Aerosol optical properties and the mixing state of black carbon at a background mountainous site in Eastern China

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ABSTRACT

In-situ measurements of aerosol optical properties were conducted at Mt. Huang from September 23 to October 28, 2012. Low averages of 82.2, 10.9, and 14.1 Mm−1 for scattering coefficient (σsp, neph, 550), hemispheric backscattering coefficient (σhbsp, neph, 550), and absorption coefficient (σap, 550), respectively, were obtained. Atmospheric aging process resulted in the increase of σap, 550 but the decrease of the single scattering albedo (ω550) at constant aerosol concentration. However, the proportion of non-light-absorbing components (non-BCs) was getting higher during the aging process, resulting in the increase of aerosol diameter, which also contributed to relatively higher σsp, neph, 550 and ω550. Diurnal cycles of σap, neph, 550 and σap, 550 with high values in the morning and low values in the afternoon were observed closely related to the development of the planetary boundary layer and the mountain-valley breeze. BC mixing state, represented by the volume fraction of externally mixed BC to total BC (r), was retrieved by using the modified Mie model. The results showed r reduced from about 70% to 50% when the externally mixed non-BCs were considered. The periodical change and different diurnal patterns of r were due to the atmospheric aging and different air sources under different synoptic systems. Local biomass burning emissions were also one of the influencing factors on r. Aerosol radiative forcing for different mixing state were evaluated by a “two-layer-single-wavelength” model, showing the cooling effect of aerosols weakened with BC mixing state changing from external to core-shell mixture.

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Introduction

Black carbon (BC) is considered as the most efficient light absorbing aerosol species in the atmosphere (Moffet and Prather, 2009) and hence contributes a considerable amount of heating to the atmosphere. However, there exist large uncertainties in the amount of heating due not only to the highly inhomogeneous spatial and temporal distributions of...
BC (IPCC, 2013), but also to the lack of knowledge about the mixing state of BC with other aerosol species (Tan et al., 2016).

There are three popular concepts to describe the mixing state of BC: external mixture (BC is distinct from other aerosol species), internal mixture (BC is incorporated homogeneously within the non-light-absorbing components (non-BCs) in aerosol particles) (Bohren and Huffman, 2008), and core-shell mixture (BC acts as a core surrounded by well-mixed non-BCs) (Jacobson, 2001), which is a special kind of internal mixture. BC is generally externally mixed with other aerosol chemical species once it is emitted into the atmosphere. As governed by the atmospheric aging processes, such as collisions with ambient particles, condensation of vapors on the surface producing hygroscopic coatings (Shiraiwa et al., 2007), and reactions with gases, BC tends to mix with other chemical components (Riemer et al., 2004) and hence gradually become internally or core-shell mixed.

Li et al. (2018) demonstrated the enhancement of BC absorption coefficient ranged from 1.58 to 1.64 with the evolution of its mixing state and thus, the direct radiative forcing of BC ranged widely at the top of the atmosphere (Jacobson, 2000; Chung and Seinfeld, 2002), which indicated the sensitivity of the optical properties of BC to the mixing state (Khalizov et al., 2009). Additionally, the aged particles can act more readily as cloud condensation nuclei (CCN) and ice nuclei (IN), which modify the formation processes, optical properties, and life time of clouds (Andreae and Rosenfeld, 2008; Rose et al., 2011). Thus, the mixing state of BC is critical for adequate simulations of its effect on climate (Jacobson, 2001).

Various experimental and numerical investigations have been undertaken to explore how BC mixed with other aerosol components. The use of transmission electron microscopy (TEM) (Naoe et al., 2009) and single-particle soot photometer (SP2) (McMeeking et al., 2011) provided an intutionistic image to show the mixing state of BC. Recently, some indirect observational methods by using aerosol time-of-flight mass spectrometer (Bi et al., 2011; Wang et al., 2015), Humidified Tandem Differential Mobility Analyzer (HTDMA) (Tan et al., 2013; Mahish and Collins, 2017), and Volatile Tandem Differential Mobility Analyzer (VTDMA) (Cheng et al., 2009; Cheung et al., 2016; Tan et al., 2016) were widely applied to explore the size-resolved chemical components, hygroscopicity, and volatility, which could be used to infer BC mixing state. Moreover, optical closure study with Mie model were also applied to retrieve BC mixing state (Bohren and Huffman, 2008). This method can not only provide a numerical way to investigate the complex relationships between aerosol optical properties and physicochemical characteristics, but also offer a convenient platform that sensitivity studies and parameterization can be conducted on. Related studies were carried out mainly distributed in the Pearl River Delta (Cheng et al., 2006) and the North China Plain (Ma et al., 2012) in China. They defined the mixing state of BC as the ratio of externally mixed BC to the total mass of BC. Aerosol optical properties were calculated using Mie model with aerosol particle number size distributions (PNSDs) and BC fraction as input parameters. A proper mass ratio of externally mixed BC was yielded from minimizing the discrepancies between the measured and calculated optical properties. These articles gave reliable information about aerosol optical properties associated with physicochemical characteristics and provided convenient approaches to investigate BC mixing state in China.

With the rapid development of economy, emissions from urbanization, industrial and traffic activities have increased dramatically in China, resulting in rather complex microphysical features of aerosol and severe pollution events (Han et al., 2016; Sun et al., 2016; Wang et al., 2016; Yu et al., 2017), especially in the Yangtze River Delta (YRD) region (Yu et al., 2011; Yu et al., 2018), one of the largest developed megacity clusters and also one of the most polluted areas in eastern China. Recently, there have been lots of in-situ measurements carried out at this region, focusing on the physical, chemical, or optical properties of aerosols (Zhuang et al., 2014; Wang et al., 2015; Yu et al., 2016; Gong et al., 2016; Qi et al., 2016; Wang et al., 2018). However, very few measurements were conducted to explore the complex relationships between aerosol optical, microphysical and chemical characteristics and to further investigate the mixing state of BC. To fill these gaps, in-situ measurements of aerosol optical and microphysical and chemical properties were conducted at Mt. Huang (the Yellow Mountain), a continental background mountainous site in eastern China, where air masses could not only have the regional representation, but also allow us to study the exchanges of air between the planetary boundary layer (PBL) and the upper troposphere and to compare the discrepancy of aerosol properties with the site at the lower altitude (Chen et al., 2014; Li et al., 2014; Yuan et al., 2016). Thus, the aims of this study are: (1) to investigate the unique influencing factors on the variation of aerosol optical properties at Mt. Huang; (2) to obtain the mixing states of BC with non-BCs and discuss the reasons dominating the change of the mixing states; and (3) to evaluate the effect of BC mixing state on aerosol direct radiative forcing.

1. Measurements and methodology

1.1. Site description

All the data were collected at Mt. Huang (30.12° N, 118.19° E) from 267 to 301 day of year (DOY) (September 23–October 28), 2012, which locates approximately 300 km southwest of the megacity cluster of the Yangtze River Delta in eastern China. Fig. 1 shows the map of the locations of Mt. Huang and the relatively lower aerosol optical depth (AOD) around Mt. Huang compared to surrounding regions, suggesting that Mt. Huang is one of the cleanest regions due to the few industrial activities in eastern China. The observation site is on the mountainside of Mt. Huang and 869 m above mean sea level and thus, can be considered as a continental background mountainous site.

An automatic meteorological station (Vantage Pro2, Davis, USA) was located on the roof of Yungu resort, a three-story building (approximately 10 m above ground level), in which all of the aerosol sampling instruments were installed. The weather conditions were either clear or cloudy and there were two obvious rain events on 291 and 296 DOY. T and RH show evident diurnal cycles with average values of 16.3 ± 3.5°C and
70.9% ± 14.2%, respectively. The wind direction (WD) was dominated by north and southwest with average wind speed (WS) of 0.4 ± 0.3 m/s, and the atmospheric pressure was periodically fluctuating (Fig. S1).

1.2. Aerosol sampling

The sampling system was installed in a temperature-controlled room at Yungu resort during the campaign as Fig. 2 shows. It contained a community air-sampling system, a scanning mobility particle sizer (SMPS) (Model 3936, TSI, St. Paul, MN, USA), an aerodynamic particle sizer (APS) (Model 3321, TSI, St. Paul, MN, USA), a three-wavelength (450, 550, and 700 nm) integrating nephelometer (Model 3563, TSI, St. Paul, MN, USA), and a aethalometer (Model AE31, Magee Scientific, Berkeley, CA, USA). A vacuum pump was used to keep the aerosol flow rate at 10.97 L/min in the community air-sampling system, which was consisted of a stainless steel pipe with a diameter of 3/4 in., putting out of the window at approximately 8 m aboveground. A Nafion Dryer (PD-100T-24MSS, Perma Pure LLC, Lakewood, NJ, USA) was connected upstream of all the instruments to ensure that RH of aerosol sample was lower than 20%. The sample flow was split to the different instruments through stainless steel tubes and conductive rubber tubes by the pump located inside or outside each of the instrument.

