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Characterization of aerosol optical properties, chemical composition and mixing states in the winter season in Shanghai, China

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ABSTRACT

Physical and chemical properties of ambient aerosols at the single particle level were studied in Shanghai from December 22 to 28, 2009. A Cavity-Ring-Down Aerosol Extinction Spectrometer (CRD-AES) and a nephelometer were deployed to measure aerosol light extinction and scattering properties, respectively. An Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) was used to detect single particle sizes and chemical composition. Seven particle types were detected. Air parcels arrived at the sampling site from the vicinity of Shanghai until mid-day of December 25, when they started to originate from North China. The aerosol extinction, scattering, and absorption coefficients all dropped sharply when this cold, clean air arrived. Aerosol particles changed from a highly aged type before this meteorological shift to a relatively fresh type afterwards. The aerosol optical properties were dependent on the wind direction. Aerosols with high extinction coefficient and scattering Ångström exponent (SAE) were observed when the wind blew from the west and northwest, indicating that they were predominantly fine particles. Nitrate and ammonium correlated most strongly with the change in aerosol optical properties. In the elemental carbon/organic carbon (ECOC) particle type, the diurnal trends of single scattering albedo (SSA) and elemental carbon (EC) signal intensity had a negative correlation. We also found a negative correlation ($r = -0.87$) between high mass-OC particle number fraction and the SSA in a relatively clean period, suggesting that particulate aromatic components might play an important role in light absorption in urban areas.

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Introduction

Atmospheric aerosols have a “direct effect” on climate by scattering or absorbing solar radiation and an “indirect effect” by acting as cloud condensation and ice nuclei (Pöschl, 2005). The magnitude of these effects has still considerable uncertainties, especially the indirect effect (Forster et al., 2007; Schiermeier, 2010). In order to estimate the direct and indirect effect of...
aerosols, further understanding of aerosol optical properties is urgently needed.

The optical properties of aerosols govern their interaction with sunlight and are important parameters for estimating radiative forcing in modeling studies (Fischer et al., 2011). Studies have shown that aerosol optical properties are determined by particle size distribution, chemical components, and mixing state (Seinfeld and Pandis, 2006), with the latter being the most challenging to understand (Cappa et al., 2012; Huang et al., 2013). Different chemical species, especially soot and brown carbon (Lack and Cappa, 2010), can be mixed within a single particle (internal mixing) or across different particle types (external mixing); the exact mixing can be mixed within a single particle (internal mixing) under certain conditions (Cappa et al., 2012; Huang et al., 2013). Different studies have shown that the theoretical model does not fit all cases (Cappa et al., 2012), and more work still needs to be done to investigate the influence of particle mixing state on aerosol optical properties.

Measurements of optical properties of aerosols along with mixing state within a single particle have been crucial in estimating aerosol radiative forcing (Pratt and Prather, 2010; McMeeking et al., 2011). Single particle mass spectrometers, such as the Aerosol Time-of-Flight Mass Spectrometer (ATOFMS), can provide information on the size-resolved chemical composition and internal mixing state of particles (Schwarz et al., 2006; Onasch et al., 2012; Pratt and Prather, 2012). Since SP-AMS and Aethalometer and the Particle Soot Absorption Photometer (SP2), can provide information on the size-resolved chemical composition and internal mixing state of particles (Schwarz et al., 2006; Onasch et al., 2012; Pratt and Prather, 2012). Since SP-AMS and SP2 only measure material that is sufficiently light absorbing at 1064 nm (i.e., soot particles, and only the non-refractory aerosol component with SP-AMS), the ATOFMS is preferred for full chemical measurements in regions where sea salt or mineral dust is an important contributor to the aerosol.

