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Size-resolved effective density of urban aerosols in Shanghai

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HIGHLIGHTS

- Effective density of atmospheric aerosols was measured online using DMA–APM system.
- Effective density increased considerably with increasing particle size.
- Density variation was highly correlated with the mass fraction of secondary inorganic aerosols.
- Aitken mode particles had a rapid increase in the effective density during a new particle formation event.
- Precipitation scavenging had significant impact on both particle mass loading and effective density distribution.

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ABSTRACT

Size-resolved effective density of 50–400 nm urban particles was determined by a TDMA–APM system in Shanghai during wintertime. The average effective density ranged from 1.36 to 1.55 g cm^{-3}, increasing with the particle diameter. The size dependent increase of density was consistent with previous hygroscopic measurements. We attributed the increase in density to the condensation of hygroscopic secondary aerosols and large massive organics. The diurnal variation of effective density was pronounced for smaller particles. A similar diurnal pattern was observed between particle density and the contribution of secondary NH_4NO_3 and $(NH_4)_2SO_4$ to $PM_{1.0}$, suggesting that density change in response to particle compositions. The effective density of Aitken mode particles had a considerable increase during the NPF event, in agreement with the contribution of sulfate. Particle mass distribution was derived from particle number distribution in combination with effective density. $PM_{0.6}$ was highly correlated with $PM_{1.0}$, revealing that secondary aerosols tend to condense on smaller particles.

1. Introduction

Aerosol particles are of great importance in atmosphere due to their strong impact on climate change, visibility impairment, and public health. Adverse health effects related to fine and ultrafine particles largely depend on particle concentration, chemical composition, and deposition efficiency in human respiratory tract, while the latter is mostly associated with particle size, shape, and density (Cao et al., 2012; Pitz et al., 2008). In combination with the dynamic shape factor, density relates electrical mobility diameter of a particle to its aerodynamic diameter, which is a key parameter in deposition model (Hinds, 1999; Khlystov et al., 2004). Furthermore, density can be utilized in converting particle number concentration to particle mass loading, which is a crucial air quality index regulated in all countries (McMurry et al., 2002; Schmid et al., 2007). Additionally, time-series density can serve as a tracer for particle formation and aging process, since density changes in response to chemical reaction, condensation, and restructuring agglomerates (Katrib et al., 2005; Spencer et al., 2007; Zhang et al., 2008).

Several techniques for online measurement of particle density have been developed, which provide real-time monitoring of density variation. For example, Pitz et al. (2003) calculated the apparent particle density as the ratio of hourly $PM_{2.5}$ mass to hourly number-derived volume concentration. Khlystov et al. (2004) developed a density algorithm by merging electrical mobility with aerodynamic size distributions. Kostenidou et al. (2007) determined organic aerosol density by combining an aerodyne aerosol mass spectrometer (AMS) with a scanning mobility particle sizer (SMPS). McMurry et al. (2002) developed a novel technique for online measurement of size-resolved effective density through coupling a tandem differential mobility analyzer (TDMA) with an

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aerosol particle mass analyzer (APM). Since the pioneering work of McMurry et al. (2002), DMA–APM system has been applied in extensive laboratory experiments as well as field measurements (Geller et al., 2006; Malloy et al., 2009; Nakao et al., 2013; Zhang et al., 2008).

In the last decade, numerous field campaigns have been deployed in China for the purpose of better understanding physiochemical properties and atmospheric processing of ambient aerosols. However, density measurement is still limited (Hu et al., 2012). When density data was not available, researchers had to estimate $PM_{1.0}$ (particulate matters less than 1.0 μm in aerodynamic diameter) mass concentration using an assumed bulk aerosol density (Achtert et al., 2009; Massling et al., 2009). In this study, we conducted the first observation of size-resolved effective density of urban aerosols in Shanghai using DMA–APM system. Particle size distribution, $PM_{1.0}$ and chemical composition were also measured simultaneously to reveal the possible mechanism of density change.

2. Experimental

2.1. Sampling site

All measurements in this study were deployed at the main campus of Fudan University (31.30°N, 121.5°E). With the mixture of residential, traffic and industrial emissions, this measurement site is a good representation of urban area of Shanghai. Density measurement was conducted at the Department of Environmental Science and Engineering from December 6, 2012 to January 12, 2013, representing the typical wintertime conditions. Ambient aerosols were sampled from the inlet about 1 m above the roof of the building. The particle size distribution, $PM_{1.0}$ mass loading and chemical compositions were measured online at the supersite next to the Department of Environmental Science and Engineering with a distance of about 100 m.