In addition, a single particle aerosol mass spectrometer (SPAMS) (Hexin Analytical Instrument Co., Ltd., Guangzhou, China) with a homemade silica gel diffusion dryer and a separate inlet system using a flow rate of 0.08 L/min was installed in parallel with the community air-sampling system to get the size-resolved BC fraction.

Aerosol particle number size distributions (PNSDs) were determined continuously by the SMPS and APS, which were calibrated before the campaign. The sample flow rate of SMPS and APS were 0.30 ± 0.02 and 1.00 ± 0.02 L/min, respectively. And respective sheath-to-sample flow ratio were 10 and 4 in the SMPS and APS. Both the two instruments were calibrated every two days. The data from these two instruments were converted and combined to yield the PNSDs with Stokes equivalent diameter from 10 nm to 20 μm (Yuan et al., 2016). Only two PNSDs were available per hour for the post processing due to the synchronous size-resolved activation experiment with the SMPS (Gu, 2013).

The integrating nephelometer was operated to measure the aerosol scattering coefficient (σsp, neph) and the hemispheric backscattering coefficient (σhbsp, neph). It was also calibrated with particle-free air as the low span gas and CO2 (purity of 99.99%) as the high span gas, prior to the campaign (Anderson and Ogren, 1998). The flow rate of 7.76 L/min was maintained in the nephelometer and the temporal resolution was 5 min for this measurement. Zero baseline check was carried out automatically, once an hour, to ensure the stability of the instrument during the sampling period.

The BC mass concentrations at 7 wavelengths (370, 470, 520, 590, 660, 880, and 950 nm) with a time interval of 5 min were measured by the calibrated aethalometer. The flow rate of the aethalometer was set to 2 L/min with a variation of ±2%. The absorption coefficient at 532 nm (σap, 532) was calculated using Eq. (1), which was the result of intercomparison between an aethalometer at 880 nm and a photoacoustic spectrometer at 532 nm in the Pearl River Delta region of China (Wu et al., 2009).

\[
\sigma_{ap, 532} = 8.28 \cdot M_{BC, 880} + 2.23
\]

where, σap, 532 (Mm⁻¹) was the absorption coefficient at 532 nm measured by a photoacoustic spectrometer, M_{BC, 880} (μg/m³) was the BC mass concentration at 880 nm directly recorded by aethalometer without any corrections, and the constant 8.28 (m²/g) was the conversion factor, which was
applied in Mt. Huang previously by Yuan et al. (2016). This factor may result in a conservative uncertainty of 20% for the calculation of the absorption coefficient due to the lack of comparison study at this site.

Due to the different wavelength of the scattering coefficient and absorption coefficient, $\sigma_{ap, 532}$ was converted to the absorption coefficient at 550 nm ($\sigma_{ap, 550}$) to match with the scattering coefficient at 550 nm ($\sigma_{sp, neph, 550}$) following the inverse wavelength "Power Law" (Bergstrom et al., 2002):

$$\sigma_{ap, 550} = \sigma_{ap, 532} \cdot \left( \frac{532}{550} \right)^{1.8/C_1}$$

BC fraction has a great influence on aerosol optical properties. Yuan et al. (2016) reported that the BC size resolution was more important than its time resolution in retrieving aerosol absorption coefficient, so the BC fraction obtained by the SPAMS were processed to the high size-segregated BC number fraction ($\varepsilon_{N}(lgD_p)_BC$) averaged over the study period with aerodynamic diameters from 0.2 to 2.5 μm, which was converted to Stokes equivalent diameter with the same size bins of PNSDs in Mie model. The detailed setup of the SPAMS in this campaign was described by Chen et al. (2014).

Corrections considering the diffusion losses in the inlet of SMPS, APS, nephelometer, and aethalometer was conducted following the method provided by Kulkarni et al. (2011). All the instruments connecting the community air-sampling system were shut down for 30 min for cleaning every two days. The data from the first 5 min after the reboot of the instruments and the data when the corresponding flow rate exceeded the range of the set value by more than ±2% for the SMPS and APS and ±5% for the other instruments were manually eliminated. Then the filtered data were calculated to hourly arithmetic means and used as input parameters in the following model.

1.3. Methodology

1.3.1. Two-component optical aerosol model

Due to the insensitivity of aerosol scattering coefficient to the fraction of non-BCs (Wex et al., 2002), a two-component aerosol model used in Ma et al. (2011) and Yuan et al. (2016) was applied to calculate the aerosol optical properties, although aerosols in the atmosphere comprise various chemicals. In the model, aerosol components were divided into a light-absorbing component, which was dominated by BC, and non-BCs that included sulfate, nitrate, ammonium, organic carbon, and undetermined compounds. This model has been tested by Yuan et al. (2016), who verified its applicability on aerosols at Mt. Huang.

The refractive indices of those two components, which are of great importance to calculate the optical properties of aerosol particles, are needed as the input parameters of the Mie model (Bohren and Huffman, 2008). They were set as the same as Yuan et al. (2016) ($m_{BC}=1.80-0.54i$ and $m_{nonBC}=1.50-10^{-7}i$), according to the open literature listed by Cheng et al. (2006) and the previous studies about continental aerosols in China (Cheng et al., 2008; Ma et al., 2011; Shen, 2012).

For the mixing state of BC, Yuan et al. (2016) has demonstrated that aerosol scattering coefficient and absorption coefficient measured by the nephelometer were just between the calculated values with the assumptions of external and core-shell mixtures. In this study, the hemispheric backscattering fraction $\beta$ (the fraction of the hemispheric backscattering coefficient ($\sigma_{hbsp}$) to the total scattering coefficient ($\sigma_{sp}$), $\beta = \frac{\sigma_{hbsp}}{\sigma_{sp}}$), provided by the nephelometer ($\beta_{neph}$),
is also between the values calculated with these two extreme assumptions (εcore-shell and εext) at 550 nm (Fig. S2). This definitely suggests that BC particles at Mt. Huang are externally mixed in part and core-shell mixed in another part. To quantify the mixing state of BC at Mt. Huang, r was defined as the volume fraction of externally mixed BC (VBC-ext) in total BC (VBC), as Eq. (3), which equaled to the number fraction of externally mixed BC.

\[ r = \frac{V_{BC \text{ ext}}}{V_{BC}} = \frac{N_{BC \text{ ext}}}{N_{BC}} \tag{3} \]

r of 1 indicated all BC particles were completely externally mixed while r of 0 indicated all BC particles were core-shell mixed that covered by non-BCs. Thus, r varied between 0 and 1 in the real atmosphere.

### 1.3.2. Mie model and the retrieval algorithm

A modified BHMIE code and a modified BHCOAT code (Bohren and Huffman, 2008; Cheng et al., 2009) were utilized to retrieve BC mixing state. In the modified Mie model, the total PNSDs given by the SMPS and APS were partitioned into the PNSDs of BC (N(lgdDp)_BC) and non-BCs (N(lgdDp)_non-BC) based on ε_{BC} and N(lgdDp)_BC measured by the SMPS as shown in Eqs. (4) and (5):

\[
N(\text{lgDp})_{\text{BC}} = N(\text{lgDp})_{\text{measured}} - N(\text{lgDp})_{\text{BC}} \tag{4}
\]

\[
N(\text{lgDp})_{\text{non-BC}} = N(\text{lgDp})_{\text{measured}} - N(\text{lgDp})_{\text{BC}} \tag{5}
\]

where, D_{pBC} (µm) is the geometric diameters of the particles, and N(lgdDp)_measured (#/m^3) was the PNSD measured by the SMPS and APS.

In previous studies, BC mixing state were just considered two parts, one was externally mixed BC, and the other one was the rest BC that core-shell mixed with all the non-BCs (Cheng et al., 2006; Ma et al., 2012). However, there also exist some externally mixed non-BCs in the atmospheric aerosols (Cheung et al., 2016; Tan et al., 2016), and they play a critical role on affecting aerosol optical properties. Therefore, two scenarios of BC mixing state (r_1 and r_2) were retrieved to reflect the actual situation in this study (Fig. S3). One considered the existence of externally mixed non-BCs and the other one did not. The comparison of these two scenarios aimed to explore the impacts of externally mixed non-BCs on BC mixing state.

