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Morphology, composition and mixing state of individual carbonaceous aerosol in urban Shanghai

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834 individual aerosol particles were collected during October and November 2010 in urban Shanghai, China. Morphologies, compositions and mixing states of carbonaceous aerosols were investigated by transmission electron microscopy (TEM) coupled with energy-dispersive X-ray (EDX). Structures of some particles were verified using selected-area electron diffraction (SAED). Among the aerosol particles observed, carbonaceous aerosols were categorized into five types: polymeric organic compound (POC), soot, tar ball, char, and biogenic particle. Based on the detailed TEM-EDX analysis, most of particles were coated with secondary organic aerosols (SOA), which commonly formed through condensation or heterogeneous reactions of precursor gases on pre-existing particles. The internally particles of sulphates, organics and soot were encountered frequently. Such internally mixed particles may be preferentially formed during a stagnated air mass which often occurred during serious pollution events, such as a haze episode on 13 November. Although relative number counts varied with different species, sulphates (38%–71%) and soot (11%–22%) constituted the most dominant species observed in the samples. With an exception of the sample collected during a dust storm on 12 November, soil-derived particles (68%) were relatively more frequently observed. Of particular interest was the biogenic particles encountered almost as frequently as soot on the sample collected on 13 November (18% vs. 22%). The result from air mass back-trajectory analysis indicated that these particles were marine-originated, most likely from the Yellow Sea.

1 Introduction

Carbonaceous aerosols exert great influence on climate by changing the energy transfer through the atmosphere, and potentially affect public health as carriers of toxic chemicals (Jacobson, 2001; Ramana et al., 2010; Utsunomiya et al., 2002; Menon et al., 2002). Carbonaceous aerosols also supply surfaces for heterogeneous chemical

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reactions to occur upon in atmosphere, and alter the regional biogeochemical cycle by their long-range transport with nutrient species (Adachi et al., 2010; Geng et al., 2010a; Ro et al., 2005; Utsunomiya et al., 2004). Generally, carbonaceous aerosols in ambient are broadly differentiated into two main fractions: Elemental carbon (EC) and organic carbon (OC). EC is often used interchangeably with black carbon (BC) in terms of light absorbing, which is considered only to occur in soot (Jacobson, 2001; Adachi and Buseck, 2010). OC in aerosols ranges from small molecules such as oxalic, to polycyclic aromatic hydrocarbons, to viable bacteria, fungi, and spores, to secondary OC aerosols formed initially by oxidation of volatile organics (Pan et al., 2007).

Carbonaceous aerosols have direct effects on climate by scattering and absorbing solar radiation. Soot particles produce a net warming effect through absorption of sunlight (Jacobson, 2001). The IPCC report indicates that their global, annual mean clear-sky radiative forcing is approximately 0.34 Wm^{-2} , making them the largest contributor to global warming after carbon dioxide and methane (IPCC, 2007). In high pollution areas such as Mexico City and Beijing, much of the soot particles are embedded with OC together with materials such as ammonium sulphate and nitrate (Adachi and Buseck, 2008; Li et al., 2010; Li and Shao, 2009a). These embedding materials and coatings act as lenses that focus light on soot and thus amplify absorption (Adachi et al., 2007). Jacobson (2001) believed that internally mixed soot particles could be the second most significant component of global warming, as commonly the case in the atmosphere. OC consists of primary organic aerosols and secondary organic aerosols, having highly variable optical properties. Light-absorbing organic aerosol is tentatively named “brown carbon” and may be associated with high molecular weight humic-like substances (HULIS) from biomass burning or soil deflation (Alexander et al., 2008; Hoffer et al., 2006). HULIS not only leads to the efficient absorption of solar radiation in the UV and visible range, but also exhibits much stronger wavelength dependence at shorter wavelengths than EC (Alexander et al., 2008). Atmospheric models of the climate effects of carbonaceous aerosols assume that no light-absorbing particles are produced in the air by secondary mechanisms. The main optical effect of light-coloured

OC from secondary emission is thought to be scattering of sunlight, resulting in a net cooling effect on global climate (Chung and Seinfeld, 2002).

Besides, carbon-bearing particles can serve as cloud condensation nuclei (CCN) and may affect the formation, coverage, and lifetime of clouds, thereby having an indirect effect on climate (Sun and Ariya, 2006). Recent studies on atmospheric aerosols have shown that OC aerosols are an important part of the global CCN budget. Their activation capability is assumed to be comparable to that of sulphate aerosols, which is considered the most effective CCN (Sun and Ariya, 2006). Both organic acids and HULIS have been identified as the predominant constituents of organic CCN (Sun and Ariya, 2006). Furthermore, OC aerosols can alter the hygroscopic properties and CCN activity of inorganic particles by their mixing states. Inorganic particles with hygroscopic OC coatings tend to be more spherical and larger and more hydrophilic, enhancing their light scattering and CCN activity, both of which have cooling effects on the climate (Freney et al., 2010; Semeniuk et al., 2007). Field measurements have shown that a significant fraction of both continental and marine inorganic aerosols are coated by organic films (Li et al., 2003a; Niemi et al., 2006; Russell et al., 2002). This widespread occurrence of mixed organic and inorganic species within the same particle implies a broad impact on global radiation balance. BC may play an important, but as yet undetermined, role in the cloud formation processes. Decesari et al. (2002) reported that the soot oxidation process caused the formation of HULIS, which may be potential CCN precursors. The CCN ability of collapsed aged soot particles was further recognized by Zuberi et al. (2005) as part of laboratory studies. In light of these observations Sun and Ariya (2006) speculated that the CCN activity of soot particles may not be neglected when considering their indirect radiative forcing.

Carbonaceous aerosol emissions in China are large, which are estimated to account for around one-fourth of global anthropogenic carbonaceous aerosols (Menon et al., 2002; Zhou et al., 2009). Enhanced emissions due to the increased usage of fossil fuels, combined with biomass burning and soil dust have been causing serious air pollution in urban areas and frequently extend to regional haze episodes (Li et al., 2010;

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Li and Shao, 2009a, 2010). It was well known that carbonaceous particles emitted from intense biomass burning contribute significantly to the seasonal brown hazes in northern China (Li et al., 2010). Anthropogenic aerosols emitted from the developing megacities in China may have altered the regional atmospheric circulation, probably leading to increased summer flooding in the south and enhanced drought in the north (Menon et al., 2002). Clearly, a complete understanding of unique characteristics of anthropogenic aerosols, particularly carbonaceous aerosols, in the chemically rich atmosphere of China, must be conducted before the climate impacts of aerosols can be evaluated for China.

Our knowledge of Chinese urban aerosols is mostly indebted to extensive studies using bulk analysis methods. These studies have provided useful insights into the general characteristics of aerosols, including their concentrations, distributions and seasonal patterns (Zhou et al., 2009; Sun et al., 2006). However, urban aerosols are chemically and morphologically heterogeneous, so that the average composition does not describe well the population of the particles. Direct evidence of the composition and morphology of aerosol particles can be provided by single particle analysis (Geng et al., 2010b; Ro et al., 2005; Utsunomiya et al., 2004). The analytical TEM has been proven extremely useful for characterizing aerosols, especially for internally mixed particles, which is a unique source of information on particle coatings, agglomeration, and possible atmospheric reactions (Adachi et al., 2007; Freney et al., 2010). By using TEM techniques, Buseck et al. (2010) supplied visual evidence that the radiative property of soot was determined, to a large extent, by the mixing state of soot within individual particles, suggesting that the external mixing assumption is unrealistic for many atmospheric situations (Adachi et al., 2008, 2010; Freney et al., 2010). Based on the outstanding work of Buseck's group, we can suppose that the core-shell model used in current studies does not properly represent the shapes of ambient soot particles. Very recently, Buseck reviewed the results of individual particle studies that use microscopy-based techniques, emphasizing TEM and focusing on achievements of the past ten years (Pósfai and Buseck, 2010).

