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The variation of characteristics of individual particles during the haze evolution in the urban Shanghai atmosphere

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ABSTRACT

The severe long-lasting haze episode in December 2013 provided a unique opportunity to track the variation of aerosol particles in Shanghai, China. Concentrations and sources of the pollutants varied greatly in severe haze-fog episode (P1), moderate haze episode (P2), and clear episode (P3). Both low wind speed and high relative humidity (RH) during P1 resulted in the high level pollutants of $PM_{2.5}$ ($240.3 \pm 167.9 \ \mu g \ m^{-3}$), SO_2 ($37.9 \pm 20.7 \ \mu g \ m^{-3}$), NO_2 ($111.5 \pm 50.2 \ \mu g \ m^{-3}$) and total water-soluble ions ($58.73 \pm 28.87 \ \mu g \ m^{-3}$), indicating a strong accumulation of local pollutants and secondary species formation. During P2, air masses from the north decreased the concentration level of particles ($116.1 \pm 65.5 \ \mu g \ m^{-3}$) and increased the visibility, resulting in a moderate degree of pollution. Most of the pollutants dropped to the lowest concentration levels due to the rainfall in P3, and the haze episode ended at 13 December. Single particle analysis showed that C-rich particles exhibited the highest number percentages (30%) in the samples of P1, S/N-rich species (35%) dominated the particles in the samples of P2, and Al/Si-rich particles (23%) were most abundant in the samples of P3. The TEM-EDS analysis confirmed that particles contained more internally mixed components during P1 and P2 than those during P3, suggesting that the particles during P1 and P2 underwent more intense aging in the atmosphere. The single particle analysis indicated that trace metals may promote the heterogeneous transformation of SO_2 and NO_2 on the surface of the particles during P1, which was in agreement with the highest sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) observed in the haze-fog episode. Such information will deepen our understanding on the evolution of haze and fog pollutions in China, which will help the government to establish efficient control strategy for air pollution prevention.

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1. Introduction

China is currently suffering from serious atmospheric pollution due to the fast development of economy and urbanization (Wang et al., 2013; Zhang et al., 2015). Extremely severe haze pollutions presented in most parts of central-eastern China have attracted a lot of attention over the world (Shen et al., 2015; Wang et al., 2013). The haze episodes are characterized by low visibility, high particle mass loading and aerosol optical depth (Che et al., 2009; Wang et al., 2014), which has caused significant impacts on the local and/or regional air quality (André, 2005; Zhang et al., 2015).

A growing body of researches has focused on size distributions and chemical components of the haze particles (Han et al., 2015; Sun et al., 2006; Zhao et al., 2015). Chemical analyses showed that the fine particles, including organic matter, black carbon, nitrate, sulfate, ammonium, and fly ash, are the dominant contributors to the regional haze pollution in China (Feng et al., 2006; Pui et al., 2014; Wang et al., 2006). It has been well documented that temporal and spatial distributions of haze events are different in specific seasons and regions (Huang et al., 2013; Kim et al., 2000; Yan et al., 2015). Several studies pointed out that anthropogenic activities and stagnant meteorological conditions are linked to the severe haze formation in megacities (Shen et al., 2015). Despite the wealth of information that is available on haze particles, there is still a need to further study on aerosol particles in detail, especially at a single particle level.

Recently, analytical transmission electron microscopy (TEM) has been proven to be an effective tool for identifying the properties of particles, which can detect the composition, morphology, structure, and mixing states of individual aerosol particles synchronously (Moffet et al., 2008a; Smith et al., 2012). By using the TEM, Okada et al. (2001) characterized the aerosol particles collected in the Indonesia haze episode, and found that particles emitted from the biomass burning were mainly presented as internal mixture morphologies. Li et al. (2011)

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Table 1
Sampling time, weather conditions and particle numbers for the TEM/EDS analysis.

Sampling time (BST[a])			Type	Particle numbers (TEM/EDS analysis)
Date	Starting	Duration		
Dec 4	9:30	2 min	Severe haze-fog (Period 1)	411
Dec 6	9:30	1 min		
Dec 8	9:30	8 min	Moderate haze (Period 2)	436
Dec 11	9:30	8 min		
Dec 14	9:30	15 min	Clear episode (Period 3)	116
Dec 18	9:30	18 min		

[a] Beijing standard time (8 h prior to GMT).

investigated the features of aerosol particles from the regional brown hazes in northern China, and found that particles collected on the haze days presented larger sizes than those collected on clear days. Hu et al. (2015) recommended that Fe-, Zn-, and Pb-bearing particles during the haze and fog episodes in Beijing originated mainly from local industrial emissions.

The commercially available online analyzer for Monitoring of Aerosols and Gases (MARGA) is also a powerful technique to study particle components (Du et al., 2010; Leng et al., 2015; Pathak et al., 2011). By using MARGA, Wang et al. (2015) conducted 3-year on-line measurements of $PM_{2.5}$ chemical components in Shanghai, and found that mass concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ decreased gradually before the year of 2008. Kong et al. (2014) further confirmed that significant negative correlation between the mass fractions of SO_4^{2-} and NO_3^- in the Yangtze River Delta.