For the first scenario, the total BC particles were divided into externally mixed BC (N(lgdDp)_ext-BC) (#/m^3), which existed distinct from other aerosol particles, and core-shell mixed BC with the whole non-BCs (N(lgdDp)_core-shell) (#/m^3) based on a given r_1:

\[
N(\text{lgDp})_{\text{ext-BC}} = N(\text{lgDp})_{\text{BC}} \cdot r_1 \tag{6}
\]

\[
N(\text{lgDp})_{\text{core-shell}} = N(\text{lgDp})_{\text{measured}} - N(\text{lgDp})_{\text{ext-BC}} \tag{7}
\]

Additionally, the sizes of the BC cores in the particles are also a crucial parameter, which are generally different in the particles with the same diameters, for calculating the optical properties of the core-shell mixed particles (Yuan et al., 2016). To simplify the optical aerosol model, the core-shell mixed particles with the same diameters were assumed to have BC cores of the same sizes (Ma et al., 2012; Yuan et al., 2016), which were calculated with the volume fraction of core-shell mixed BC:

\[
D_{\text{core}}(D_p) = D_p \cdot \left( \frac{N(\text{lgDp})_{\text{BC}} - N(\text{lgDp})_{\text{ext-BC}}}{N(\text{lgDp})_{\text{core-shell}}} \right)^{\frac{1}{3}} \tag{8}
\]

where, D_{core}(D_p) (µm) was the diameter of the BC core at size D_p, which could be derived by combining the Eqs. (4), (6), (7), (8):

\[
D_{\text{core}}(D_p) = D_p \cdot \left( \frac{\varepsilon_1(\text{lgDp})_{\text{BC}} \cdot (1-r_1)}{(1-\varepsilon_2(\text{lgDp})_{\text{BC}} \cdot r_1)} \right)^{\frac{1}{3}} \tag{9}
\]

Then, the scattering coefficient and hemispheric backscattering coefficient for the first scenario (σ_{sp (hisp)}, r_1) were calculated by summing the scattering and hemispheric backscattering of the externally mixed BC and core-shell mixed particles, respectively, both of which were integrated mathematically across all size bins based on the assumption of spherical particles according to the Mie model (Bohren and Huffman, 2008) as shown in Eq. (10):

\[
\sigma_{sp (hisp)} = \int_D Q_{sp (hisp), \text{ext-BC}} \cdot \frac{\pi D_p^2}{4} \cdot N(\text{lgDp})_{\text{ext-BC}} \cdot d \text{lgDp} + \int_D Q_{sp (hisp), \text{core-shell}} \cdot \frac{\pi D_p^2}{4} \cdot N(\text{lgDp})_{\text{core-shell}} \cdot d \text{lgDp} \tag{10}
\]

where, Q_{sp (hisp), \text{ext-BC}} and Q_{sp (hisp), \text{core-shell}} (dimensionless values) were the scattering efficiency and backscattering efficiency for externally mixed BC and core-shell mixed particles, respectively. They are functions of scattering angle, refractive index, and the dimensionless size parameter in the Mie model (Cheng et al., 2006; Bohren and Huffman, 2008).

For the second scenario, the total BC were divided into externally mixed BC (N(lgdDp)_ext-BC) (#/m^3) with the same fraction of non-BCs (N(lgdDp)_non-BC) (#/m^3), and core-shell mixed BC, mixing with the rest of non-BCs (N(lgdDp)_core-shell) (#/m^3) for r_2:

\[
N(\text{lgDp})_{\text{ext-BC}} = N(\text{lgDp})_{\text{BC}} \cdot r_2 \tag{11}
\]

\[
N(\text{lgDp})_{\text{non-BC}} = N(\text{lgDp})_{\text{measured}} - N(\text{lgDp})_{\text{ext-BC}} \tag{12}
\]

\[
N(\text{lgDp})_{\text{core-shell}} = N(\text{lgDp})_{\text{measured}} - N(\text{lgDp})_{\text{non-BC}} \tag{13}
\]

And D_{core}(D_p) could be calculated by the same way as Eq. (9):

\[
D_{\text{core}}(D_p) = D_p \cdot \left( \frac{\varepsilon_1(\text{lgDp})_{\text{BC}}}{1-\varepsilon_2(\text{lgDp})_{\text{BC}} \cdot r_2} \right)^{\frac{1}{3}} \tag{14}
\]

Similarly, the scattering coefficient and hemispheric backscattering coefficient for scenario two (σ_{sp (hisp)}, r_2) were calculated by:

\[
\sigma_{sp (hisp)} = \int_D Q_{sp (hisp), \text{ext-BC}} \cdot \frac{\pi D_p^2}{4} \cdot N(\text{lgDp})_{\text{ext-BC}} \cdot d \text{lgDp} + \int_D Q_{sp (hisp), \text{non-BC}} \cdot \frac{\pi D_p^2}{4} \cdot N(\text{lgDp})_{\text{non-BC}} \cdot d \text{lgDp} + \int_D Q_{sp (hisp), \text{core-shell}} \cdot \frac{\pi D_p^2}{4} \cdot N(\text{lgDp})_{\text{core-shell}} \cdot d \text{lgDp} \tag{15}
\]
where $Q_{\text{ap(besp)}, \text{non-BC}}$ (dimensionless values) was the scattering or backscattering efficiency for the externally mixed non-BCs.

Note that the sensing angles of TSI 3563 nephelometer are restricted between 7° and 170° and between 90° and 170° for $\sigma_{\text{ap, neph}}$ and $\sigma_{\text{besp, neph}}$, respectively, due to the instrument’s design constraints. And the light source of the nephelometer can result in a non-ideal angular response (Anderson et al., 1996). This angular response was taken into consideration in the Mie calculations for this campaign instead of correcting the data measured by the nephelometer. Therefore, Qs in Eqs. (10) and (15) were replaced by corrected ones (Cheng et al., 2006; Bohren and Huffman, 2008) based on the nephelometer angular response obtained by Anderson et al. (1996).

As shown in the equations above, the input parameters of the Mie model were the functions of the parameter $\beta_1$ or $\beta_2$. Therefore, the modeled hemispheric backscattering fraction ($\beta_1$ and $\beta_2$) also depended on $r_1$ or $r_2$ (Eq. (16)):

$$
\beta_{\text{neph}}(r) = \frac{\sigma_{\text{besp, neph}}(r)}{\sigma_{\text{ap, neph}}(r)}
$$

So, the parameter $r_1$ and $r_2$ could be retrieved by minimizing the discrepancies ($\chi^2$) between $\beta_{\text{neph}}$ and the corresponding $\beta_1$ and $\beta_2$ by the modified Mie mode, which was quantified by linear least squares as Eq. (17):

$$
\chi^2 = \sum \left( \frac{\beta_{\lambda, \text{neph}} - \beta_{\lambda, \text{Mie}}}{\beta_{\lambda, \text{Mie}}} \right)^2
$$

where, $\lambda$ (450, 550, 700 nm) denoted the three operation wavelengths of the nephelometer. $\beta_{\lambda, \text{neph}}$ was the hemispheric backscattering fraction calculated with Mie model and $\beta_{\lambda, \text{Mie}}$ was the measurement of the nephelometer at wavelength $\lambda$. Finally, two time series of $r$s were subsequently retrieved by Eq. (17).

2. Results and discussion

2.1. Analyses of measured aerosol optical properties

2.1.1. Overview

$\sigma_{\text{ap, neph}}$, $\sigma_{\text{besp, neph}}$, and $\sigma_{\text{ap, 550}}$ are so-called aerosol extensive optical properties since they can represent the aerosol loading to a certain extent (Cheng et al., 2008). An optical closure study on $\sigma_{\text{ap, neph}}$ and $\sigma_{\text{ap, 550}}$ has been conducted by Yuan et al. (2016), confirming the reliability of the measured aerosol microphysical and chemical properties during the campaign.

In addition, aerosol intensive optical properties, which are derived from the extensive optical properties, are independent of aerosol loading and can represent some microphysical and chemical properties of aerosols (Cheng et al., 2008). Such as $\beta_{\text{neph}}$ (Eq. (16)) and Angström exponent ($h_{\text{neph}}$) (Eq. (18)), they are closely related to the mean size of aerosol particles. Single scattering albedo ($\omega$), the ratio of the scattering coefficient to the extinction coefficient (the sum of the scattering coefficient and absorption coefficient) (Eq. (19)), can indicate the fraction of BC in aerosols. They are given based on the measurements to further investigate the variation of optical properties at Mt. Huang.

$$
\ln \frac{\sigma_{\text{ap, neph}, \lambda}}{\sigma_{\text{ap, neph}, \lambda}} = - \frac{1}{\beta_{\lambda, \text{neph}}} \ln \frac{\lambda}{\lambda_{\text{cut-off}}}
$$

(18)

$$
\omega_{550} = \frac{\sigma_{\text{ap, neph}, 550}}{\sigma_{\text{ap, neph}, 550} + \sigma_{\text{ap, neph}, 550}}
$$

(19)

Fig. 3 shows the time series of aerosol extensive optical properties and PNSDs with average effective particle diameter $D_{\text{p, eff}}$ throughout the measurement campaign. The extensive optical properties follow essentially the same trends. Although large temporal variations can be found for the extensive optical properties, most of the values still keep very low level, which are smaller than 200 Mm$^{-1}$ for $\sigma_{\text{ap, neph}, 550}$ and 20 Mm$^{-1}$ for both hemispheric scattering coefficient at 550 nm ($\sigma_{\text{neph, neph}, 550}$) and $\sigma_{\text{ap, 550}}$ with campaign mean values (standard deviations) of 82.2 (57.0), 10.9 (6.5), and 14.1 (6.7) Mm$^{-1}$, respectively.