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Shanghai is an international metropolis near East China Sea with a population of over 18 million (31°23' N, 121°48' E), who is home to China's largest petrochemical complex, steel makers, incinerators, and a seaport. The large usage of coal and bio-fuel burning, the increasing number of automobiles, rapid urbanization, and flourishing construction activities are all causing the high aerosol loadings (Gao et al., 2009; Ramana et al., 2010; Zhou et al., 2009). These factors make Shanghai air pollution very complicated (Fu et al., 2008). To date, carbonaceous aerosols emitted from Shanghai are still not well known, especially by single particle analysis, although they may have a significant impact on not only air quality of Yangtze River Delta but also climate changes of east China. Toward this end we have employed TEM-EDX technique to characterize carbonaceous aerosols in Shanghai. HAADF-STEM was used to create maps of element distributions of a single particle, and chemical inhomogeneities can be visualized within complex particles. We expected to gain insight into their formation and sources on local, regional, and long-range levels, and to possibly make a contribution to the determination of the impact of these aerosols on regional air pollution in east China.

2 Experiments and methodologies

2.1 Sampling

Overall, 4 sets of aerosol samples were collected during October and November 2010 at Fudan University (31°18' N, 121°29' E), Shanghai, China (Fig. 1). The sampling site is located on the rooftop of a five-storey building (about 20 m above the ground) on the campus. Surrounding the sampling site mostly consist of commercial properties and residential dwellings. An incineration facility (Jiangqiao) with a capacity of 1500 t d⁻¹ is situated 13 km west. Further into Shanghai's industrial Boshan district, some 20 km north of the site, are several power plants with capacities over 1200 MW. The other (Yuqiao), located 16 km to the south of the site, could process

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1200 t of solid waste per day. Apart from the point sources, vehicular traffic may also have affected the measurements made at the study site. There is a local road (Guoding road) with light traffic 300 m east of the observation site, and a heavily trafficked road (central ring road) is about 150 m south of the site. The site at Fudan University can be treated as representative urban site influenced by mixture of emission sources, but not dominated by one of these.

Particles were collected onto the 300-mesh copper TEM grids coated with carbon films using a single-stage cascade impactor with a 0.5-mm-diameter jet nozzle with a flow rate of 1.0 L min^{-1} . The sampler has a collection efficiency of 100% at $0.5 \mu\text{m}$ aerodynamic diameter if the density of the particles is 2 g cm^{-3} . More information about the sampler can be found elsewhere (Li et al., 2010; Li and Shao, 2010). The grids contain fiber-like carbon substrates that minimize particle overlap, and TEM images show well-separated individual particles (Fig. S1). Sampling times were mostly between 60~90 s, although they ranged from 30~180 s, depending on the visibility and thus likely particle loading. The collected samples were put in plastic carriers, sealed, and stored in a desiccator to minimize exposure to ambient air and preserve it for further analysis.

Measurements of wind speed/direction, relative humidity, and ambient temperature were automatically recorded by a Kestral 4000 Pocket Weather Tracker (Nielsen-Kellermann Inc., USA). O_3 was measured by pulsed UV fluorescence (Thermo Fisher Scientific, Co., Ltd, Model 49i). NO_x was detected with a modified commercial MoO /chemiluminescence analyzer (Thermo Fisher Scientific, Co., Ltd, Model 42i). Visibility, API, and mass concentrations of SO_2 and PM_{10} were friendly provided by Shanghai Meteorological Bureau. All these information are shown in Table 1.

A Wide-Range Particle Spectrometer (WPSTM, MSP Corporation model 1000XP) was used to measure size distributions in the range of $0.01\text{--}10 \mu\text{m}$. The instrument is an aerosol spectrometer that combines the principles of Differential Mobility Analyser (DMA), Condensation Particle Counter (CPC) and Laser Particle Spectrometer (LPS) (Gao et al., 2009). A model ADI 2080 online analyzer for Monitoring of Aerosols

and Gases (MARGA, Applikon Analytical B.V. Corp., the Netherlands) with a particulate matter sampler (PM_{2.5}) was used to measure mass concentrations of major water-soluble inorganic ions in aerosols (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, SO₄²⁻, NO₃⁻, and Cl⁻) with one hour resolution (Du et al., 2010).

Backward air mass trajectories were produced using the Hybrid Single-Particles Lagrangian Integrated Trajectory (HYSPLIT4) model available at the NOAA/ARL's (U.S. National Oceanic and Air Administration/ Air Resources Laboratory) web server. The Final Run (FNL) meteorological data were used for the trajectory calculation (Draxler and Hess, 1998).

2.2 TEM Analysis

The TEM grid samples were examined with a JEOL-2100F field emission high-resolution transmission electron microscope (FE-HRTEM) equipped with an Oxford EDX, a scanning TEM unit with a high-angle annular dark field (HAADF) detector. The TEM was operated on an accelerating voltage of 200 kV and with a low beam current to minimize particle decomposition during spectrum acquisition. EDX spectra were recorded in TEM image mode and then quantified using ES Vision software that uses the thin-foil method to convert X-ray counts of each element into atomic or weight percentages. Electron diffraction patterns of the crystalline phases were recorded in SAED. EDX, SAED and HRTEM were conducted on some of the same particles. EDX spectra provided information on chemical compositions, while SAED and HRTEM were used to examine the structure of crystalline particles.

The X-ray counts from carbon coating of TEM grids were estimated by analysing blank areas between particles. The net X-ray counts of each particle analysed were calculated, and their proportions were normalized to 100%. Copper was not considered because of interferences from the copper TEM grid. Elemental mapping on some typical particles was conducted using HAADF-STEM with an EDX mapping system (Emispec, ES Vision ver. 4.0) on a micrometer scale.

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The strong vacuum ($\sim 10^{-7}$ torr) and beam exposure causes evaporation of semivolatile compounds from particles, and for that reason, water, ammonium nitrate and semivolatile organic compounds were lost, as is typical in electron microscopy (Niemi et al., 2006).

3 Results and discussion

3.1 Air quality and meteorology during sampling periods

The samples were collected on 15 October, 12 November, 13 November, and 24 November, with the API values are 71, 298, 370 and 51, respectively (Table 1). According to National Ambient Air Quality Standard (NAAQS) in China, two heavily polluted days occurred on 12 November and 13 November. The daily average concentrations of the inhalable particle (PM_{10}) was 418 and $476 \mu\text{g m}^{-3}$ on 12 November and 13 November respectively, nearly 3 times higher than Grade (II) of NAAQS in China ($150 \mu\text{g m}^{-3}$). PM_{10} concentrations on 15 October and 24 November were much lower than Grade (II) of NAAQS while a bit higher than Grade (I) of NAAQS ($50 \mu\text{g m}^{-3}$); therefore they were considered as “two moderate days”.

To better understand the sources of the particulate matter during sampling, we computed the backward air trajectories at three altitudes of 200, 500 and 1000 m above ground level (AGL), and the results are shown in Fig. 2. It is clear that the air masses on 12 November originated from Mongolia, then passed through the desert and the semi-desert regions in western Inner Mongolia, carrying high concentrations of dust particles, and finally reached Shanghai along a northwest direction within 3 days. The air masses at 500 m and 1000 m fell and moved very slowly when they arrived at Shanghai, and may impact the ground-level air quality in Shanghai. The air masses on 13 November mainly originated from Jiangshu and Anhui, and arrived at Shanghai from the direction of East China Sea. Furthermore, the back-trajectories of the air masses at 500 and 1000 m show that the air masses just passed by the upper atmosphere in

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Shanghai and did not impact the ground-level air quality. The air masses at 200 m on both 24 November and 15 October. originated from Shandong and Bo Sea, both of which have a long distance to pass over Yellow Sea before arriving at Shanghai. However, the air masses at 500 and 1000 m may have little influences on ground-level air quality.