Shanghai is the biggest city in China, with a subtropical climate under the influence of Asian monsoon. It is well known that Shanghai is suffering from serious haze pollutions, especially in winter, due to intensive anthropogenic activities and energy consumption (Wang et al., 2006). Apart from the primary emissions, heterogeneous transformations of SO_2 and NO_2 on the surface of particles contributed much to high concentrations of secondary SO_4^{2-} and NO_3^- in the Yangtze River Delta, resulting in the regional hazes (Shen et al., 2015). Haze pollutions not only impact the visibility of atmosphere, but also result in serious economic losses (Gultepe et al., 2007). It was estimated that the total economic cost of health impacts caused by air pollution in shanghai is approximately 625.40 million dollars in 2001 (Kan and Chen, 2004), and the value increases by four folds in 2004 (Zhang et al., 2008). Moreover, fine particles during high pollution episodes have a significant ecotoxicity (Liu and Zhang, 2015; Lu et al., 2008; Turóczi et al., 2012). Therefore, further understanding on the haze pollutions in Shanghai is very important to figure out the formation and evolution patterns, which could contribute to air protection strategy for the government.

In this work, the TEM analysis coupled with the MARGA technique were used to characterize the aerosol particles during a long-lasting haze episode in December 2013. We observed the temporal variations of water-soluble ions (NH_4^+, Na^+, Mg^{2+}, K^+, Ca^{2+}, Cl^-, SO_4^{2-}, and NO_3^-) in $PM_{2.5}$, and analyzed individual particles using TEM-EDS in detail. The data shown herein will deepen our understanding on the long-lasting haze pollution in the megacities of China.

2. Experimental methods

2.1. Sampling site

The aerosol samples were collected from 4 to 18 December 2013, in Shanghai, China. The sampling site (31°18′N, 121°29′E) is located on the rooftop of a five-storey building (about 20 m above the ground) on the campus of Fudan University, and no high buildings scatter around within 100 m. The surroundings of the sampling site mainly consist of commercial properties and residential dwellings. Baosteel factory and

National Container Processing Company are located at 21 km and 15 km north of the site, separately. Two waste incineration facilities, Jiangqiao and Yuqiao, locate 13 km to the west and 16 km to the south, respectively. Waigaoqiao No. 3 Power Plant and Wujing Power Plant are located 13 km to the east and 12 km to the south of the site, respectively. Apart from the point sources, vehicle emissions could also affect the study site. Central Ring Road with heavy traffic loading is about 150 m south, and Wudong Road with light traffic is situated at about 120 m north of the sampling site. The site can be treated as a representative urban site influenced by the mixture of residential, traffic, marine, construction and industrial sources, but not dominated by one of these sources (Fu et al., 2012).

2.2. TEM sampling and analysis

Aerosol particles for TEM analysis were collected onto the copper grids with carbon films (carbon type-B, 300-mesh copper, Tianld Co., China) by using a single-stage cascade impactor with a 1.0-mm-diamater jet nozzle with a flow rate of 0.5 l min^{-1}. The sampler has a collection efficiency of 100% at 0.5 μm aerodynamic diameter if the density of the particles is 2 g cm^{-3} (Fu et al., 2012). According to the particle loading, the sampling duration varied from 1 to 20 min. As the particles were impacted onto the TEM grids, few of the overlapping particles could not be avoided. After collection, each sample was preserved in a sealed dry plastic carrier, and then stored in a desiccator to avoid contamination.

Particles morphology, compositions and crystallography of interested particles on the TEM copper grids were examined with a 200-kV FEI Tecnai F20 field emission high-resolution transmission electron microscope (FE-HRTEM) equipped with an Oxford energy-dispersive X-ray spectrometer (EDS). Particles on the grids were not uniformly distributed. To ensure that the analyzed particles were representative of the entire size range, three to four areas were chosen from the center to the periphery in a line on each grid (Hu et al., 2015). The normalized atomic or weight percentage of each element was quantified by using EDS, which was collected for 15 to 30 s to minimize the radiation exposure and potential beam damage. Copper and carbon were not considered because of the interferences from copper-carbon grids. Semivolatile species, ammonium nitrate and water cannot be detected in the strong vacuum and beam exposure (Cong et al., 2010). Electron diffraction patterns of the particles of interest were recorded in selected area electron diffraction (SAED) to get the information on crystalline phases. The specific chemical forms could be identified by comparing the d-spacings of SAED patterns or HRTEM images with the crystallographic data from International Center for Diffraction Data (ICDD) inorganic compound powder diffraction file (PDF) database (PCPDFWIN software: Version 2.02) (Hu et al., 2015; Song et al., 2014). Particle sizes under the TEM were measured by DigitalMicrograph™ (Version 3.9.1) from the best fitting ellipse, with the arithmetic mean of its short and long axes in two dimensions (Li and Shao, 2009). The analysis was done by labor-intensive manual operations of TEM. Therefore, only limited numbers of particles could be selected for EDS, SAED and/or HRTEM performance. Overall, 3 sets of samples (4, 6, 8, 11, 14, 18 December) were selected for analysis (Table 1).

Furthermore, we defined the weight fraction P(X) for an element X in individual particles as its fraction relative to the selected species. P(X) = X / (N + F + Na + Mg + Al + Si + S + Cl + K + Ca + Mn + Fe + Cr + Zn + Pb + Ti + V). When the fraction of X was the highest among the 17 elements, the particle was classified as X-rich (Hu et al., 2015; Zaizen et al., 2014), unless the fraction of C was >80% in weight, in which case the particles were classified as C-rich. Following this criterion, 411 particles in the samples of P1, 436 particles in the samples of P2, and 116 particles in the samples of P3 were analyzed and classified. All of statistics in the present study were based on the number concentration (Duo et al., 2015).