The time series of aerosol intensive optical properties shows both $\beta_{\text{neph}}$ and $\beta_{\text{neph}}$ have the same trends and they are wavelength dependent (Fig. S4). $\beta_{\text{neph}}$ increases with increasing wavelength due to decreasing size parameters, while $\beta_{\text{neph}}$ increased for the longer wavelength pairs. The mean values (standard deviations) of $\beta_{\text{neph}}$, 450–700, $\omega_{550}$, and $\beta_{\text{neph}}$, 550 are 2.16 (0.23), 0.84 (0.05), and 0.14 (0.02), respectively, for the whole campaign.

To compare with some earlier related measurement campaigns, the scattering coefficient, absorption coefficient, and single scattering albedos observed in this study and in selected other studies are summarized in Table 1. It reveals clearly that the aerosol extensive properties measured at our site are remarkably lower in magnitude than those observed at other urban and rural sites in China and some sites in other countries. For example, the mean value of $\sigma_{\text{ap, neph}, 550}$ and $\sigma_{\text{ap, 550}}$ from this campaign are 2.5–5 times lower than the observations carried out in the urban site of Beijing (Jing et al., 2015), Shanghai (Xu et al., 2015), Nanjing (Yu et al., 2016), Wuhan (Gong et al., 2017), and Taiyuan (Li et al., 2015). They are also a factor of 1/6–1/2 lower than the results in some rural sites of China, such as Shouxian, in Anhui (Fan et al., 2010), Yufa, in Beijing (Garland et al., 2009), and a rural site in Guangzhou (Garland et al., 2008). The value of $\sigma_{\text{ap, neph}, 550}$ lies even approximately 1/3 of the values obtained in Linan (Yan, 2006) and Shangdianzi (Yan et al., 2008), where aerosol loadings are considered to be at a background level. However, the difference for $\sigma_{\text{ap, 550}}$ between this study and the two background sites is not as large as $\sigma_{\text{ap, neph}, 550}$.

Compared to some sites outside of China, the average value of $\sigma_{\text{ap, neph}, 550}$ in Mt. Huang is half of the values in Asian cities, e.g., Tokyo (Nakayama et al., 2010) and Delhi (Son et al., 2010), but comparable to that achieved in Granada (Lyamani et al., 2008), a European city, which is one of the cleanest cities in the world. However, $\sigma_{\text{ap, 550}}$ of 14.1 Mm$^{-1}$ in our study is much smaller than those obtained in Delhi and Granada but similar with the result in Tokyo.

Different from $\sigma_{\text{ap, neph}, 550}$ and $\sigma_{\text{ap, 550}}$, there is no obvious discrepancy for $\omega_{550}$ between this study and others in China. The mean value of $\omega_{550}$ (0.84) obtained during this study falls
Effective particle diameter measured during the observation period.

Fig. 3 – Time series of aerosol extensive optical properties and the particle number size distributions (PNSDs) with average effective particle diameter measured during the observation period.

Table 1 – Comparisons of the aerosol optical properties with the results from other sites in China and some other countries.

<table>
<thead>
<tr>
<th>Site</th>
<th>Study period</th>
<th>( \sigma_{sp} ) (Mm(^{-1}))</th>
<th>( \sigma_{ap} ) (Mm(^{-1}))</th>
<th>( \omega )</th>
<th>Instruments Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing, China (Urban)</td>
<td>2009-06-2010.05</td>
<td>360.0 ± 405.0 (525 nm)</td>
<td>64.0 ± 62.0 (525 nm)</td>
<td>0.82 ± 0.09</td>
<td>Nephelometer Aurora-1000 (Ecotech)</td>
</tr>
<tr>
<td>Shanghai, China (*) Urban</td>
<td>2010.12–2011.03</td>
<td>292.8 ± 206.4 (532 nm)</td>
<td>65.8 ± 46.8 (532 nm)</td>
<td>0.81 ± 0.04</td>
<td>Nephelometer M9003 (ECOTech)</td>
</tr>
<tr>
<td>Nanjing, China (62 m a. s. l., Urban)</td>
<td>2011.03–2011.04</td>
<td>303.3 ± 290.4 (532 nm)</td>
<td>28.0 ± 17.6 (532 nm)</td>
<td>0.89 ± 0.08</td>
<td>Nephelometer 3563 (TSI) PASS (DMT)</td>
</tr>
<tr>
<td>Wuhan, China (*) Urban</td>
<td>2009.12–2014.03</td>
<td>377.5 ± 305.0 (520 nm)</td>
<td>119 ± 92 (520 nm)</td>
<td>0.73 ± 0.16</td>
<td>Nephelometer 3563 (TSI) AE31 (Magee Scientific)</td>
</tr>
<tr>
<td>Taiyuan, China (778 m a. s. l., Urban)</td>
<td>2013.08</td>
<td>188.8 ± 110.0 (550 nm)</td>
<td>*</td>
<td>*</td>
<td>Nephelometer 3563 (TSI)</td>
</tr>
<tr>
<td>Tokyo, Japan (*) Urban</td>
<td>2007.08–2007.09</td>
<td>130.8 ± 81.4 (532 nm)</td>
<td>113.6 ± 9.2 (532 nm)</td>
<td>0.88 ± 0.07</td>
<td>Nephelometer 3563 (TSI) PSAP</td>
</tr>
<tr>
<td>Delhi, India (235 m a. s. l., Urban)</td>
<td>2008.07–2008.09</td>
<td>95.3 ± 49.5 (550 nm)</td>
<td>51.0 ± 43.6 (550 nm)</td>
<td>0.69 ± 0.07</td>
<td>Nephelometer NGN-3A (OPTEC) AE42 (Magee Scientific)</td>
</tr>
<tr>
<td>Granada, Spain (680 m a. s. l., Urban)</td>
<td>2005.12–2006.02</td>
<td>84.0 ± 62.0 (550 nm)</td>
<td>28.0 ± 20.0 (550 nm)</td>
<td>0.66 ± 0.11</td>
<td>Nephelometer 3563 (TSI) MAAP 5012 (Thermo)</td>
</tr>
<tr>
<td>Shouxiwan, China (23 m a. s. l., Rural)</td>
<td>2008.05–2008.12</td>
<td>401.2 ± 314.3 (550 nm)</td>
<td>29.4 ± 31.1 (550 nm)</td>
<td>0.92 ± 0.03</td>
<td>Nephelometer 3563 (TSI) PSAP</td>
</tr>
<tr>
<td>Yufa, China (*) Rural</td>
<td>2006.08–2006.09</td>
<td>361.0 ± 295.0 (550 nm)</td>
<td>51.8 ± 36.5 (550 nm)</td>
<td>0.86 ± 0.07</td>
<td>Nephelometer 3563 (TSI) PAS (Desert Research Institute)</td>
</tr>
<tr>
<td>Guangzhou, China (*) Rural</td>
<td>2006.07</td>
<td>151.0 ± 103.0 (550 nm)</td>
<td>34.3 ± 26.5 (550 nm)</td>
<td>0.82 ± 0.07</td>
<td>Nephelometer 3563 (TSI) PAS (Desert Research Institute)</td>
</tr>
<tr>
<td>Linan, China (*) Rural</td>
<td>2004</td>
<td>229.4 ± 104.8 (550 nm)</td>
<td>44.3 ± 19.7 (550 nm)</td>
<td>0.82 ± 0.03</td>
<td>*</td>
</tr>
<tr>
<td>Shangdianzi, China (293 m a. s. l., Rural)</td>
<td>2004.9–2004.11</td>
<td>215.1 ± 222.9 (550 nm)</td>
<td>16.7 ± 11.6 (550 nm)</td>
<td>0.88 ± 0.06</td>
<td>Nephelometer M9003 (ECOTech)</td>
</tr>
<tr>
<td>Mt. Tai, China (1534 m a. s. l., Mountain)</td>
<td>2010.09–2011.10</td>
<td>144.5 ± 134.6 (550 nm)</td>
<td>20.0 ± 15.5 (550 nm)</td>
<td>0.87 ± 0.04</td>
<td>Nephelometer 3563 (TSI) MAAP 5012 (Thermo)</td>
</tr>
<tr>
<td>Mt. Huang (1840 m a. s. l., Mountain)</td>
<td>2011.06–2011.08</td>
<td>62.6 ± 49.2 (550 nm)</td>
<td>5.5 ± 3.7 (550 nm)</td>
<td>0.89 ± 0.04</td>
<td>Nephelometer 3563 (TSI) PSAP</td>
</tr>
<tr>
<td>Mt. Huang (869 m a. s. l., Mountain)</td>
<td>2012.09–2012.10</td>
<td>82.2 ± 57.0 (550 nm)</td>
<td>14.1 ± 6.7 (550 nm)</td>
<td>0.84 ± 0.05</td>
<td>Nephelometer 3563 (TSI) AE31 (Magee Scientific)</td>
</tr>
</tbody>
</table>

* represents the lack of information.
in the range of the single scattering albedos in the sites of China listed in Table 1, which varies from 0.73 to 0.92. However, it is approximately 0.2 higher than the value of 0.63 and 0.66 in Delhi and Granada, (Lyamani et al., 2008; Soni et al., 2010), which is mainly due to the different composition of aerosol particles in different sites.