In different regions of China, the majority of studies have been focused on the effect of the chemical mass concentration, aerosol physical properties and water content on the optical properties (Che et al., 2009; Guo et al., 2009; Jung et al., 2009a; Yang et al., 2009; Yu et al., 2009; Eck et al., 2010; Huang et al., 2010; Wang et al., 2010). Jung et al. (2009b) found that under polluted conditions in the urban area of Beijing, ammonium sulfate, ammonium nitrate, and organic carbon contributed to the increases of single scattering albedo. Yao et al. (2010) analyzed atmospheric light extinction properties and chemical speciation of fine particulates in Shenzhen and concluded that the organic matter in PM2.5 contributed about 45% to the observed aerosol light extinction. Huang et al. (2011) measured black carbon (BC) mass loadings, size distributions and mixing state information in the Pearl River Delta region and estimated the potential contribution of BC mass to the radiative forcing. But studies of aerosol optical properties and their relationship with aerosol mixing state are very limited.

Cavity ring down spectroscopy (CRDS) has recently been used for measuring aerosol extinction and absorption coefficients in field and laboratory studies (Butler et al., 2007; Dinar et al., 2008; Zhang et al., 2008; Khalidov et al., 2009; Xue et al., 2009; Li et al., 2011; Li et al., 2013). Compared with filter based techniques like the Aethalometer and the Particle Soot Absorption Photometer (Bond et al., 1999; Sheridan et al., 2005), CRDS offers rapid real-time measurement of absorption coefficients (Busch and Busch, 1999; Pettersson et al., 2004; Bulatov et al., 2006). Huang et al. (2013) employed ATOFMS and CRDS to study the evolution of aerosol chemical and optical properties during a period in Shanghai when pollution was highly present. They found that organic carbon coatings could dramatically change aerosol optical properties, suggesting that this combination of measurements is ideal for elucidating the impact of particle mixing states on aerosol optical properties.

In this study, a Cavity-Ring-Down Aerosol Extinction Spectrometer (CRD-AES) (Li et al., 2011) and a nephelometer were used in Shanghai from 22 to 28 December, 2009 for the measurements of extinction and scattering coefficients, respectively. Simultaneously, an ATOFMS was used to obtain both positive and negative mass spectra from individual particles, and thus provide information on aerosol mixing state (Murphy, 2007). Examining these measurements concurrently, the sources of particles and the aerosol optical properties as a function of particle size distribution, chemical composition and mixing states are investigated.

1. Experimental

Measurements were carried out in the laboratory building of the Department of Environmental Science and Engineering at Fudan University (31°17′47.14″N, 121°30′14.94″E) in Shanghai from December 22 to December 28, 2009 (24 hr per day). This site is near residential, traffic, and construction emissions sources and represents a typical urban area. Ambient air was drawn from a height of about 5.5 m above the ground through a half-inch diameter, six-meter long, stainless steel tube at a flow rate of 6.0 L/min. A scanning mobility particle sizer (SMPS, Model 3936, TSI, Minneapolis, Minnesota) was used to monitor the size distribution of particles in the range of 15–550 nm during this period (Appendix A Fig. S1). Hourly averaged concentrations of PM10 (Appendix A Fig. S2) and the meteorological data including temperature, relative humidity (RH), wind speed and direction were provided by the Shanghai Meteorological Bureau.

1.1. Single particle measurements

The ATOFMS (Model 3800, TSI, Minneapolis, Minnesota) has been described in detail elsewhere (Gard et al., 1997). Briefly, air is introduced into a vacuum region through an aerodynamic focusing lens (Model 3801-100, TSI, Minneapolis, Minnesota) whose optimum operating range is from 100 nm to 3 μm. Each particle is sized by measuring its flight time between two orthogonal continuous diode-pumped green lasers when accelerated to a terminal velocity that depends on its aerodynamic size. The time taken for a particle to move between the lasers is recorded by a logic circuit, which controls the firing of a pulsed ultraviolet laser (frequency-quadrupled Nd: YAG laser, 266 nm) to desorb/ionize chemical species from the particle. Both positive and negative ions generated from laser ablation are analyzed simultaneously. In this work, polystyrene latex spheres (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto, California) from 0.22–2.00 μm diameter were generated via an atomizer (Model 3076, TSI, Minneapolis, Minnesota) to create monodisperse aerosols for size calibration. Ambient air passed through a dryer tube before entering the ATOFMS. No scaling was done to adjust the ATOFMS particle counts.