The obvious increase of the particle mass concentrations in the size range 10 nm~10 μm in Fig. 3a and b illustrates the occurrence of dust storm in Shanghai after 00:00 local time (LT) on 12 November. With the given assumption, the maximum mass concentration of the dust particles observed was approximately 250 μg m⁻³, and the particles with D_p > 1 μm accounted for more than 90 % of the total mass concentrations which only accounted for around 35 % the day before 12 November, indicating that anthropogenic fine particles emitted from local sources were cleared out when the dust storm approached the sampling site and that the dust particles were mostly dominant during the storm period. Until 10:00 LT on 13 November, the influence of the dust storm became less and the dust mode of the mass-concentration distributions disappeared.

The concentrations of water-soluble ions in PM_{2.5} provided the additional proof for the dust event on 12 November (Fig. 3). Mg²⁺ and Ca²⁺ were mainly from crustal sources, such as resuspended road dust, soil dust, and construction dust, and SO₄²⁺, NO₃⁻, and NH₄⁺ represented the secondary pollution sources from the transformation of their precursors of SO₂ and NO₂ (Hwang et al., 2008; Jeong, 2008; Sun et al., 2006). The concentrations of Mg²⁺ and Ca²⁺ at 00:00 LT on 12 November increased gradually and peaked at 08:00 LT on 12 November. The peak values of Mg²⁺ and Ca²⁺ during the dust storm were 0.6 and 7 μg m⁻³ respectively, which were about 10 and 14 times higher than 00:00 LT on 11 November (the day before the dust storm). The concentrations of SO₄²⁺, NO₃⁻ and NH₄⁺ decreased by a factor of 1.6–4.7 times from 9.5, 12.1, and 7.1 μg m⁻³ to 6.0, 5.3, and 1.5 μg m⁻³ respectively, which could be the dilution effect of the dust storm. Variations of water-soluble ions were consistent with the backward trajectory analysis and the meteorological conditions.

3.2 Major type and microstructure of carbonaceous aerosol

Here, we put more emphasis on carbonaceous aerosols collected from the urban Shanghai atmosphere, since they are major fraction of the aerosols by number in urban atmosphere, and are hence relevant for studying radiative effects and CCN properties of aerosols. Based on their morphologies and X-ray spectral data, carbonaceous aerosol occurring in the samples were categorized into the following five types: (1) polymeric organic compound, (2) soot, (3) tar ball, (4) char, and (5) biogenic particle. It must be noted that, since many different types of internally mixed particles were identified, for clarity, the particles were grouped according to chemical species with the highest content present in the particles. Based on this criterion, the particles with organic coating were not listed as a separate type of carbonaceous aerosol, but they were discussed later in detail.

3.2.1 Polymeric organic compounds (POCs)

The bulk of particles were that the sum of the C and minor O and/or N contents was more than 90 % in atomic fraction based on X-ray spectral data. Such particles ranged in diameter from 200 nm to 1.5 μm , mostly from 200 nm to 1 μm . They typically displayed rounded, relatively non-descript shapes, as shown in Fig. 5. Since EDX analyses only gave elemental compositions, we had not direct evidence that C in these particles occurred in organic compounds. However, it was widely assumed that all of EC in the tropospheric aerosols was within soot particles (Jacobson, 2001). Because these particles lacked the typical concentrically stacked graphitic layers of soot, we assumed they consisted of organic substances. Unlike organic coating (will be discussed later), POCs were not beam sensitive and did not evaporate under prolonged exposure to the electron beam, as indicated by a couple of TEM analysis. Such insusceptibility against the electron beam lead to the hypothesis that POCs may be high-molecule organic compounds, such as HULIS (polycyclic aromatic hydrocarbons), which has been hypothesized to form from the incomplete breakdown of polymeric carbohydrates in the atmosphere (Alexander et al., 2008; Hoffer et al., 2006). HRTEM (the inset of Fig. 4d)

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exhibited completely amorphous structure of the POCs. In this work, we defined these particles as POCs.

Most of POCs contain soil-like elements such as Al, Mg, Si, and Ca. Particularly, they were coated or embedded with Si-rich particles (Fig. 5a and b). It has been reported that many soil-derived aluminosilicate particles contained carbonaceous species which probably came from humic substances in soil (Geng et al., 2010; Jeong, 2008; Ro et al., 2001). Based on EDX data, some of Si-rich components were identified as quartz (Fig. 5a and b). Quartz is the most common mineral in soils but can also form during fossil fuel combustion processes (Li and Shao, 2009b). However, soil-derived quartz particles formed by mechanical processes are irregularly shaped. Fly ash particles produced during high-temperature combustion are typically spherically shaped (Geng et al., 2010). This type of POCs encountered more frequently in the sample of 12 November, collected during a dust storm event. Some of POCs contained K, in addition to Cl, S and Si (Fig. 4d and e). The potassium enrichment in aerosols has been used as a fingerprint of their biomass-burning origin (Pósfai et al., 2003; Pósfai et al., 2004; Li et al., 2003b). Previous field-measurements have proposed that biomass burning was an important origin of HULIS in East Asia (Alexander et al., 2008; Hoffer et al., 2006). POCs were often found to be coated by S- or N-rich rim (Fig. 4c and d), indicated that they were readily oxidized by common atmospheric gases such as NO_x and SO₂. Figure 4f shows a typical POC particle with S-rich coating. Cube-like aggregated crystals (arrowed) indexed by the inset fast Fourier transform (FFT) pattern as CaSO₄.

3.2.2 Soot

Soot was common in all samples, which was believed to be formed via a vaporization-condensation mechanism during combustion processes (Chen et al., 2005, 2006a; Li et al., 2003b). Typical Soot aggregate had spherical primary particles and fractal-like chain structures that can extend to a couple of micrometers or more (Fig. 6a and e). HRTEM image of the soot spheres shows onion-like structures of curved, disordered

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graphitic layers (Fig. 6d). STEM-EDX mapping shows the soot aggregate mainly contained C and minor O (Fig. 6b and c). Typical SAED patterns of soot aggregates (Fig. 6g) exhibited three distinct rings, which were indexed to the crystalline structure of graphite (Viktória et al., 2006). The SAED pattern obtained from soot aggregates shows broad and diffuse 002 and hk rings, indicating a microstructure consisting of randomly distributed crystallites that had a fine size and did not possess long range order, which was consistent with the previous study (Chen et al., 2005). Dark-field image (Fig. 6f) was used to visualize individual microcrystallites. The bright spots in the dark-field image were produced by diffraction from the 002 planes of microcrystallites. These bright spots were distributed unevenly within the particles. Such patterns observed could be due to a different density of circumferential 002 lattice planes parallel to the electron beam (Chen et al., 2005; Viktória et al., 2006).

Besides the major component of C and O, soot may also contain variable, trace amounts of S, K, Si, Ca, Fe, Mn and Zn. These external inorganic species may constitute an important fingerprint that could be used to identify their possible combustion and fuel sources (Chen et al., 2005). The type of the soot aggregates shown in Figure 6a often contained trace K element, suggesting the soot aggregate with larger particles was most likely originated from biomass burning. The soot aggregates with smaller primary particles often exhibited trace Si and Ca, which may originate from vehicle exhaust since Si can be found in the fuel, and Ca is a frequent additive in oil (Kocbach et al., 2005; Vernooij et al., 2009). It has been reported that the smaller diameters of primary particles from vehicle exhaust could be due to the higher flame temperatures for engines (approximately 2000 °C) (Kocbach et al., 2005). Trace Fe ingredient, often coupled with Mn and Zn in soot aggregates, may be used as indicators for coal combustion (Chen et al., 2005). Soot aggregates exhibiting a discernible S have previously been observed from the atmosphere of Kentucky, which were prominently derived from the combustion of coal and residual oil (Chen et al., 2006b). However, the S tracer was present in almost all of soot aggregates in our samples, indicating the S-content in soot aggregates might be due to a reaction with ambient air rather than a source difference.