As tourist regions with few industrial activities, σsp, neph, 550 and σsp, 550 at Mt. Huang are far below and almost half of that observed at the summit of Mt. Tai (Shen, 2012) located in eastern China with an elevation of 1534 m, although the observational site in this campaign was on the mountainside, about half lower than the altitude of Mt. Tai. The result is slightly higher than that on the summit of Mt. Huang obtained by Yuan et al. (2013) due to its lower altitude. Thus, from the comparison above, it can be concluded that Mt. Huang has lower average aerosol optical properties than the urban, rural, and mountain regions and it is one of the cleanest regions in central and eastern China.

2.1.2. Aerosol optical properties during the pollution episodes

As can be seen in Fig. 3, three heavy pollution events (episode) can be identified on 280, 284, and 301 DOY, which are defined as significant rises in σsp, neph and σsp, 550, satisfying that the rises of both σsp, neph and σsp, 550 lasted for consecutive hours and exceeded three standard deviation of the period average (Cheng et al., 2008).

Table 2 lists the averages of aerosol optical properties and the major meteorological parameters for the complete campaign, the campaign without the episode days, and the episode days (280, 284, 301 DOY). As can be seen from Table 2, the mean values of the extensive optical properties at 550 nm for the episode days, including σsp, neph, 550, σsp, 550, and σap, 550, were 188.8, 22.7, and 26.1 Mm⁻¹, which were more than twice the average values of 71.7, 9.8, and 13.0 Mm⁻¹, respectively, for the rest of the campaign. However, Δneph, 450-700 and Δneph, 550 had clear decreasing trends for each episode (Fig. S4), with mean values of 2.02 and 0.12, respectively. It indicated some pollutants with slight increasing diameter occurred during these three days, which was confirmed by the variation of PNSDs showed in Fig. 3.

To further explore the factors resulting in the three episodes, Fig. 4 displays the details of aerosol properties around these periods. σsp, neph, 550 and the PNSDs around the three episode days are presented in Fig. 4a, c, e, respectively. The corresponding meteorological factors including T, RH, and wind are showed in Fig. 4b, d, f. The episodes are shaded in red.

Fig. 4a, c, e shows that the high level of σsp, neph, 550 during the three episodes were all contributed by the high concentration of aerosol particles of accumulation mode with diameter ranging from 100 to 300 nm. This part of aerosols is mainly originated from condensation and coagulation of Aitken mode aerosols and the high-temperature steam emitted by combustion process (Shen, 2012). Thus, the episodes were possibly due to the regional transmission or intense biomass burning during the campaign.

There were no distinct differences between the averages of T, RH, and WS on the episode days and the rest days. However, there existed some differences among each episode. RH was lower, but WS was a little higher on 284 DOY. Combining with their hourly variation in Fig. 4b, d, f, it could be seen that the diurnal pattern of WD was different from the other two episode days, WD was dominated by north with the highest WS of larger than 1.5 m/sec in the daytime on 284, while the wind was from southwest with WS of lower than 1.0 m/sec in the noon and almost kept calm condition in the afternoon on 280 DOY. On 301 DOY, the wind always kept calm condition. It is worth noting that the top value of σsp, neph, 550 was corresponding to high north wind on 284 DOY, but calm conditions on 280 and 301 DOY. So, it can be concluded that the high values of σsp, neph, 550 on 284 DOY could be partly due to the regional transmission from the north. Nevertheless, the high values of σsp, neph, 550 during the episodes on 280 and 301 DOY could be attributed to the intensive surrounding biomass.

| Table 2 – Averages of aerosol optical properties and the major meteorological parameters for the complete campaign, the campaign without the episode days, and the episode days (280, 284, 301 DOY). |
|--------------------------------|--------------------------------|--------------------------------|
|                                | All campaign | Campaign without the episode days | The episode day |
|                                | Mean ± S. D. | Mean ± S. D. | Mean ± S. D. |
| σsp, neph, 450 (Mm⁻¹)         | 118.5 ± 78.1 | 104.3 ± 49.7 | 262.0 ± 142.8 |
| σsp, neph, 550 (Mm⁻¹)         | 82.2 ± 57.0  | 71.7 ± 35.8  | 188.6 ± 104.0 |
| σsp, 700 (Mm⁻¹)               | 46.6 ± 33.4  | 40.4 ± 20.9  | 109.5 ± 60.9  |
| σhhsp, neph, 450 (Mm⁻¹)       | 14.5 ± 8.6   | 12.9 ± 5.5   | 29.8 ± 16.1   |
| σhhsp, neph, 550 (Mm⁻¹)       | 10.9 ± 6.5   | 9.8 ± 4.2    | 22.7 ± 12.2   |
| σhhsp, neph, 750 (Mm⁻¹)       | 8.2 ± 5.1    | 7.2 ± 3.2    | 17.5 ± 9.5    |
| Δneph, 450-400                 | 14.1 ± 6.7   | 13.0 ± 4.8   | 26.1 ± 10.9   |
| Δneph, 450-700                 | 1.88 ± 0.26  | 1.90 ± 0.25  | 1.69 ± 0.23   |
| Δneph, 550-700                 | 2.16 ± 0.23  | 2.17 ± 0.22  | 2.02 ± 0.21   |
| Δneph, 550                      | 2.39 ± 0.21  | 2.40 ± 0.21  | 2.30 ± 0.20   |
| σ550                           | 0.84 ± 0.05  | 0.84 ± 0.05  | 0.86 ± 0.05   |
| Δneph, 450                     | 0.13 ± 0.01  | 0.13 ± 0.01  | 0.12 ± 0.01   |
| Δneph, 550                     | 0.14 ± 0.02  | 0.14 ± 0.02  | 0.12 ± 0.01   |
| Δneph, 700                     | 0.18 ± 0.02  | 0.19 ± 0.02  | 0.17 ± 0.02   |
| T (°C)                         | 16           | 16           | 17            |
| RH (%)                         | 70           | 69           | 72            |
| WS (m/s)                       | 0.4          | 0.4          | 0.5           |
burning, which accumulated at the observation site under the steady synoptic condition. This result was consistent with Chen’s report (Chen et al., 2014), who showed there was a biomass burning event around 280 DOY at surrounding areas. And, it was also confirmed by the 72-hr backward trajectories, which showed that the air mass came from a farther source region on 284 DOY than that on 280 and 301 DOY. The 72-hr backward trajectories were calculated by the Hybrid Single Particle Lagrangian Integrated Trajectory-4 (Hysplit-4) model (Draxler and Rolph, 2003). The American meteorological center global environmental prediction data assimilation system (NECP, GDAS) 1° × 1° meteorological field was used by the model. The end-station was Mt. Huang (30.12° N, 118.19° E) and the end-time corresponded to the time when the highest \( \sigma_{sp, neph, 550} \) occurred on the episode days.

2.1.3. Relationship between different aerosol properties

To further investigate the key factors affecting the aerosol optical properties, the relationships between different aerosol properties are drawn in Fig. 5. The data during the three episodes are highlighted by squares in this figure. The scatterplots of \( \sigma_{sp, neph, 550} \) and \( \sigma_{ap, 550} \) in Fig. 5a displays excellent agreement with a correlation coefficient \( R^2 \) of 0.94, which agree well with Fig. 2. This reveals that aerosol particles observed in Mt. Huang are both BC and the non-BCs contained.