The mass spectra were converted to a list of peaks at each m/z by setting a minimum signal threshold of 30 arbitrary units above the baseline in the MS-Analyze software (TSI). The resulting peak lists were then imported into YAADA (version 2.11, www.yaada.org), a software toolkit for single particle data analysis written in the Matlab programming language (version R2010b). An adaptive resonance theory-based clustering method (ART-2a) (Bhave et al., 2001; Rebotier and Prather, 2007) was used to classify mass spectra with a vigilance factor of 0.85, a learning rate of 0.85 and 20 iterations. The resulting clusters were regrouped by hand
based on the mass spectral patterns. 95% (141,103) of all individual particles with bipolar mass spectra were assigned into 7 general particle types that were named by the characteristics of chemical species and their likely sources, i.e., biomass burning, fresh organic carbon (OC), aged OC, high mass organic carbon (HMOC), internally mixed elemental carbon/organic carbon (EOCOC), dust, and industrial particles. Peak identifications corresponding to the most probable ions at a given m/z ratio are based on previous lab and field studies (Silva et al., 1999, 2000; Hudson et al., 2004; Spencer and Prather, 2006; Moffet and Prather, 2009; Zhang et al., 2009).

1.2. Optical measurements

A home-built CRD-AES has been described in detail elsewhere (Li et al., 2011). In brief, the cavity contains two high-reflectivity dielectric mirrors (540 nm center wavelength, 99.9985% reflectivity, 6 m radius of curvature, 0.8 in. in diameter, Los Gatos Research, Inc.), mounted on the ends of a stainless steel cell equipped with aerosol inlets and outlets at 90° to the light path. Typically the aerosol flow is 1 liter per minute (LPM) through a diffusion drier. The distance between the two mirrors is 79.4 cm and the length of the cell containing the aerosol is 58 cm. To keep the mirrors clean, a small flow of dry nitrogen (0.03 LPM) is supplied near the mirror region. A light pulse at 532 nm produced by a Q-switched pulsed laser (CrystalLaser QG-532-500, CrystalLaser, Reno, Nevada) is injected into the cavity and the ring-down signal through the mirrors is measured with a Hamamatsu R928 photomultiplier, Hamamatsu Photonics USA, Bridgewater, New Jersey. When the CRD-AES cell is filled with aerosols, the light intensity decayed faster than in an empty cavity, leading to a ring-down trace with a shorter time scale. The extinction coefficient $\alpha_{\text{ext}}$ can be found using the expression:

$$\alpha_{\text{ext}} = \frac{L}{k_1(T_1 - T_0)}$$  \hspace{1cm} (1)

where, $T_0$ is the ring-down time of the air sample without particles, $T_1$ is the ring-down time of the air sample with aerosols present, $L$ is the optical cavity length, $k_1$ is the length of the cavity occupied by particles and $c$ is the speed of light. Measurements of NO$_2$ concentration were performed using a separate inlet occupied by particles and present

(1.45 × 10$^{-5}$ M, Moffet and Prather, 2009; Zhang et al., 2009).

The SAE has been shown to be a good parameter to represent the aerosol size that contributes to the aerosol extinction coefficient (Seinfeld and Pandis, 2006). Generally, a low SAE value (<1) indicates dominance of larger-size particles and a high SAE value (>1) indicates the dominance of smaller-size particles (Dubovik et al., 2002). The scattering coefficient at 532 nm ($\alpha_{\text{scat},532}$) was calculated according to equation:

$$\alpha_{\text{scat},532} = \frac{\alpha_{\text{scat},532}}{\lambda^{d}}$$  \hspace{1cm} (3)

The single scattering albedo ($\omega$) is the ratio of the scattering coefficient over the extinction coefficient at a given wavelength:

$$\omega = \frac{\alpha_{\text{scat}}}{\alpha_{\text{ext}}}$$  \hspace{1cm} (4)