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Some of the soot particles showed a modified morphology, which most likely resulted from atmosphere aging (Fig. 6h and i). Once emitted into the air, the irregular geometry and complex microstructure of soot aggregates may provide active sites for deposition of common atmospheric gases such as O₃, NO₂, and SO₂, which could readily oxidize soot surfaces (Decesari et al., 2002). The soot-O₃ reaction is particularly rapid, and prolonged exposure to ozone under laboratory conditions may lead to the collapse of the graphitic structure (Zhang et al., 2008).

3.2.3 Tar ball

Tar balls were readily recognized in TEM images (Fig. 7a and b) by their spherical shape, which are produced by a gas-to-particle transformation followed by condensational growth in biomass smoke (Hand et al., 2005; Pósfai et al., 2003). Tar balls had a diameter range from 100–500 nm with a few particles larger than 1 μm. HRTEM images (Fig. 7c) of tar balls did not indicate any semioordered graphitic microstructure typical of soot. Their EDX spectra indicated elemental compositions consisting of C and O with trace amounts of S, K, Cl and Si. Internal mixing of tar balls with other particle types was rarely observed.

In contrast to other widespread and spherical aerosol particle types, such as sulphate and K-rich particles, tar balls were stable and did not change visibly under prolonged exposure to the electron beam, suggesting they were composed of refractory material. It has been reported that the chemical compositions, densities, and carbon functional groups of tar balls were distinctly different from soot and black carbon and more closely resemble high molecular weight polymeric humic-like substances, which could account for their reported optical properties (Pósfai et al., 2004; Li et al., 2003b).

Of special interest was to compare tar ball with K-containing POCs (as noted previously), both of which showed similar element compositions with comparable amounts, amorphous microstructures, overlapped sizes, and strong resistances against electron bombardment. Since Posfai et al. (2003) proposed that tar balls were probably correspond to an intermediate stage in the aging of organic particles from biomass burning,

we strongly suspected that a fraction of K-containing POCs could be originated from tar balls. A typical POC particle with S-rich coating is shown in Fig. 7d. When exposed to electron beam, surface sulphates sublimated when the particle exposed to electron beam (Fig. 7e). Element maps proved that C, O, and Si elements homogeneously distribute within the bulk of the particle. Homogeneous internal distributions of C and O in tar balls were previously reported (Hand et al., 2005). Also our assumption was supported by a few field studies performed on southern Africa and California (Hand et al., 2005; Pósfai et al., 2004, 2003). Both tar balls and the organic particles with minor K, Cl, and S contents were characteristic products in aged biomass plumes. Given the small number of particles analyzed in this study, it was difficult to evaluate the validity of this scenario, but it was certain that both K-containing POCs and tar balls observed in the atmosphere of Shanghai come from biomass burning.

3.2.4 Char

Two char particles with submicron sizes were also observed in the sample on 15 October. They had compact and irregular-shaped morphologies, quite different from soot aggregates and “tar ball” (Fig. S2a). HRTEM shows that the char particles exhibited short and discontinuous graphitic layers, and infrequently, the concentric onion-like microtextures were also observed (Figs. S2b and 2c). Char particles in the urban atmosphere often derived from coal or residual oil combustion (Chen et al., 2005). The relative number concentrations of these particles were so low that they were not discussed further.

3.2.5 Biogenic particle

Biogenic particles are a special type of organic particles with special morphologies, ranging in size from millimeters down to tens of nanometers. The number concentrations of biogenic particles range from minor fractions of the total aerosol in oceanic (1 %) and continental (2 %–3 %) settings, to ~25 % in a continental aerosol and 35 %

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in Amazonia (Wittmaack et al., 2005). The simultaneous presence of minor N, P, S, Si and Cl with C and O was considered as “biogenic fingerprint” in the previous studies (Geng et al., 2010b; Pósfai and Buseck, 2010; Niemi et al., 2006). Most biological particles originate from terrestrial plants; while the ocean with the “bubble-burst” mechanism is also an important producer (Wittmaack et al., 2005). In this work, biogenic carbonaceous particles have also been observed in the urban air of Shanghai. Figure 8 shows the TEM images of several typical biogenic particles. The morphology of these particles varied strongly from simple bar to complicated biological structures. The HRTEM image exhibited completely amorphous structure.

Particles having interesting, flower-like morphologies with diameters around 400 nm, occurred in the sample collected 15 October (Fig. 8a). They contained mostly of C and O and also contained significant Si, which was believed to serve as a highly water repellent body coating of leafhoppers (Pósfai et al., 2010). They might originate mainly from local forests. Leafhopper is a common insect in Shanghai, and widely distributed in east China. Particles with similar morphologies and compositions were observed in other geographically diverse regions, such as southern Africa, Munich and Kentucky (Pósfai et al., 2010; Chen et al., 2005; Pósfai et al., 2003). The particles shown in Fig. 8d and e abundantly encountered in the sample collected on 13 November, but they were absent in the other samples. These particles have never been observed in previous studies. Most of the biological particles (Fig. 8b–e) were likely insect and/or algae. Bunch of identical bioaerosols shown in Fig. 8f, may be presumably bacteria. The detailed classification of these particles was beyond the scope of this work.

3.3 Mixing states of carbonaceous particles and formation mechanisms

3.3.1 Particles with organic coatings

Several TEM studies have shown the inorganic particles with organic coating were widespread in urban atmosphere (Adachi and Buseck, 2008; Li and Shao, 2010). Similar results were well observed in our samples. Most of the particles, including S-rich

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particles, fly ashes, mineral dusts and metal-rich particles were coated with a carbonaceous film, and a few typical particles with organic coating are shown in Fig. 9a–c. Similar particles, with coatings of various thickness of organic coating, have been widely observed in a variety of samples, including those from pristine marines and polluted continental environments (Adachi and Buseck, 2008; Li and Shao, 2010; Russell et al., 2002; Niemi et al., 2006). Organic coatings were lost under strong beam bombardment although they were less sensitive to the electron beam than sulphates and nitrates, which were different from tar ball and POCs. It was believed that organic coating was composed of second organic aerosol (SOA), which commonly forms through condensation of precursor gases on pre-existing particles such as soot, ammonium sulphate, and primary organic aerosol as well as through homogeneous nucleation (Fan et al., 2006). The high ozone and VOC concentrations in urban Shanghai atmosphere suggested that the formation of SOA in the vapour phase and their subsequent condensation may be a significant pathway in the formation of organic coating. Previous studies have suggested that ozone, hydroxyl radical, nitrate radical, and other oxidants presented during atmospheric transport played a central role on the formation of SOA in Beijing atmosphere (Li and Shao, 2010). In Shanghai, about half of VOCs come from motor vehicles, and 10~35 % of VOCs was from industrial activities, indicating the organic coating in these aerosol particles were likely formed by VOCs from fuel combustion, and a lesser extent, from industrial activities (Geng et al, 2009). Tar balls were an indicator of biomass and biofuel burning (Hand et al., 2005; Pósfai et al., 2004). The low abundance of tar balls indicated little influence from biomass burning on the formation of organic coating (see the section of *relative abundances*). Laboratory experiments have found that SOA is slightly hygroscopic and exhibits a smooth water uptake with increasing (Varubangkul et al., 2006). Therefore, the circle stamps in the grid indicate that their organic coatings likely held water before they was sampled, suggesting the formation of such coating by aqueous-phase processing of the particles during transport in atmosphere. Organic coatings could modify the particle hygroscopicity, CCN abilities and heterogeneous chemical reactivity, indicating that the

ubiquitous presence of this particle type in urban Shanghai atmosphere had important ramifications of the regional climate (Adachi et al., 2008; Russell et al., 2002; Li et al., 2003a).