The changes of the single scattering albedo can reflect the variations in aerosol composition (e.g., the fraction of BC and its mixing state in aerosols). Fig. 5b shows the relationship between \( \omega_{550} \) and \( \sigma_{ap, 550} \) as well as \( \sigma_{sp, neph, 550} \). Combine with the color bar coded by \( \sigma_{sp, neph, 550} \) in Fig. 5b, it was clear that \( \omega_{550} \) generally increased with increasing \( \sigma_{sp, neph, 550} \) and \( \sigma_{ap, 550} \). This was consistent with the result for typical polluted continental aged aerosols (Kim et al., 2005). However, it is worth noting that \( \sigma_{ap, 550} \) could increase when aerosol concentration kept constant (\( \sigma_{sp, neph, 550} \) remains unchanged), which resulted in the decrease of \( \omega_{550} \). This can be explained by the aging process of aerosol in the atmosphere, which led to the enhancement of BC light-absorption capacity, resulted in the decrease of \( \omega_{550} \) at constant aerosol concentration. Additionally, the decreasing rate of \( \omega_{550} \) with increasing \( \sigma_{ap, 550} \) became smaller when aerosol concentration gets higher (high level of \( \sigma_{sp, neph, 550} \)). This revealed that the increasing rate of the fraction of non-BCs was more rapid than BC when aerosol concentration was increasing. This sensitivity of \( \omega_{550} \) to \( \sigma_{sp, neph, 550} \) and \( \sigma_{ap, 550} \) was basically consistent with that in Xinken, a rural site in Pearl River Delta of China (Cheng et al., 2008), where a slight difference was that \( \omega_{550} \) was more sensitive to \( \sigma_{ap, 550} \) in their study.

The variations in the single scattering albedo can be generally driven not only by changes in the particle composition but also by changes in the particle size, which influences the scattering and absorption efficiency according to the Mie model (Garland et al., 2008). To investigate the impact of particle size on \( \omega_{550} \), Fig. 5c displays \( \omega_{550} \) plotted against \( D_{p, eff} \). Clearly, \( \omega_{550} \) and \( D_{p, eff} \) showed a positive correlation with \( R^2 \) of 0.46. The increasing rate of \( \omega_{550} \) became smaller as \( D_{p, eff} \) increases, and it kept almost a constant for \( \omega_{550} \) occurred at \( D_{p, eff} \) of 300–350 nm. This result confirmed that the change in \( \omega_{550} \) were also driven by the change of particle diameter, which could be explained by that BC was coated by the non-BCs during the aging process in the atmosphere, which enlarges the aerosol diameter that leads to the increase of \( \sigma_{sp, neph, 550} \) and thus, \( \omega_{550} \) increases (Liu et al., 2017). Fig. 5d confirms this result, which displays the scatterplots of \( D_{p, eff} \) and \( \sigma_{ap, 550} \) and a positive relationship between \( D_{p, eff} \) and \( \sigma_{sp, neph, 550} \) was found.

Thus, a conceptual model of aerosol aging process in the atmosphere can be drawn in Fig. 6 by combining Fig. 5b, c, d.
Fig. 6 considers two conditions that describe aerosol aging process. On the one hand, if BC is considered solely in the initial state (Fig. 6a), the coating of non-BCs component on the surface of BC in the atmosphere will contribute to increasing aerosol diameter with high absorption and higher scattering coefficients leading to higher SSA compared to the initial state according to the modified Mie model. This explains the increase of $\omega_{550}$ and $\sigma_{\text{sp, neph, } 550}$ in Fig. 5c, d. On the other hand, if the initial state contains both externally mixed BC and externally mixed non-BCs, and the later will cover the surface of externally mixed BC in the aging process (Fig. 6b), this will lead to large enhancement of absorption coefficient and almost constant scattering coefficient compare to the initial state, which results in a relatively lower SSA. And this can explain the decreasing $\omega_{550}$ with increasing $\sigma_{\text{ap, } 550}$ at a constant aerosol concentration (Fig. 5b).

Additionally, Fig. 5d also reveals that the higher the aerosol loading is, the more contribution is from the relatively larger particles to $\sigma_{\text{sp, neph, } 550}$. However, $D_{\text{p, eff}}$ of lower than 360 nm indicates that $\sigma_{\text{sp, neph, } 550}$ is still dominated by the fine particles. This is in compliance with the result from Yuan et al. (2016), who demonstrated that the scattering coefficient and absorption coefficient were dominated by the fine particles with diameters ranging from 150 to 1000 nm.

2.1.4. Diurnal variations of aerosol optical properties

Fig. 7 shows the diurnal cycles of $\sigma_{\text{sp, neph, } 550}$, $\sigma_{\text{ap, } 550}$, $\omega_{550}$, and PNSDs with error bars of one standard deviation based on their hourly averages. The boundary layer height (BLH) calculated by the Hysplit-4 model is also drawn in Fig. 7a, b and $D_{\text{p, eff}}$ is added in Fig. 7d.

Although similar diurnal patterns were found for these two properties, the ranges of variations kept very small.
σ_{sp, neph, 550} was elevated from 63.8 Mm$^{-1}$ at 06:00 LT in the morning to a maximum mean value of 77.5 Mm$^{-1}$ around 9:00 LST (Local Standard Time) and then fell gradually and continuously between 11:00 LST and the next day 06:00 LT with two small peaks occurred around 16:00 LST and 22:00 LST. The diurnal cycle for σ_{ap, 550} was more pronounced than that of σ_{sp, neph, 550}. The mean value was enhanced from 10.6 Mm$^{-1}$ at 06:00 LT and reached the highest value of 16.2 Mm$^{-1}$ at 09:00 LST but then decreased sharply and almost followed the similar trend with σ_{sp, neph, 550}, with two small peaks appeared around 16:00 LST and 22:00 LST.

As this campaign was conducted at a mountain site, the diurnal patterns were found to be different from that in the sites at lower altitude such as Wuqing in the North China Plain (Ma et al., 2011; Han et al., 2014), Nanjing, in the Yangtze River Delta (Yu et al., 2016), and Guangzhou in the Pearl River Delta (Garland et al., 2008). In their studies, the maximum values of σ_{sp, neph, 550} and σ_{ap, 550} occurred in earlier time around 06:00–08:00 LST due to the enhanced emissions in the morning and the average values of σ_{sp, neph, 550} and σ_{ap, 550} were lower in the daytime because of the turbulent dilution with the PBL development. However, there were no local rush hours with enhanced traffic emissions at our site during the morning, as Fig. 7a, b shows, the pollutants in the lower level of the atmosphere before sunrise could be elevated with the development of PBL. Aerosol concentration reached the highest resulting in the top values of σ_{sp, neph, 550} and σ_{ap, 550} during 09:00 and 10:00 when the PBL reaches the height of our site (the boundary layer height of about 400–500 m above ground level around 09:00 LST was almost equal to the altitude of 869 m above sea level of our site) (Yuan et al., 2013; Li et al., 2014). Then, aerosols were diluted with the continuously elevated PBL height. This led to a decrease of aerosol concentration after about 09:00 LST and 10:00 LST. In the late afternoon, σ_{sp, neph, 550} and σ_{ap, 550} began to rise and reached the second peak at 16:00 LST, just corresponding to the time that the PBL declined to height of the observation site. This indicated the diluted pollutants due to PBL development in the morning fell back and accumulated in this site. In the nighttime, the decrease of σ_{sp, neph, 550} and σ_{ap, 550} from the midnight to the early morning suggested a removal of aerosol particles by dry deposition.

Additionally, the topography-induced local circulation, such as the mountain–valley breeze, due to the special geographic location, could also have some impact on the transport of the pollutants to the site. A modeling study at Mt. Huang conducted by Wang et al. (2013) demonstrated that an up-slope flow started to develop and flushed out from the valley due to the enhanced solar radiation around 09:00 LST. This up-slope flow could also carry the pollutant from the low level to our site in the morning, while in the afternoon, the down-slope wind generated and brought the pollutants back to the site.

This unique cycle was also different from that at relatively higher altitude like the summit of Mt. Tai (Shen, 2012) and Mt. Huang (Yuan et al., 2013), who obtained higher concentrations in the middle and the afternoon of the day (12:00–18:00 LST). The peak time of the diurnal cycles for both σ_{sp, neph, 550} and σ_{ap, 550} in this campaign were just between the time of urban area in the plain and summit of high altitude. This corresponded to the evolution of BLH and the mountain–valley breeze with time.

The diurnal cycles of ω_{550} and PNSD could reflect the different degree of the peak-to-trough diel variation in

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**Fig. 6 – The conceptual model of aerosol aging process in the atmosphere.**
The whole period. As Fig. 7b, c shows, the low value of $\omega_{550}$ in the morning corresponded to the obviously increase of $\sigma_{ap, 550}$. This could be explained by the rapid atmospheric aging process of BC showed in Fig. 6b, which was discussed in Section 2.1.3. However, the appearance of non-absorbing secondary aerosols, which was more likely to scatter the incident light, generated from the photochemical reactions in the afternoon (10:00–14:00 LST) (Fig. 7d) led to the increased $\omega_{550}$ and decreased $D_{p, eff}$ correspondingly. This was also the reason that $\sigma_{sp, neph, 550}$ did not decrease as sharply as $\sigma_{ap, 550}$.