Based on validation experiments (Li et al., 2011), the uncertainty in $\omega$ was believed to be less than 12% under field conditions. The absorption coefficients ($\alpha_{\text{abs},532}$) was obtained by

$$\alpha_{\text{abs},532} = \alpha_{\text{ext},532} - \alpha_{\text{scat},532}.$$  \hspace{1cm} (5)

2. Results and discussion

2.1. Meteorology and optical measurement

The temporal profiles of temperature, relative humidity (RH), wind speed, and wind direction during the sampling period are shown in Fig. 1a. The time series of the aerosol optical properties at 532 nm, including the aerosol extinction, scattering and absorption coefficients are shown in Fig. 1b. The scattering Ångström exponent ($\omega_{520/700}$, SAE) and single scattering albedo (SSA) are shown in Fig. 1c covering the entire sampling period. The backward air trajectories at 10 m height were determined with the HYbrid Single Particle Lagrangian Integrated Trajectory (HYPLIT-4) model developed by NOAA/ARL, and are shown in Fig. 2.

A diurnal variation of temperature and RH can be observed clearly on December 23 and 24, when the SAE was relatively constant at around 1.4–1.6. Air parcel back-trajectory analysis shows that the air parcel moved slowly around Shanghai on December 24 and 25, 2009, with an average wind speed of 1.8 m/sec. The extinction, scattering, and absorption coefficients were generally high with mean values of 792 ± 154, 591 ± 143, and 201 ± 51 mol/min, respectively, and maximum values about 1251, 1029, and 304 mol/min, respectively. After mid-day on December 25, 2009, a strong wind (average wind speed of 6.5 m/sec) changed from north-west to north, bringing significantly colder air parcels (cyan area in Fig. 1), accompanied by sharp decreases of extinction and scattering coefficients but an increase of PM$_{10}$ concentration (Appendix A Fig. S2). SAE and SSA declined at first and then increased again. A short period of snowy weather occurred around noon on December 27, 2009 (yellow area in Fig. 1) and the extinction roughly doubled after that period. Toward the end of the sampling period, the extinction coefficient returned to over 400 mol/min and the SAE returned to around 1.6. Over the whole sampling period, the aerosol extinction coefficients had...
a better correlation with the scattering coefficients than the absorption coefficients ($R^2 = 0.97$ and 0.77, respectively), indicating that aerosol scattering played a dominant role in extinction during that measurement period.

The entire sampling period was classified into three categories (Yang et al., 2012) based on the aerosol extinction coefficients (dashed lines in Fig. 1b): heavy haze (aerosol extinction coefficient (AEC) > 800 mol/min, visibility < 5 km), light haze (400 < AEC < 800 mol/min, 5 km < visibility < 10 km), and clean (AEC < 400 mol/min, visibility > 10 km), with visibility calculated at $3.91 / (\alpha_{\text{ext}})$ (Seinfeld and Pandis, 2006). Particle number concentrations of fine particles, ranging in size from 15–550 nm, were generally low on clean days and significantly higher during haze periods (Fig. 1b and Appendix A Fig. S1).

Li et al. (2013) reported that there was a clear relationship between the aerosol optical properties and the wind direction during April 2010 in Shanghai. We plot the extinction coefficients relative to wind direction in Fig. 3a. During the sampling period, the wind was predominantly from the west and northwest, corresponding mostly with light or heavy haze (green and red bars). When the wind blew from the north and northeast, it was predominantly the clean condition. Shanghai is located in the Yangtze River Delta, with the highly industrialized Jiangsu and Zhejiang Provinces to the west, and the East China Sea to the east and northeast. The back trajectories in Fig. 2 show that the air parcels arriving in Shanghai from the west carried atmospheric pollutants from Jiangsu and Zhejiang Provinces (December 22–25 and 28, 2009) but predominantly clean air from the East China Sea (December 26–27, 2009).

