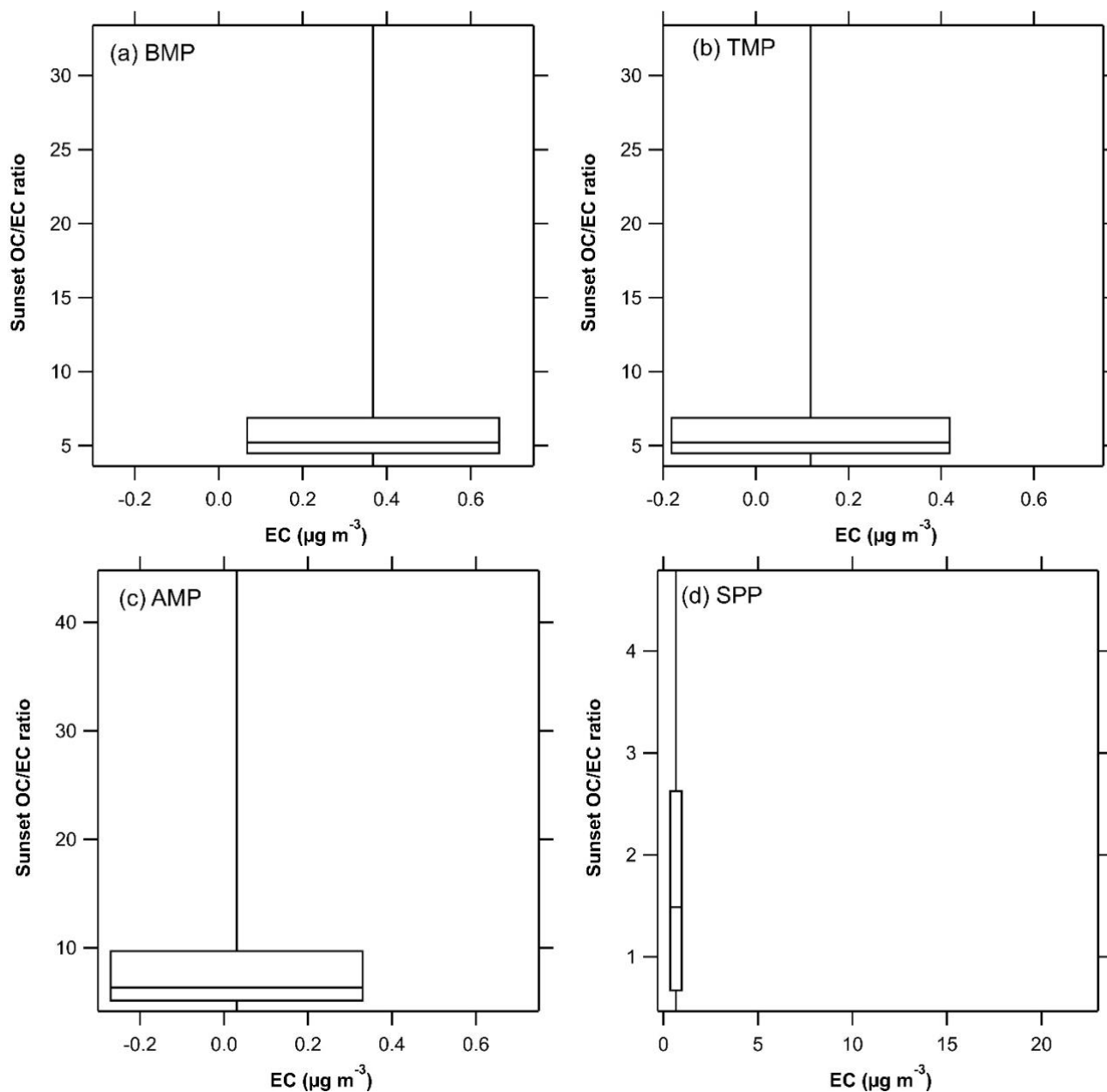
Figure 8. **The time series of fire spots distribution and the 72-h backward trajectories over the South China Sea (SCS) during the campaign. The solid circles were dated by the intensity bar at the top, representing the detected fire spots using MODIS satellite with a confidence threshold of >80%. The light grey, grey and black 72-h backward trajectories were obtained at AGL heights of 100, 500 and 1000 m using the HYSPLIT model.**

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Figure 9. Box and whisker plots of the OC/EC ratio vs the EC concentration for (a) before the monsoon period (BMP), (b) transition

monsoon period (TMP), (c) after the monsoon period (AMP), and (d) ship pollution period (SPP) based on the data from the Sunset