3.3.2 Internally mixed particles

S-rich particles, likely ammonium sulphate, dominated in most of samples. In TEM images, these particles were euhedral or rounded. Their size distributions were bimodal, with most particle diameters < 500 nm or from 800 nm to 1.5 μm . Close examination of TEM-EDX showed many of the ammonia sulphate grains consisted of organic components, which exhibited carbon peaks higher than those seen from background. The sulphates readily decomposed when exposed to an electron beam (Fig. 9d–f). When decomposing, they left a similar carbonaceous residue. Laboratory studies showed that sulphate nucleation was often coupled with aromatic acids (Zhang, 2004); thus, it was not surprised that organics were present in small sulphate particles. A smaller size of the sulphate grains seemed homogeneous and were commonly coated by organic layer, while the larger ones were commonly internally mixed with soot and organic matter (or more chemical species) (Fig. 9g and h). Within the internally mixed particles, most of organics may be beam-sensitive SOA (Fig. 9d and e). Consistent with the usual findings that SOA was coupled with S-rich particles (Kanakidou et al., 2005). However, some particles also contained beam-resistant dark inclusions without clear morphological characteristics, which may be POCs, collapsed soot or tar ball. Previous water dialysis experiments of individual particles have demonstrated that the coatings were water soluble, while organic inclusions were insoluble (Li and Shao, 2010).

Such internally mixed particles may be preferentially formed in an aerosol mass stagnates which often occurs during episodes of serious pollution (such as urban haze), when there is insufficient wind velocity to carry pollutants away from the city. During these periods of pollutant retention, aerosols continue to collide and combine with each other, resulting in larger average sizes and complex components. Larger sizes are commonly associated with polluted environment and adverse meteorological

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conditions (Li et al., 2010). In high pollution areas such as Mexico City, over half of the aerosol particles consist of internally mixed soot, organic matter, and sulphates (Adachi and Buseck, 2008). Sulphate coatings can have either negative or positive effects on the radiative forcing of BC. On one hand, the internally mixed sulphates can make organic matter and soot more hydrophilic and eventually make them efficient CCN. While, on the other hand, embedding sulphates act as lenses that focus light on soot and thus amplify absorption of the internally particles (Adachi and Buseck, 2008; Adachi et al., 2010).

3.3.3 Aged biogenic particles

The aged biogenic particles were relatively frequently observed in both clean and polluted environments (Fig. 9i and S3). The particles shown in Fig. 8a commonly embedded in or aggregated with soot aggregates, but still retain their whole flower-like morphology. The surface of the aged particles changed apparently under electron bombardment, suggesting that they may be coated by sulphates (Fig. S3h and S3i). The attached sulphates could change them from hydrophobic to hydrophilic, indicating the possibility of the importance of such particle acting as CCN. The marine-originated bioaerosols shown in Fig. 8c and d often presented flawed morphologies, and/or coated by organics and unknown material. These biogenic particles were encountered frequently in the sample of 13 November. Previous studies have reported that biogenic particles may act as CCN and played an important role for the long-range transport of trace elements into and away from specific biomes (Witmaack et al., 2005).

3.4 Relative abundances and possible sources

Figure 10 shows the relative number percentages of major chemical species in the samples collected at different times. Although there was a variation in the relative number counts of different species, sulphates (15%–71%), followed by soot (7%–22%), constituted the most dominant species observed in the samples. The sulphur in these

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particles was probably present mainly as ammonium sulphate salts, because most of the particles did not have a satellite droplet rings around them, which was characteristic of such acid sulphates as H_2SO_4 particles (Li et al., 2010; Zhang et al., 2000). The high concentrations of SO_4^{2-} and NH_4^+ measured by ion chromatography also supported the dominance of ammonium sulphate salts (not shown). In urban areas, it was well-known that ammonium sulphate particles were major chemical species, which was mostly from the reaction of atmospheric SO_2 with NH_3 under high relative humidity (Zhang et al., 2000; Geng et al., 2010; Chen et al., 2006). Particles containing abundant ammonia sulphate species, either as single species or mixed with others, has been frequently observed in Mexico City, Kentucky, and Qingdao (Adachi and Buseck, 2008; Chen et al., 2006; Zhang et al., 2000). The carbonaceous particles comprise mostly soot aggregates, which was consistent with the previous observations of urban atmosphere (Adachi and Buseck, 2008; Chen et al., 2006). Urban areas generally undergo high loads of carbonaceous particles from heavy traffic, emissions from industrial plants, and intensive energy consumption. Previous work has demonstrated the poor correlation between BC and SO_2 in Shanghai, suggested that diesel vehicles were the dominant sources of BC (Zhou et al., 2009). Only minor tar balls were present in the samples; the low abundance of these particles indicated biomass burning was not a main source of BC during sampling.

As shown in Table 1, the API values of 13 November, 24 November, and 15 October are 370, 51 and 71, with the wind speeds of 0–1.9, 0–6.2, and 0–3.7 $\text{m}\cdot\text{s}^{-1}$, respectively. Pollutant concentrations in Shanghai were greatly influenced by weather conditions, especially wind speeds. Strong negative correlation between average wind speeds and pollutant concentrations was found in Shanghai (R^2 of -0.74), when significant wind speed changes existed (Feng et al., 2006). On 13 November, the high pollution was related to low wind speeds of 0–1.9 $\text{m}\cdot\text{s}^{-1}$ from east south direction. This suggested that the main sources of pollutants were local in Shanghai. The larger sizes of internally mixed particle, often containing soot, sulphates and organic matters, were more common on the sample of 13 November as compared to the samples of

24 November and 15 October, suggesting the weather condition did not favour dispersion and transport of air pollutants, resulting in more collisions, combinations and coagulations among particles, and thus more complex morphologies and larger sizes of aerosols.

Of particular interest was the biogenic particles encountered almost as frequently as soot on the sample collected on 13 November (18 % vs. 22 %). The back-trajectories of air masses support that these particles were marine-originated, most likely from the Yellow Sea. Indirect conclusions could be drawn regarding the strong changes were seen in the presence of sea salt particles in the same sample (4 %). Abundant biogenic aerosols from the Yellow Sea in the summertime atmosphere of Seoul have been widely reported (Geng et al., 2009, 2010; Ro et al., 2002). Visibility is an important indication of regional haze, which is inversely proportional to the bulk aerosol concentration. Because of their abundance and large sizes (most is larger than 1 μm), it was believed that these biogenic particles make a significant contribution to visible degradation of the city on 13 November. As discussed previously, aged biogenic particles could be the potential CCN. The important source of biogenic organic CCN from the ocean was omitted from current cloud research in east China and should be taken into account.

With an exception of the sample collected at 12 November, soil-derived particles (mainly aluminosilicates and quartzes, 68 %) were relatively more frequently observed as compared to sulphates (15 %) and soot (7 %). The backward air mass trajectories showed that the air masses originated from Mongolia and Gobi desert of China, which belonged to typical source regions of Asian dust storm. On one hand, local pollutants will be diluted by long-range transport of dust plumes. On the other hand, the formation of ammonium sulphate/bisulphate might be suppressed as sulphuric acid was taken up by mineral particles with basic surfaces (Ro et al., 2005; Geng et al., 2009). Both of them lead to much lower contents of soot (7 %) and sulphates (15 %) on the sample of 12 November as compared to the other samples. On the basis of the back-trajectories, the air-mass fell and moved very slowly when they arrived at Shanghai, suggesting

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that dust particles had a chance to mix with local pollutants for the reactions. TEM-EDX analysis showed that most of mineral particles, especially the particle with small size, presented N-rich or S-rich coatings. It was reported that Asian dust storm events provided a removal mechanism for NO_x (or HNO₃) and perhaps contributed to nitrogen deposition in the Yellow Sea and the eastern China Sea (Geng et al, 2009; Zhang et al., 2010).