During the haze events (December 23–25, 2009, as shown in Fig. 1), SAE was higher than 1 suggesting that the major contribution to light extinction was due to fine particles, while on clean days (December 25–26, 2009), this value was lower than 1, indicating the presence of coarse particles. Fig. 3b and d shows the contour plots of PM$_{10}$ and SAE based on wind direction and speed, revealing that they were both wind dependent. Fig. 3b, d also correlates very well. The wind from the north and northeast that was higher in speed (>4 m/sec) brought a higher concentration of PM$_{10}$ that had lower SAE values, indicating that the high concentration of PM$_{10}$ was primarily due to the long range transport of coarse particles from North China starting the mid-day of December 25 (see...
2.2. Particle composition classification

The overall percentages of each particle type are summarized in Table 1. The detailed mass spectra of these particle types are shown in Appendix A Fig. S4. The biomass burning particles contained dominant potassium peaks ($^{39}$K$^+$, and $^{213}$K$_2$SO$_4$) in the positive spectra and secondary inorganic peaks ($^{64}$CN$^-$/C$_6$H$_7$, $^{46}$NO$_2$, $^{63}$NO$_3$, and $^{97}$HSO$_4^-$) in the negative spectra (Silva et al., 1999; Hudson et al., 2004; Moffet et al., 2008; Yang et al., 2009a). Recently, Wang et al. (2013) reported that this kind of particles could include coal burning emissions in Shanghai. Of the 30% of particles which were classified as organic carbon particles (OC), only 4% were fresh OC particles. As shown in Appendix A Fig. S4, the OC aerosol mass spectral signature was dominated by organic carbon markers, including m/z $^{27}$C$_{6}$H$_{7}$/CHN$^+$, $^{37}$C$_{6}$H$_{7}$/H$^+$, $^{39}$K$^+$/C$_6$H$_7$, $^{43}$CH$_3$CO$^+$/CHNO$^-$, and $^{56}$C$_{6}$H$_7$/C$_7$N$^+$ (Silva et al., 1999). Aged OC particles had stronger signal intensities of $^{46}$NO$_2$, $^{63}$NO$_3$, and $^{125}$H(NO$_3$)$_2$ in the negative mass spectra and higher peak areas of $^{18}$NH$_3$ in the positive mass spectra relative to fresh OC (Sodeman et al., 2005; Moffet et al., 2008). High mass-OC (HMOC) particles were those with signals at higher m/z (>200).

Appendix A Fig. S4 shows that they contain aromatic signals ($^{13}$C$_6$H$_7$, $^{64}$C$_8$H$_7$, $^{77}$C$_8$H$_7$, $^{91}$C$_9$H$_7$), and also $^{18}$NH$_3$, $^{43}$CH$_3$CO$^+$/CHNO$^-$, and $^{53}$C$_6$H$_7$O$^-$ in the positive mass spectra, indicating that these particles have undergone aging processes. ECOC particles were characterized by carbon cluster ions (C$_n^+$) and OC in the positive mass spectra (Spencer and Prather, 2006). The mass spectra of the dust particles were dominated by $^{27}$Al$^+$, $^{40}$Ca$^+$, $^{56}$Fe$^+$/CaO$^-$, $^{76}$SiO$_2^-$, and $^{75}$PO$_4^-$, while industrial emissions particles were mainly identified by the presence of $^{55}$Mn$^+$, $^{56}$Fe$^+$, $^{63}$Cu$^+$, $^{64}$Zn$^+$ and $^{206}$Pb$^+$. The temporal variations of each particle type are shown in Fig. 4a. Typically, biomass burning particles accounted for about 20% of all particles, with several spikes over 40% during the sampling period. HMOC particles dominated on December 22 and 23, 2009. Before mid-day on December 25, few fresh OC particles were detected. On December 24 and 25, 2009, when the air parcels mainly originated from the vicinity of Shanghai, aged OC particles accounted for over 40% of all particles. ECOC particles also accounted for a high percentage during this time. Then a sharp increase of biomass burning particles occurred, rising to nearly 1.5 times the former level, as the wind blew from the north, indicating the non-local source of these particles. The biomass burning particle number fraction decreased gradually until December 27, accompanied by a nearly constant fresh OC particle number fraction. However, no significant increase of dust particles occurred during this long range air parcel transport from North China. Toward the end of the sampling period, aged OC dominated the OC type again.