OC/EC analyzer. The whisker top, box top, box bottom, and whisker bottom are 90%, 75%, 25% and 10%, respectively.
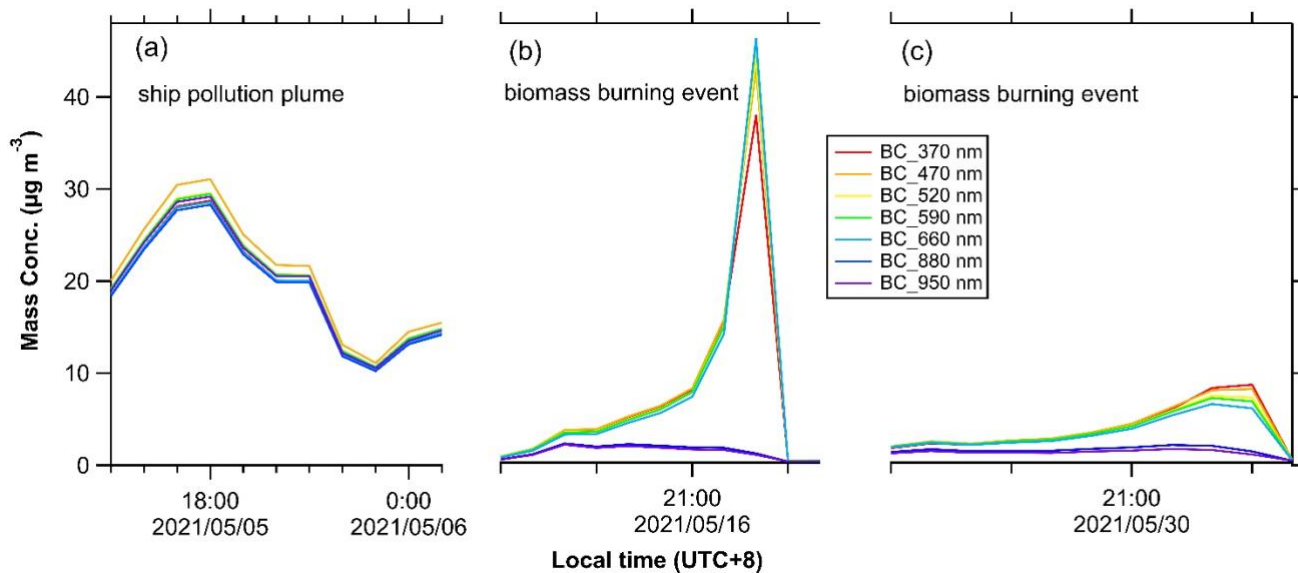
Figure 10. The wavelength-dependent mass concentration from AE33 aethalometer for example spectra for (a) example of a ship pollution plume, and (b, c) two significant biomass burning events during this campaign.
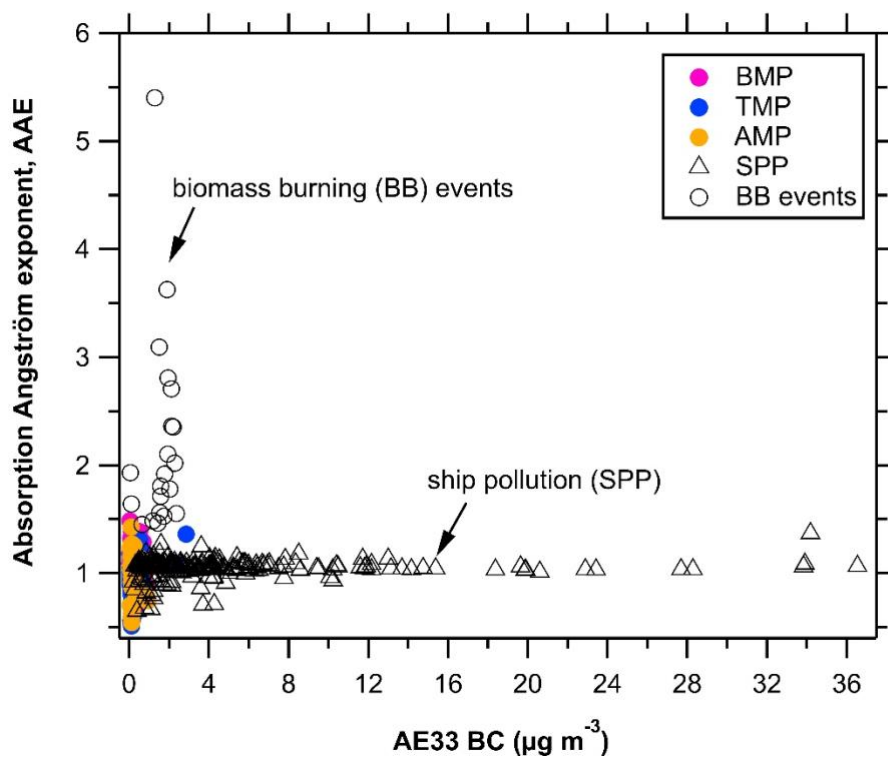
Figure 11. The absorption Angström exponent (AAE, all wavelengths) vs AE33 BC concentration for before monsoon period (BMP),