4 Conclusions

In this study, individual aerosol in the urban atmosphere of Shanghai were observed using TEM-EDX. Several types of carbonaceous particles were present in our aerosol samples, which were POC, soot, tar ball, char, and biogenic particle. Organic coating, commonly formed through condensation of precursor gases on pre-existing particles, was also widely observed in the most samples. Soot (11 %–22 %) constituted the most dominant carbonaceous species observed in the samples. Soil-derived POCs particles were relatively more frequently observed during the dust storm. Of particular interest was the biogenic particles encountered almost as frequently as soot on the sample collected on 13 November (18 % vs. 22 %), suggesting that the important source of biogenic organic CCN from the ocean in east China should be taken into account. During the polluted day, most carbonaceous particles were in aggregates, which had a significant influence on their physical and chemical properties and may change their radiative properties and thus their climatic effects.

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Supplementary material related to this article is available online at:
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**Table 1.** Sampling date, meteorological conditions, and daily averaged concentrations of atmospheric pollutants.

| No. | Sampling Date | Start of Sampling | T (°C) | RH(%) | WS (m s ⁻¹) | WD | Visibility (km) | O ₃ (ppbv) | Daily averaged concentrations | | | |
|-----|------------------|-------------------|-----------|-------|-------------------------|----|-----------------|-----------------------|-------------------------------|---------------------------------------|---------------------------------------|----------------------------------------|
| | | | | | | | | | API* | SO ₂ (μg m ⁻³) | NO _x (μg m ⁻³) | PM ₁₀ (μg m ⁻³) |
| 1 | 15 October 2010 | 15:00 | 22.3–23.7 | 53–57 | 0–3.7 | NE | 15 | 23.8–43.6 | 71 | 22 | 78 | 92 |
| 2 | 12 November 2010 | 15:00 | 15.3–15.5 | 62–66 | 1.3–7.0 | SW | 5 | 14.0–66.0 | 298 | 365 | 107 | 418 |
| 3 | 13 November 2010 | 15:00 | 17.3–17.5 | 87–89 | 0–1.9 | SE | 10 | 42.7–51.0 | 370 | 225 | 88 | 476 |
| 4 | 24 November 2010 | 15:00 | 14.4–14.9 | 57–59 | 0–6.2 | NE | 27 | 2.0–9.0 | 51 | 10 | 74 | 52 |

*Air Pollution Index (API, API = 100 corresponds to Chinese air quality standard II)

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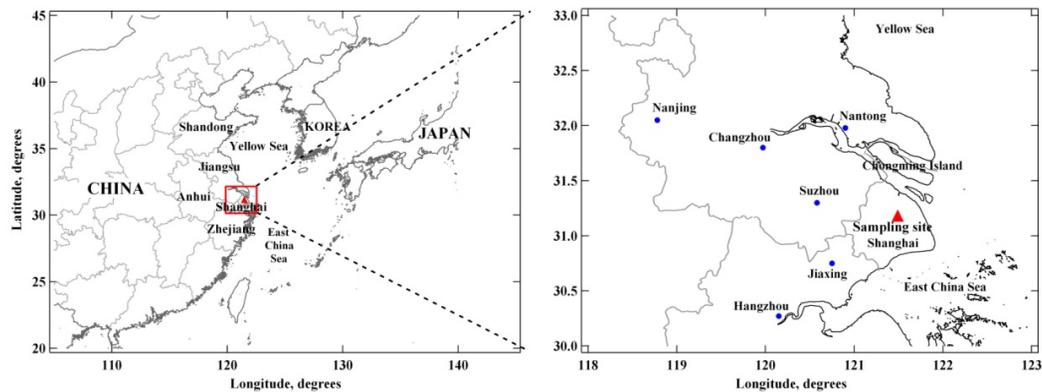


Fig. 1. Schematic map of sampling site.

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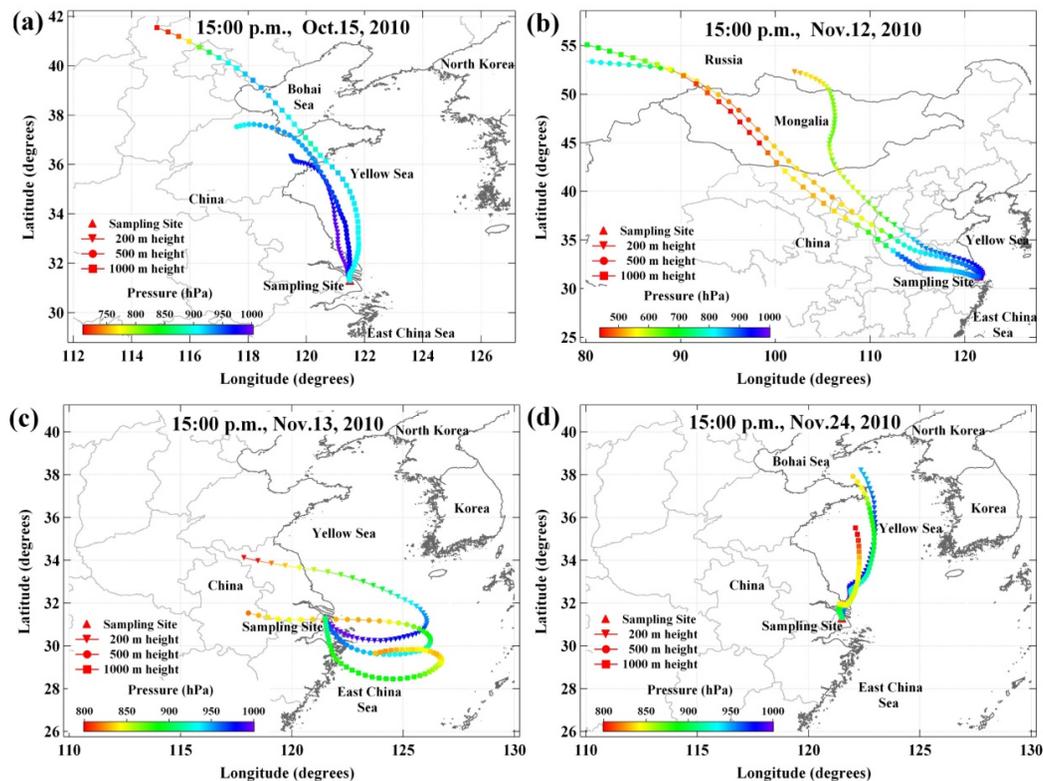


Fig. 2. The backward air-mass trajectories ending at 200 m, 500 m and 1000 m for **(a)** 15 October 2010 (48 h), **(b)** 12 November 2010 (72 h), **(c)** 13 November 2010 (48 h) and **(d)** 24 November 2010 (48 h) with the pressure indicated by color-coded line.

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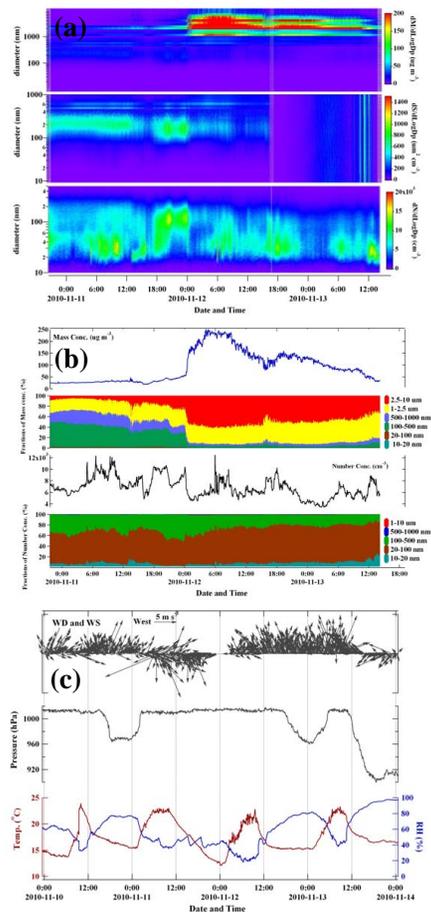



Fig. 3. The pollution event, 12–13 November 2010: **(a)** Time series of mass, surface and number size distribution, **(b)** The average fractions of the particle mass and number concentrations in different size ranges, **(c)** Hourly meteorological data (WD = wind direction, WS = wind speed, RH = relative humidity).