2.2. Mixing state of BC and the non-BCs

2.2.1. Factors influencing the variations of BC mixing state

To further trace and understand the factors affecting the optical properties of aerosols at Mt. Huang, $r_1$ and $r_2$ were inverted by using Mie model described in Section 1.3 for the whole period.

Excellent agreements with $R^2$ greater than 0.99 were achieved between the calculated hemispheric backscattering fraction based on the retrieved $r_1$ and $r_2$ ($\beta_1$ and $\beta_2$) and the measurements, at all three wavelengths (Fig. S5 and Table S1). This indicated that $r_1$ and $r_2$ were appropriate to reflect the mixing state of BC at our site. Fig. 8 presents the time series of $r_1$ and $r_2$ as well as the atmospheric pressure. As can be seen that $r_1$ and $r_2$ followed generally the similar trends and varied between 0 and 1, with averages (standard deviations) of 0.67 (0.27) and 0.48 (0.22) for the whole period, respectively, which meant that around 70% and 50% of the total BC, respectively, was externally mixed with non-BCs in the two different ways mentioned above. $r_1$ of 0.67 was just between the values of the researches conducted by Cheng et al. (2006) and Ma et al. (2012) at Xinmen (0.78) and Wuqing (0.51), and it was higher than the latest result of Tan et al. (2016) in Guangzhou (0.58), China. This indicated the large variation of BC mixing state with time and space. The discrepancy between the average values of $r_1$ and $r_2$ revealed the non-negligible influence of externally mixed non-BCs on the retrieved parameter $r$ and the existence of externally mixed non-BCs reduced the externally mixed BC at the same level of aerosol optical properties. In addition, large discrepancies between $r_1$ and $r_2$ during 280–283 DOY and 294–301 DOY can be found in Fig. 8, when $\beta_{neph, 550}$ was relatively lower than the rest of the campaign (Fig. S2), indicating that aerosol particles were relatively larger (relatively larger $D_{p, eff}$). The relative difference between $r_1$ and $r_2$ ($\Delta r = r_1 - r_2$) was positively correlated with $D_{p, eff}$ with some degree (Fig. S6a). This confirmed again the impact of externally mixed non-BCs in the relatively larger particles on the retrieved parameter $r$.

Fig. 7 also shows $r_1$ and $r_2$ varied periodically, which are negatively correlated with the variation of atmospheric
pressure to a certain extent (Fig. S6b). On one hand, when the weather was dominated by a high-pressure system, the downward flow due to the convergence in the upper level suppressed the updraft produced by the evolution of PBL and mountain–valley breeze from lower level, which led to the relatively stable synoptic conditions. Thus, the transportation of newly produced externally mixed BC in the low level was also inhibited, contributing to the relatively lower \( r_s \) (more BC particles were core-shell mixed) in our site. Whereas the low-pressure system was favorable to the transportation of the newly produced externally mixed BC from the low level, leading to the higher \( r_s \) (more BC particles were externally mixed). On the other hand, the difference of air mass source due to the different weather system could contribute to the variation of BC mixing state. The 72-hr backward trajectories ending at 12:00 LST on four days, two of which were controlled by the high-pressure system (274 and 292 DOY) and the other two of which were controlled by the low-pressure system (277 and 287 DOY) (Fig. S7). They were computed by HYSPLIT-4 model at 500 and 1500 m above the ground level. On 274 and 292 DOY, the air masses transported from the north and there was no intensive pollution source regionally around Mt. Huang from this direction. Thus, not so much fresh pollutants were emitted, and more BC were core-shell mixed. Nevertheless, on 277 and 287 DOY, the air masses originated from north, passing through the megacity cluster of the Yangtze River Delta, which brought large amount of freshly emitted pollutants, and eventually reached Mt. Huang from the east and more BC were externally mixed.

### 2.2.2. Diurnal variations of BC mixing state – case studies

The diurnal variation of BC mixing state and its influencing factors were investigated by choosing four typical days (274, 277, 287, and 292 DOY), which were selected based on the analysis in Section 2.2.1 as case studies. As discussed in Section 2.2.1, 274 and 292 DOY were controlled by the high-pressure system, while 277 and 287 DOY were controlled by the low-pressure system. Fig. 9a, b show the diurnal variations of \( r_s \) as well as \( \sigma_{ap, neph, 550} \) and \( \sigma_{ap, 550} \) for high-pressure controlled days and low-pressure controlled days, respectively. More pronounced diurnal patterns of \( r_s \) can be found in Fig. 9a with relatively lower values of \( r_s \), \( \sigma_{ap, neph, 550} \), and \( \sigma_{ap, 550} \) compared to Fig. 9b.

On the high-pressure controlled days, the transportation of newly produced externally mixed BC in the low level was inhibited by the high-pressure system, which built a clean environment around the observation site that favored the formation of new particles. This was confirmed by the diurnal variation of PNSDs in Fig. 9c, which shows there was new particle formation (NPF) event during 08:00 and 12:00 LST on these two days. This resulted in the higher values of \( \sigma_{ap, neph, 550} \) in the morning and noon (08:00–12:00 LST) as shown in Fig. 9a. Therefore, the corresponding lower \( r_s \) were mainly due to the rapid aging process that the new formed particles coated on preexisting BC, which produced large number of core-shell mixed aerosols, leading to the increase of \( \sigma_{ap, 550} \) during this time (08:00–12:00 LST) (Fig. 9a). However, the higher values of \( \sigma_{ap, neph, 550} \) and \( \sigma_{ap, neph} \) in the afternoon were mainly due to the local emissions of biomass burning. This can be also confirmed by Fig. 9c, which shows the concentration of aerosol particles with diameter of around 100–200 nm increased at dusk (16:00–21:00 LST) due to biomass burning (Reid et al., 2005; Moffet and Prather, 2009). Thus, more BC were externally mixed in the afternoon, contributing to the increasing \( r_s \).

The diurnal variation of \( r_s \) on the low-pressure controlled days (Fig. 9b) were significantly different from that on the high-pressure controlled days, thus, the influence factors could be also different. As shown in Fig. 9b, the peak values of \( \sigma_{ap, neph, 550} \) and \( \sigma_{ap, 550} \) also occurred during 08:00–12:00 LST just like the patterns in Fig. 9a. However, this was corresponding to the large number of aerosol particles with diameters larger than 100 nm during this time as shown in Fig. 9d. Considering that the low-pressure system was favorable to the transportation of newly produced aerosols, including externally mixed BC and non-BCs from the low level. Thus, the aerosols described above could be mainly from the low level with development of PBL. From the analysis above, it was not difficult to explain that the relatively lower \( r_s \) during this time were due to the rapid aging process of coating on BC during the transportation from the low level in these days. The relatively higher \( r_s \) during the rest time of these days were mainly contributed by the local biomass burning because no uplift existed but aerosol particles with diameter of around 100–200 occurred.

These different influence factors also explain the reason why \( r_s \) on the low-pressure controlled days were generally higher than that on the high-pressure controlled days, namely, more BC were external mixed on the low-pressure controlled days.

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Fig. 8 – Time series of the retrieved BC mixing state \( (r_1 \) and \( r_s ) \) as well as the atmospheric pressure.
2.2.3. The effect of BC mixing state on aerosol direct radiative forcing

As an application of the influence of different BC mixing state on aerosol optical properties at Mt. Huang, the effect of BC mixing state on aerosol direct radiative forcing ($\Delta F$) was evaluated at 550 nm.

In this study, we just investigated the relative change of $\Delta F$ due to the variation of BC mixing state rather than calculate the absolute value of $\Delta F$. Therefore, to simplify the calculation, the “two-layer-single-wavelength” model was employed (Seinfeld and Pandis, 2006):

$$\Delta F = \frac{-1}{2} S_0 \left[ T_{\text{atm}}^2 \cdot (1 - A_c) \cdot \left( 1 - R_s \cdot \tau_{\text{ap}} - 2 R_s \cdot \tau_{\text{sp}} \right) \right]$$

(20)

where, $\Delta F > 0$ indicated the heating effect due to aerosol absorption, whereas $\Delta F < 0$ indicated the cooling effect due to aerosol scattering. $S_0$ (W/m$^2$) was the solar constant, $T_{\text{atm}}$ (dimensionless values) was the atmospheric transmissivity, $A_c$ (dimensionless values) was the fraction of the surface covered by clouds ($A_c = 0$ under the clear sky condition), $R_s$ (dimensionless values) was the surface albedo ($R_s = 0.23$ for farmland and chard (Dudhia et al., 2005)), $\beta$ (dimensionless values) was the average upscatter fraction of ambient aerosol layer, which could be simply calculated by Eq. (21) (Chylek and Wong, 2005) and Eq. (22) (Yu et al., 2016):

$$\beta = \frac{(1 - g)}{2}$$

(21)

$$g = -7.143889\beta^2 + 7.46443\beta^2 - 3.9356\beta + 0.9893$$

(22)

where, $g$ (dimensionless values) was the asymmetry parameter and $\beta$ (dimensionless values) was the hemispheric backscattering fraction.