Size distributions of each particle type number fraction, seen in Fig. 4b and Appendix A Fig. S5, show that biomass burning particles constituted more than 50% of the small size range. Both fresh and aged OC particles displayed bimodal distributions. For the fresh OC type, the more-populous mode peaked at around 0.35 μm and the less-populous at around 0.55 μm. The aged OC type was similar, however the more populous size mode (0.8 μm) was higher than the less populous mode (0.4 μm), compared to the fresh OC. HMOC particles were mainly distributed between 0.4 and 0.6 μm. ECOC particles also displayed a bimodal distribution, with the smaller peak around the lower size limit 0.2 μm and the larger one at 0.9 μm, consistent with our previous observations (Huang et al., 2013). The differential mass spectra between these two modes of fine particles indicated that the larger particles contained stronger signals from ammonium ($^{18}$NH$_3$).
amines ($^{15}$N(CH$_3$)$_3$, $^{74}$NH$_2$(C$_2$H$_5$)$_2$, $^{86}$NCH$_2$(C$_2$H$_5$)$_2$), and nitrate ($^{13}$NO$_3$ and $^{125}$H(NO$_3$)$_2$), suggesting these particles had undergone heterogeneous reactions (Angelino et al., 2001; Rehbein et al., 2011; Huang et al., 2012b). On the other hand, dust and industrially emitted particles were mostly found in the coarse size range (>1.0 μm).

2.3. Influence of aerosol chemical composition and mixing states on optical properties

Aerosol optical properties are determined by several factors, including size distribution, chemical components, and particle mixing states (Seinfeld and Pandis, 2006). Here we examine the factors that impact aerosol optical properties during our sampling period.

Number concentrations of particles in the size range of 15–550 nm were measured by SMPS (Appendix A Fig. S1). Taking this size range as a representative for the size range that contributed the most to the extinction coefficient (<1000 nm) (Seinfeld and Pandis, 2006), we plotted the temporal profile of particle volume (proxy of PM$_{10}$ mass concentration) and surface concentration (based on the SMPS measurement) versus the extinction coefficient in Fig. 5a. The overall correlation coefficient ($R^2$) between the volume concentration and the extinction coefficient was 0.84, while it was 0.76 between the surface concentration and

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Percent of particles</th>
</tr>
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<tbody>
<tr>
<td>Biomass burning</td>
<td>29</td>
</tr>
<tr>
<td>Fresh OC</td>
<td>4</td>
</tr>
<tr>
<td>Aged OC</td>
<td>26</td>
</tr>
<tr>
<td>HMOC</td>
<td>24</td>
</tr>
<tr>
<td>ECOC</td>
<td>9</td>
</tr>
<tr>
<td>Dust</td>
<td>6</td>
</tr>
<tr>
<td>Industrial</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 3 – (a) Polar plot of statistic of extinction coefficients relative to wind direction. Wind speed resolved polar contour plots of (b) PM$_{10}$, (c) single scattering albedo, and (d) scattering Ångström exponent.
the extinction coefficient, indicating that the particle volume concentration (namely PM$_1$) played an important role in the determination of the aerosol extinction coefficient. Two spikes of the volume concentration and the extinction coefficient were observed (marked by arrows in Fig. 5a). The volume Peak 1 was higher than Peak 2, while the extinction Peak 1 was lower than Peak 2, suggesting that particles in Peak 2 had a larger extinction efficiency than those in Peak 1. Contributions of chemical compositions and mixing states to the particle optical properties will be discussed in detail below.

**Fig. 4** – (a) Temporal particle number fractions of biomass burning, fresh OC, aged OC, HMOC, ECOC, dust and industrial particle types, (b) size resolved particle number fractions of the 7 particle groups. The gray line indicates the fraction of particles from which mass spectra were obtained (hit particle number) as a function of size.