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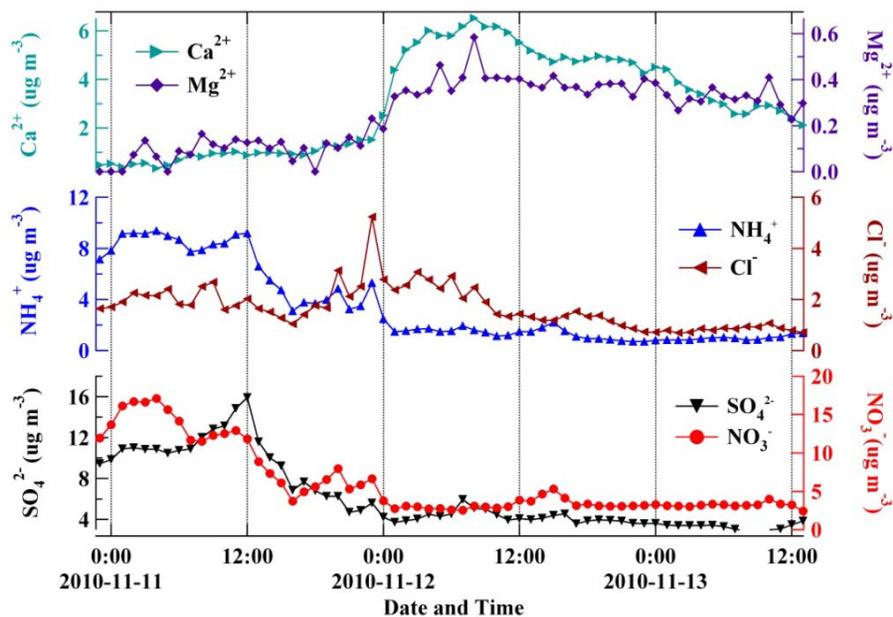


Fig. 4. Hourly concentrations of Ca^{2+} , Mg^{2+} , NH_4^+ , Cl^- , SO_4^{2-} , and NO_3^- during the dust-haze episode (12–13 November 2010).

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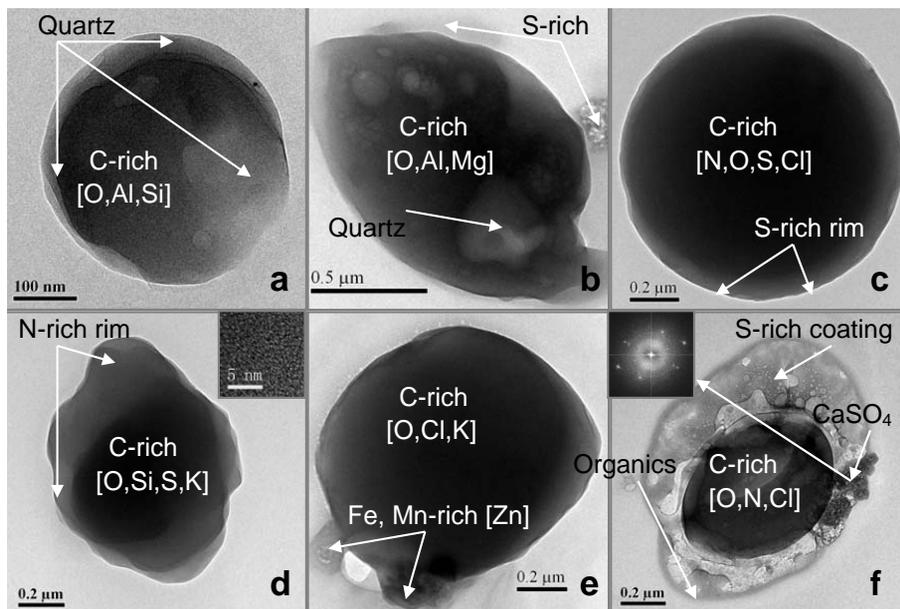


Fig. 5. TEM images of the typical POC particles collected from the atmosphere of Shanghai. Element of the detected parts of individual particles is mainly C (> 80%), and minor elements are indicated in square brackets. **(a)** C-rich particle coated by quartz layer. **(b)** C-rich particle internally mixed with quartz. **(c)** C-rich particle with S-rich rim. **(d)** C-rich particle with N-rich rim. HRTEM image in the inset shows amorphous microstructures of the particle bulk. **(e)** C-rich particle is attached to two metal-bearing particles (Fe, Mn, Zn). **(f)** C-rich particle with S-rich coating, surrounded by organic layer. Cube-like aggregated crystals (arrowed) indexed by the inset FFT pattern as CaSO_4 .

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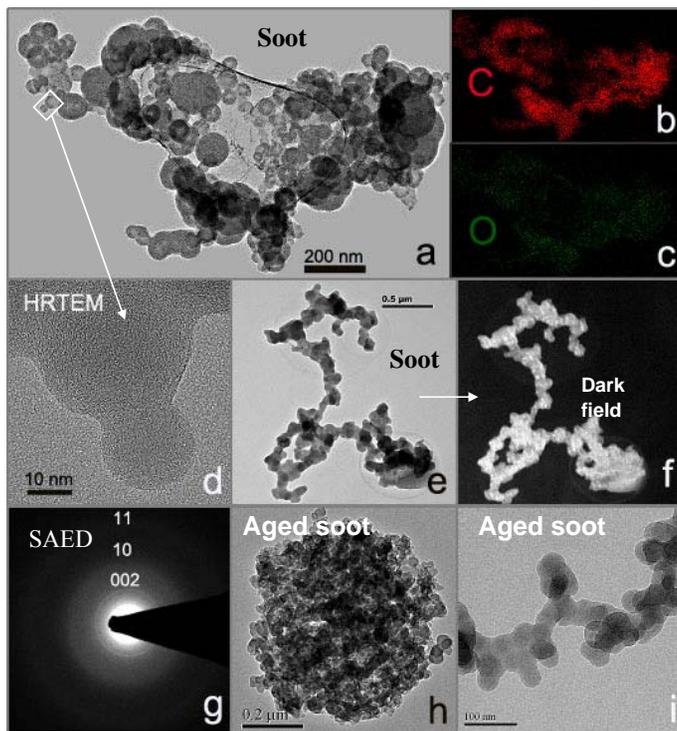


Fig. 6. TEM images of soot particles collected from the atmosphere of Shanghai. **(a)** The aggregate of chain-like soot particles with heterogeneous particle sizes ($D_p > 100$ nm or $D_p < 80$ nm). Elemental profiles obtained from STEM-EDS (HADDF-STEM mode) across the whole aggregate show the distribution of C **(b)** and O **(c)** elements. **(d)** High-resolution TEM shows the soot spheres with onion-like curved, disordered graphitic (grapheme) layers. Bright-field image **(e)** and corresponding 002 dark-field image **(f)** of a soot aggregate with homogeneous size ($D_p < 80$ nm). **(g)** Typical SAED pattern of the soot particle exhibits three distinct rings, corresponding to 002, 10 and 11. **(h)** and **(i)** Aged soot.