$\tau_{\text{ap}}$ and $\tau_{\text{sp}}$ were the optical depth of aerosol layer due to light scattering and absorption, respectively, and $\tau_{\text{ap}}$ could be expressed by Eq. (23) according to the relationship between $\tau_{\text{ap}}$ and $\tau_{\text{sp}}$:

$$\tau_{\text{ap}} = \tau_{\text{sp}} \cdot \frac{1 - \omega}{\omega}$$

(23)

where, $\omega$ (dimensionless values) was single scattering albedo.

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Fig. 9 – Diurnal variations of $r_1$ and $r_2$, $\sigma_{\text{sp, neph, 550}}$, $\sigma_{\text{ap, 550}}$, and PNSDs on high-pressure controlled days (a, c) and low-pressure controlled days (b, d).
of ambient aerosol layer and Eq. (20) could be changed to:

\[
\Delta F = -\frac{1}{2} \sigma_{\text{atm}} (T_0^2 \cdot (1 - A_0)) \cdot \tau_{\text{ap}} \cdot (1 - R_s)^2 \cdot \beta \cdot 2 R_s \cdot \frac{1 - \omega_0}{\omega_c}
\]  

(24)

According to Eq. (24), a critical value of \( \omega_c (\omega_c) \) could be obtained when \( \Delta F = 0 \), which represented aerosol cooling effect compensated the heating effect and the net direct radiative forcing of aerosol layer was 0.

So, \( \omega_c \) for different mixing state of BC could be calculated by solving the function below:

\[
(1 - R_s)^2 \cdot \beta \cdot 2 R_s \cdot \frac{1 - \omega_0}{\omega_c} = 0
\]

(25)

Table 3 lists \( \omega_c \) for external, core-shell, and the retrieved mixing state \( r_1 \) and \( r_2 \). It can be seen that \( \omega_c \) is not sensitive to the BC mixing state and the value of 0.69 is much smaller than the campaign average \( \omega \) of 0.84 at 550 nm, which reveals that the direct radiative forcing of aerosol at Mt. Huang is always negative. However, although the discrepancy of \( \omega_c \) between each mixing state is small, the average \( \omega_c \) for different mixing state during the campaign differ greatly, which can contribute to great differences of aerosol direct radiative forcing for different BC mixing states according to Eq. (24).

Therefore, Eq. (26) was applied to evaluate the ratio of direct radiative forcing (\( \xi \)) (dimensionless values) between different mixing state to external mixture based on Eq. (24).

\[
\xi = \frac{\Delta F_{\text{mix}}}{\Delta F_{\text{ext}}} = \frac{(1 - R_s)^2 \cdot \beta_{\text{mix}} - 2 R_s \cdot \frac{1 - \omega_{0\text{mix}}}{\omega_{c\text{mix}}}}{(1 - R_s)^2 \cdot \beta_{\text{ext}} - 2 R_s \cdot \frac{1 - \omega_{0\text{ext}}}{\omega_{c\text{ext}}}}
\]

(26)

where, the subscripts “mix” represented the four mixing states including external, core-shell, \( r_1 \), and \( r_2 \). The results calculated by using campaign average \( \beta \) and \( \omega_{550} \) for each mixing state are shown in Table 3.

It can be known from Table 3 that \( \Delta F \) for external mixture is the largest, follow by that for \( r_1 \) and \( r_2 \), which are factors of 0.86 and 0.79, respectively, smaller than that of externally mixed aerosols. For core-shell mixture, \( \Delta F \) is almost half (\( \xi = 0.57 \)) of the result for externally mixed aerosols. The change of \( \Delta F \) from external mixture to core-shell mixture indicated that the negative radiative forcing was decreasing with increasing fraction of core-shell mixed BC, that was, the cooling effect of aerosols was weakened due to the enhancement of aerosol absorption with increasing fraction of core-shell mixed BC. The externally mixed non-BCs in the atmosphere could contribute to the discrepancy of \( \Delta F \) between \( r_1 \) and \( r_2 \). This highlighted the non-negligible influence of externally mixed non-BCs on the assessment of aerosol direct radiative forcing.

However, the assumptions of scenarios \( r_1 \) and \( r_2 \) in this paper were not rigorous enough that \( r_0 \) were the same at all size bins and the total non-BCs were divided into the FNSDs of externally mixed with the same fraction of BC due to the lack of precise size distributions of externally mixed BC and non-BCs. Thus, it was hard to say which assumption was more appropriate for our site, and more observations focusing on accurate size distribution of total BC, externally mixed BC, and externally mixed non-BCs were urgently needed to accurately estimate the radiative forcing of aerosols.

### 3. Summary and conclusions

In-situ measurements of aerosol optical properties were conducted at Mt. Huang from September 23 to October 28, 2012. Remarkably lower averages (standard deviations) of 82.2 (57.0), 10.9 (6.5), and 14.1 (6.7) Mm^{-1}, respectively, were found for \( \sigma_{\text{ap, 550}} \), \( \sigma_{\text{ap, 550}} \), and \( \sigma_{\text{ap, 550}} \) than those observed at other urban and rural sites in China and some sites in other countries. Three pollution episodes with average \( \sigma_{\text{ap, 550}} \), \( \sigma_{\text{ap, 550}} \), and \( \sigma_{\text{ap, 550}} \) of 188.8, 22.7, and 26.1 Mm^{-1} during the campaign were all contributed by the high concentration of aerosol particles of accumulation mode with diameter ranging from 100 to 300 nm. Two of the episodes (280 and 301 DOY) were due to the biomass burning at surrounding areas and the other one (284 DOY) was partly attributed to the regional transmission from the north.

Atmospheric aging process resulted in the increase of BC light-absorption but the decrease of \( \omega_{550} \) at constant aerosol concentration. However, the proportion of non-light-absorbing components (non-BCs) was getting higher on BC aerosols during the aging process, resulting in the increase of aerosol diameter, which also contributed to relatively higher \( \sigma_{\text{ap, 550}} \) and \( \sigma_{\text{ap, 550}} \) comparing to the initial state.

The diurnal cycles of \( \sigma_{\text{ap, 550}} \) and \( \sigma_{\text{ap, 550}} \) showed the first peak occurred around 9:00 and 10:00 LST and two small peaks occurred around 16:00 LST and 22:00 LST. These patterns were closely related to the development and decay of PBL and mountain–valley breeze. However, the diurnal cycle for \( \sigma_{\text{ap, 550}} \) was more pronounced than that of \( \sigma_{\text{ap, 550}} \) which could be contributed by the photochemical reactions and the aging process.

BC mixing states \( r_1 \) and \( r_2 \) showed that about 50% and 70% of total BC were externally mixed with the non-BCs, respectively, by considering the existence of the externally mixed non-BCs or not. The periodical change of \( r_1 \) and \( r_2 \) and their diurnal variations were mainly influenced by the atmospheric aging during different vertical transport and air sources under different synoptic systems. Local biomass burning emissions were also one of the influencing factors on BC mixing state.

The direct radiative forcing (\( \Delta F \)) of aerosol evaluated by a "two-layer-single-wavelength" model at Mt. Huang was always negative. The ratios of \( \Delta F \) for the retrieved \( r_1 \), retrieved \( r_2 \), and core-shell mixture to the external mixture were 0.86, 0.79, and 0.57, respectively, indicating the cooling effect of aerosols weakened with BC mixing state changing from external mixture to core-shell mixture.

<table>
<thead>
<tr>
<th>( \omega_c )</th>
<th>Core-shell</th>
<th>Retrieved ( r_1 )</th>
<th>Retrieved ( r_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average ( \omega_{550} )</td>
<td>0.67</td>
<td>0.68</td>
<td>0.68</td>
</tr>
<tr>
<td>Average ( \sigma_{\text{ap, 550}} )</td>
<td>0.90</td>
<td>0.79</td>
<td>0.86</td>
</tr>
<tr>
<td>Average ( \beta )</td>
<td>0.36</td>
<td>0.37</td>
<td>0.36</td>
</tr>
<tr>
<td>( \xi )</td>
<td>1.00</td>
<td>0.57</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 3 - The critical single scattering albedos (\( \omega_c \)) for different mixing state and the parameters used to calculate the direct radiative forcing of aerosol as well as the results.
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Appendix A. Supplementary data

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REFERENCES