transition monsoon period (TMP), after monsoon period (AMP), and ship pollution period (SPP).
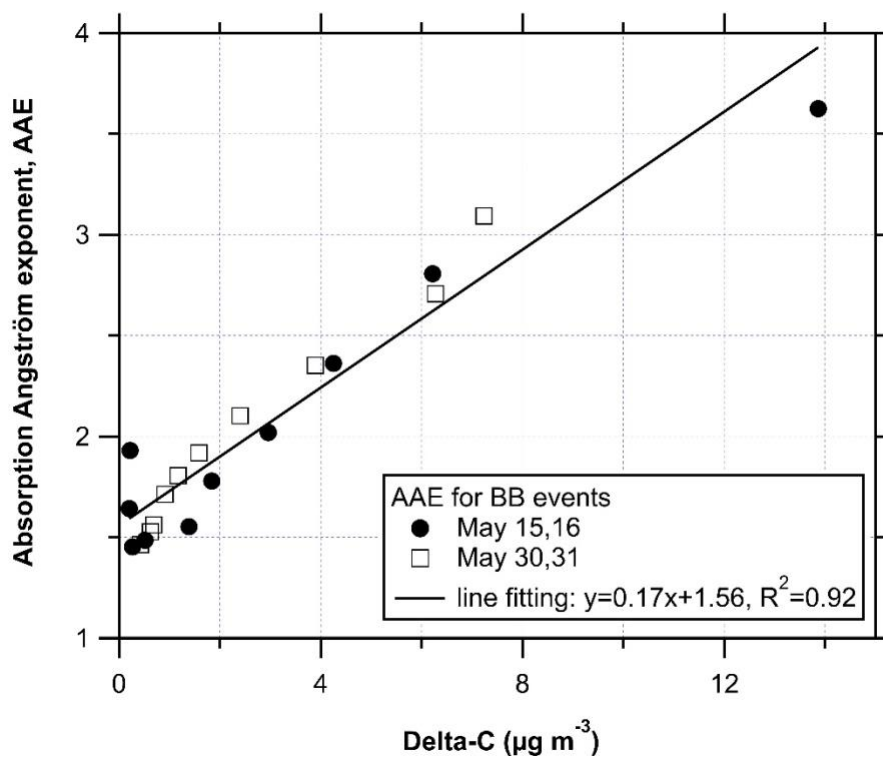
Figure 12. The absorption Angström exponent (AAE) vs the Delta-C concentration for the two biomass burning events: BB-1 at 6:00–7:00 on May 15 and 15:00–22:00 on May 16 during BMP, and BB-2 at 15:00-23:00 on May 30 and 00:00 on May 31 during TMP. The BB-1 and BB-2 data points are marked in solid circles and open squares, respectively.

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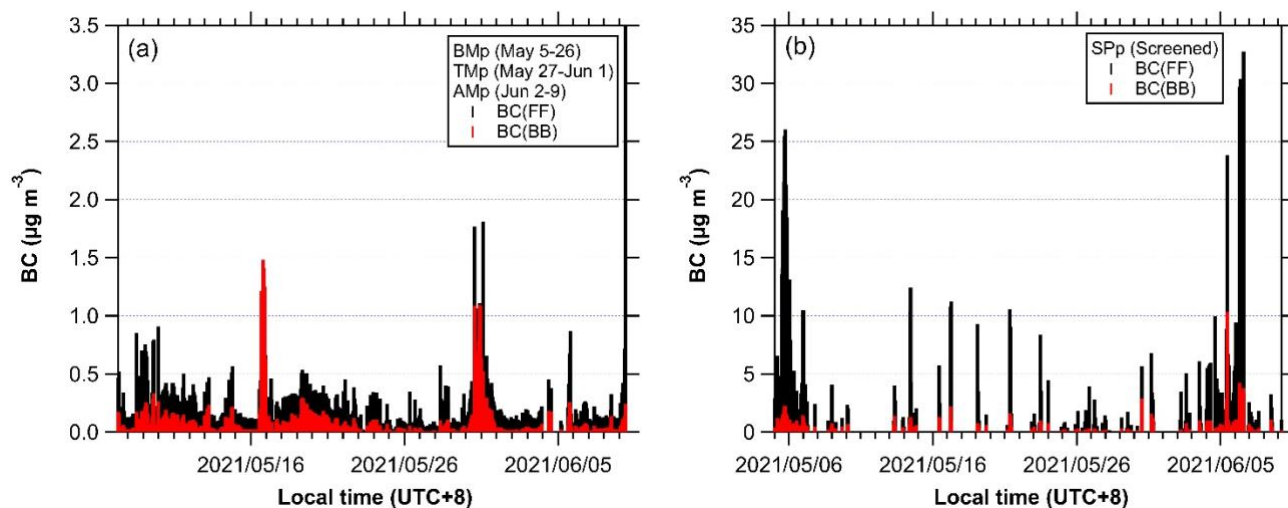
Figure 13. Source apportionment of the BC particles using the two-component AAE model (AAE=1 for foil fuel (FF) and AAE=2 for biomass burning (BB): (a) before monsoon period (BMP), transition monsoon period (TMP), after monsoon period (AMP), and (b) ship pollution period (SPP).