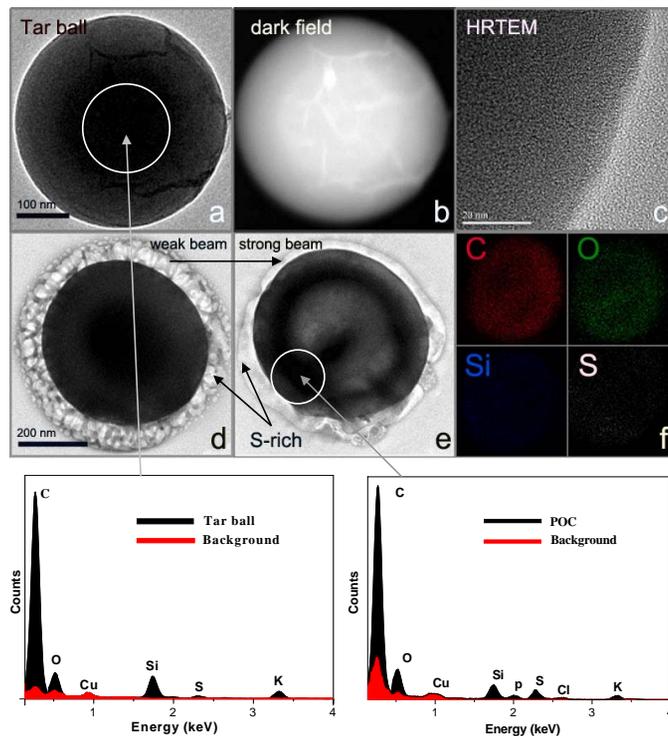


Fig. 7. TEM images of a typical spherical tar ball particle from a bright-field **(a)** and dark-field **(b)**. HRTEM image of the same particle shows amorphous microstructures **(c)**. A POC particle with sulfate-containing coating **(d)**. The same particle expose to the strong beam **(e)**. STEM-EDX maps showing the distributions of carbon element, oxygen element, silicon element, and sulfur element in the aged tar ball **(f)**. EDX **(g and h)** recorded from the corresponding regions of white circles. The tar ball and a POC particle show similar element component (C, O, Si, and K elements), but varied ratios.

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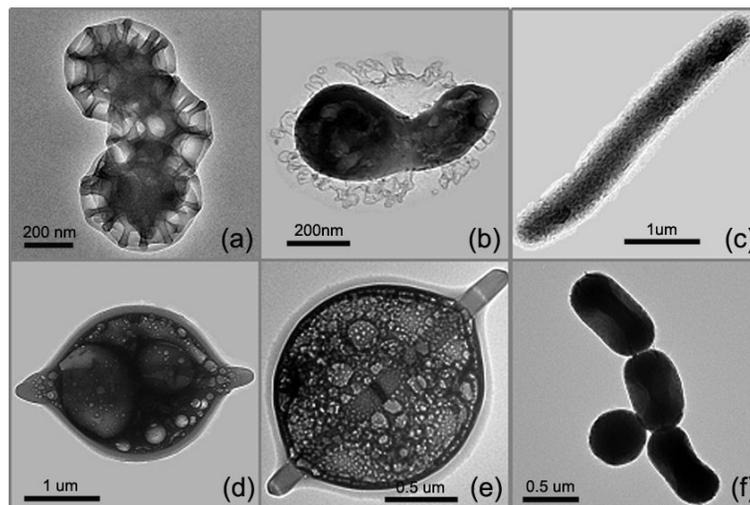


Fig. 8. TEM images of particles classified as biological particles. **(a)** agglomerate of three brocosomes produced by leaf-hopping insects as a water-repellent body coat; **(b–f)** unidentified biogenic particles in the present study. The particles **(e and d)** were abundant encountered on the sample of 13 November, which could be originated from the Yellow Sea, and may be insect and/or algae; Bunch of identical bioaerosols **(f)**, presumably bacteria.

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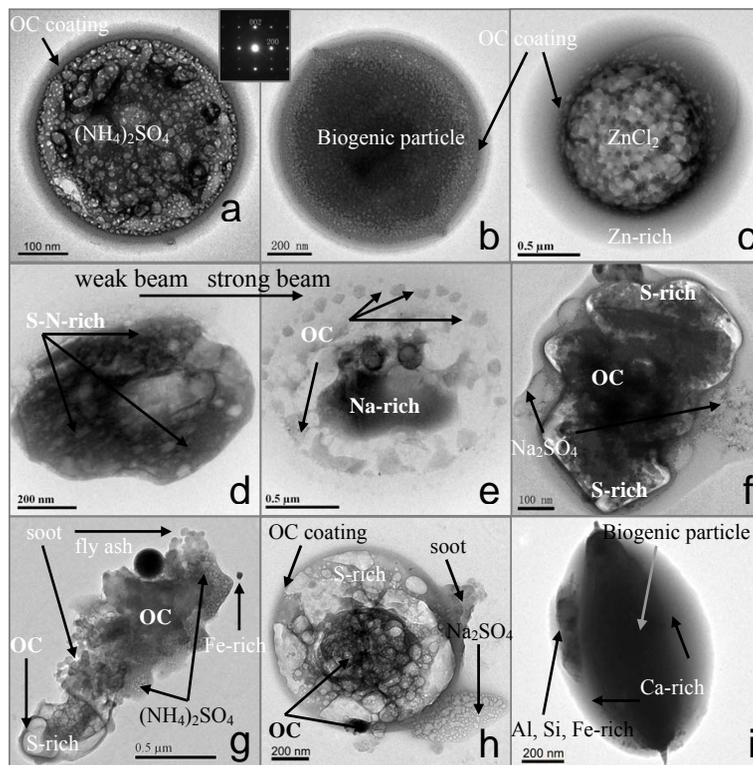


Fig. 9. TEM images of the typical C-bearing particles collected from the atmosphere of Shanghai. **(a)** A ammonium sulfate particle with organic coating. The inset is the diffraction pattern of ammonium sulfate. The diffraction pattern was obtained from a similar-looking particle, which was destroyed during electron-beam exposure. **(b)** Biogenic particle coated by thin organic layer. **(c)** ZnCl_2 particle with organic coating (arrowed), and then encapsulated in the Zn-rich layer. **(d)** Organic components embedded in the N-S-rich particle. **(e)** The exposed organic components from decomposition of the beam-sensitive N-S-rich particle. **(f)** The internally mixed organic/sulphate-containing particles (ammonium sulfate) after intentional strong beam exposure. The SAED image and EDS show the basis for the identification of the bar-shaped particles (arrowed) as Na_2SO_4 . **(g)**, and **(h)** the internally mixed particles containing soot, organic matter and sulfates. **(i)** Biogenic particle attached with Ca-rich material.

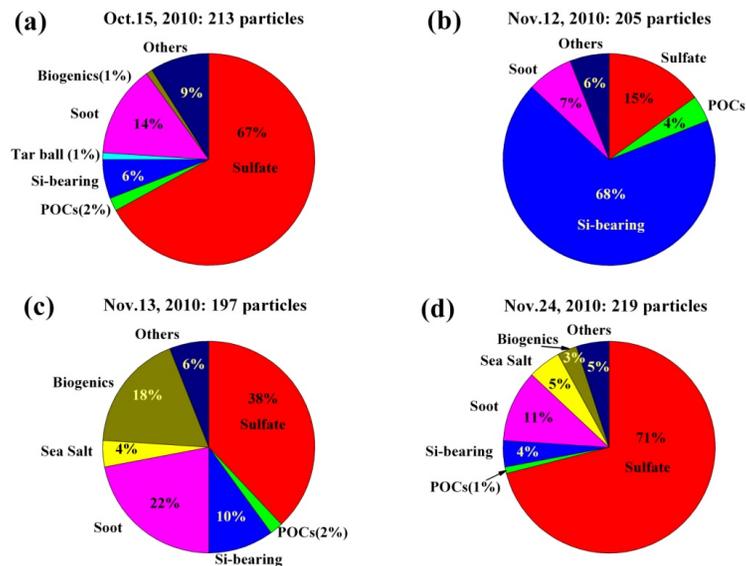


Fig. 10. The relative number percentages of major chemical species in the samples collected at Shanghai: **(a)** 15 October 2010, **(b)** 12 November 2010, **(c)** 13 November 2010, and **(d)** 24 November 2010.

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