**Fig. 5** – (a) Temporal trends of particle volume concentration and extinction coefficient. The insert shows the size distribution of the particles sampled during the two spikes (Peak 1 and Peak 2, marked by arrows), (b) Average diurnal profiles of single scattering albedo and EC signal ($^{48}$C$_2$, $^{54}$C$_2$, $^{60}$C$_2$) intensity in ECOC particle type during the sampling period, (c) temporal plots of single scattering albedo and HMOC particle number fraction between 12:00 PM on December 25 and 8:00 AM on December 27, 2009.
Markers of nitrate (46NO2−, 62NO3−, 125H(NO3)2−), sulfate (97HSO4−, 195H(HSO4)−), ammonium (18NH4+), organic carbon (27C2H3+, 29C2H5+, 37C3H+, 43C2H3O+), and elemental carbon (36C3+, 48C4+, 60C5+) (Silva et al., 2000; Liu et al., 2003; Spencer and Prather, 2006; Cahill et al., 2012) were used to identify particle mixing states in each particle type, since these five components have been reported as the main contributors to the aerosol optical properties in Shanghai (Jung et al., 2009a; Jung et al., 2009b; Huang et al., 2012a).

Fig. 6 shows the temporal profiles of the average relative intensities of the above five components in individual particles and the contribution from each particle type. The particle chemical compositions and mixing states shown in Fig. 6 changed dramatically over the period, revealing the chemical complexity underlying the good correlation between particle volume concentration and the particle extinction coefficient. Ammonium and nitrate exhibited high intensities (with the largest contribution from aged OC particle type) during December 24 and 25, 2009, corresponding to the high optical indices (as shown in Fig. 1b). As the signal intensities of these two species declined from mid-day of December 25, the optical indices similarly decreased, suggesting that these two factors contributed the most to the change in aerosol optical properties (Jung et al., 2009b; Huang et al., 2012a, 2013). Over the whole sampling period, averaged sulfate and organic carbon signal intensities changed much less than ammonium and nitrate in individual particles, regardless of the drastic shifts of particle types from aged to fresh, suggesting that sulfate and organic carbon were both distributed broadly over different particle types and played a smaller role in the change of aerosol optical properties.

The weak intensities of ammonium and nitrate during the period of Peak 1 suggested that the first peak of aerosol extinction coefficient in December 23 was mostly due to the high particle volume concentration. During the second peak of aerosol extinction coefficient in December 25 high concentration secondary materials (ammonium, nitrate, and sulfate as shown in Fig. 6) in aerosols increased the aerosol extinction efficiency significantly by scattering light, although the particle volume concentration was low during this time. Particles during Peak 2 were larger in size (as shown in the insert layer in Fig. 5a) than those during Peak 1. As discussed above, in Peak 2 more scattering materials, such as ammonium, nitrate and sulfate, contributed to the larger particle diameter and hence higher extinction efficiency (Seinfeld and Pandis, 2006).

Elemental carbon (EC) in aerosols usually plays the role of absorbing light (Jacobson, 2001). EC signals were widely distributed among all the particle types except the dust and industrial types, especially in ECOC, OC and biomass burning particles. During our sampling period, the correlation coefficient (r) between EC-containing particle number fraction and SSA was −0.61, demonstrating the contribution of EC to the light absorbing efficiency. As shown in Fig. 6, ECOC and aged OC particles contributed the most to the high EC signal intensity during December 24 and 25, 2009, when the absorption coefficient was high. After the mid-day of December 25, biomass burning and fresh OC particles contributed to more EC signal intensity. Among all the particle types, only the average diurnal pattern of EC signal intensity in the ECOC particle type showed a relatively strong negative correlation.
$r = -0.71$ with the SSA (Fig. 5b). The diurnal EC signal in ECOC particles has a dual-peak pattern, with one peak at 6–10 AM and the other at 10 PM, revealing its origin from diesel engine emissions (Wu et al., 2013).