2.2. Instrumentation and measurements

2.2.1. Effective density

The effective density in dry mobility diameter of 50–400 nm was determined by the TDMA–APM system at 8:00–19:00 local time from December 6, 2012 to January 12, 2013. The custom-built TDMA has been described in detail elsewhere (Ye et al., 2009). A compact aerosol particle mass analyzer (APM, Model 3601, Kanomax Inc.) was used to classify aerosol particles according to their mass-to-charge ratio. The classification principle of the APM was previously reviewed in detail by Tajima et al. (2011). A laboratory test showed that the performance of the Model 3601 compact APM operating at the aerosol flow rate of $0.3\ l\ min^{-1}$ was comparable to that of the Model 3600 APM at $1.0\ l\ min^{-1}$ (Tajima et al., 2013). The lower limit selected for the density measurement was 50 nm in mobility diameter in this study, because the mass of particles in the diameter of 30 nm or smaller could be significantly underestimated (Tajima et al., 2011, 2013). Briefly, the ambient aerosol was charged with a Kr^{85} neutralizer (Model 3077, TSI Inc.) and subsequently dried with a silica gel type diffusion drier and a Nafion drier (PD-50T-12ss, Perma Pure Inc.) before entering DMA1. The sample flow and the sheath flow were 0.3 and $3.0\ l\ min^{-1}$, respectively. Particles with a known size classified by DMA1 were introduced into the APM where particles passed through the rotating cylinders to the downstream Condensation Particle Counter (CPC) when the radial electrical and centrifugal forces were in balance. Mass distribution was then obtained by voltage scanning and particle counting. The effective density can be calculated by the following equation:

$$\rho_{\text{eff}} = \frac{m}{V} = \frac{m}{\frac{\pi}{6}D_p^3} \qquad (1)$$

where m is the particle mass and D_p is the particle mobility diameter.

Before the field observation, the TDMA–APM system was calibrated using 40–450 nm NIST-Traceable PSL particles. The average effective density $\rho_{\text{eff}} = 1.07 \pm 0.01\ g\ cm^{-3}$ was obtained, in good agreement with the material density ($1.05\ g\ cm^{-3}$).

2.2.2. Particle size distribution, $PM_{1.0}$ and chemical composition

Particle size distributions in the range of 10–500 nm were determined by a wide-range particle spectrometer (WPS™, Model 1000XP, MSP Inc.). The WPS consists of a DMA–CPC system to measure particle number distribution of 10–500 nm in mobility diameter, and a Laser Light Scattering (LPS) to characterize particles in the aerodynamic size range of 0.35–10 μm. Detailed description can be seen in Zhang et al. (2010). In this work, the WPS was operated in DMA mode, since the LPS system failed to work. The $PM_{1.0}$ mass loading was continuously measured with high time-resolution using a Thermo Scientific™ 5030 SHARP Monitor. An hourly based online measurement of 8 water-soluble inorganic ions (Cl^-, SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) in $PM_{1.0}$ was conducted with a Monitor for AeRosols and Gases (MARGA, Model ADI 2080, Applikon Analytical B.V.). This instrument has been described elsewhere (Du et al., 2010).

2.2.3. Meteorological conditions

Hourly meteorological data (temperature, relative humidity, wind speed and direction, and precipitation) were continuously measured by an automatic meteorological station (Model CAWS600, Huayun Inc., China) equipped with a high-performance temperature and RH sensor (Model HMP155, Vaisala Inc.).

3. Results and discussions

3.1. Overview of meteorological conditions

Shanghai is characterized as subtropical monsoon climate. Fig. 1 shows the hourly variations of temperature, relative humidity (RH), wind direction and speed, and precipitation during the whole observation. On average, the temperature was 4.8 ± 3.78 °C, with the highest hourly temperature of about 18 °C and the lowest hourly temperature below −3 °C. The average relative humidity was 68 ± 17.1%. In general, the changing trend of RH was roughly similar to temperature while the temporal variation pattern of RH was the inverse of temperature. The prevailing wind direction varied from northwest to northeast, with an average wind speed of $2.3\ m\ s^{-1}$. Occasionally, the prevailing wind was from south. There were 15 rainy days during the 38-day observation, with a total precipitation of 77.6 mm. The heaviest rainfall lasted from December 26 to 30, and accumulated around 40 mm precipitation.

3.2. Dependence of effective density on dry mobility diameter

Fig. 2 illustrates a set of typical density scans for particles in dry diameter of 50–400 nm. This set of samples was taken on January 6, 2013. Gaussian model was applied in fitting each density scan to determine the effective densities of the preset particles selected by DMA. The peak-fitted curves usually matched well with the measured density distributions. The effective density of 400 nm particles was not obtained in some cases (e.g. heavy precipitation) when the particle counts were below the detection limit. Single-peak density distribution was dominant during the observation.