Although biomass burning particles, reported to be light absorbing (Adler et al., 2011), accounted for more than 50% in number since the mid-day of December 25 (Fig. 4a), we found no obvious correlation between the number fraction of biomass burning particles and the SSA. However, the HMOC particle number fraction was found to correlate quite well with the SSA ($r = -0.87$, Fig. 5c) from noon on December 25 to 8 AM on December 27, corresponding to the clean period when the wind blew from North China. The mass spectra show that in addition to aromatic fragment peaks, the HMOC particles contained many polycyclic aromatic hydrocarbons (PAHs), identified by peaks such as $^{115}$C$_6$H$_7$$^{+}$, $^{165}$C$_{16}$H$_{10}$$^{+}$, $^{178}$C$_{14}$H$_{10}$$^{+}$, $^{229}$C$_{18}$H$_{12}$$^{+}$, and $^{252}$C$_{20}$H$_{12}$. Studies have shown that aromatics are associated with “brown” light absorbing carbon (Andreae and Gelencsér, 2006), which can yield fragment ions such as $^{135}$C$_6$H$_7$$^{+}$ and $^{146}$C$_6$H$_7$$^{+}$ (Silva et al., 1999), which are observed in HMOC particle mass spectra. There were also peaks corresponding to $^{135}$C$_6$H$_7$NO$_3$$^{−}$ and $^{169}$C$_{16}$H$_{10}$NO$_3$$^{−}$. It has been reported that emissions of NOx and precursor non-methane volatile organic compounds (NMVOCs), which result in the increase of anthropogenic secondary organic aerosols, have significant impacts on the overall enhancement in aerosol optical depth in China (Lin et al., 2010). A recent field study also showed that these nitro-aromatic compounds were light absorbing materials (Zhang et al., 2013). Hence we tentatively identify these HMOC particles as light absorbing particles. However, the good correlation between HMOC and SSA was only found on clean days. The correlation between the HMOC particle number fraction and the SSA over the whole sampling period was not as good. Fig. 6 shows that compared to the clean period, the HMOC particles during haze periods (e.g., December 23) presented intense signals of ammonium, nitrate, and sulfate, suggesting that these three secondary inorganic components in HMOC particles had changed their mixing states and thus, their absorbing efficiencies.

### 3. Conclusions

Measurements of aerosol optical and chemical properties were conducted from December 22 to December 29, 2009 in Shanghai, China. The aerosol optical properties were found to be dependent on the wind direction, and thus, are dependent on the source of the particles as well. The westerly wind usually brought particles with high extinction coefficient to the sampling site. The wind speed-resolved polar contour plots of PM$_{10}$ and scattering Ångström indicated that particles originating in the northwest were fine particles, while strong wind blowing from the north and northeast brought coarse particles.

The particle type-resolved temporal variations of ammonium, nitrate, sulfate, organic carbon (OC), and elemental carbon (EC) signal intensities uncovered the impacts of particle mixing state on aerosol optical properties. Changes in ammonium and nitrate contributed the most to the changes in aerosol optical properties, while total sulfate and OC contributed much less. The diurnal patterns of single scattering albedo (SSA) and EC signal intensity in the ECOC particle type correlated relatively well ($r = -0.71$), suggesting the direct impact from the vehicle emitted internally mixed EC particles on the SSA. HMOC particles, presumably containing light absorbing materials, e.g., aromatic and nitro-aromatic compounds, also correlated negatively with the SSA, especially on clean days.

Our observations suggest that the shift of particle types contributes to the change in aerosol bulk optical properties. Though organic carbon was found to play only a small role in this process, the negative correlation between SSA and the HMOC particle type indicates that organic carbon could influence the aerosol absorption efficiency. More work is needed to explore the contribution from other forms of organic carbon (such as PAHs) to aerosol absorption and scattering properties. In addition, the optical properties of internally mixed EC particles should be explored by more field observations and laboratory experiments.

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### Appendix A. Supplementary data

Supplementary data associate with this article can be found in online version at http://dx.doi.org/10.1016/j.jes.2014.03.002.

### References


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