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# Measurements of nonvolatile size distribution and its link to traffic soot in urban Shanghai

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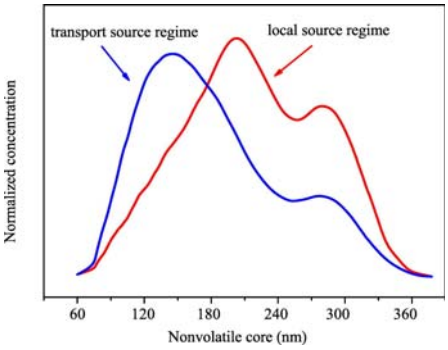
## HIGHLIGHTS

- Temporal variations of volatility shrink factor distribution is present.
- The concentration of nonvolatile mode particles is highly consistent with that of $NO_x$.
- The aerosol volatility is significantly different between haze and clean days.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Measurements of particle size distribution and size-resolved particle volatility were conducted using a volatility tandem differential mobility analyzers (V-TDMA) in the urban area of Shanghai during wintertime in January 2014. The nonvolatile mode particles with VSF exceeding 0.85 were always externally mixed with more-volatile mode particles. The average VSF ranged from 0.58 to 0.65 for 100–400 nm particles, increasing with the increase of particle size. On average, the nonvolatile mode contributed 15–20% of number fraction for 50–400 nm particles. Due to their hydrophobic nature, the nonvolatile particles were not easily removed by wet deposition. The concentrations of the nonvolatile mode particles and $NO_x$ were well correlated, indicating that the nonvolatile mode particles were mostly attributed to be fresh traffic soot. The diurnal variations in ensemble VSF and number fraction of nonvolatile mode particles exhibited two peaks in clean days, corresponding to morning and evening rush hours. The VSF distributions of 50 nm particles were similar during a transition between haze to clean periods whereas in the accumulation mode range, the number fraction of more-volatile mode and the amount of volatile materials in the more-volatile mode particles during haze periods are considerably larger than those in clean periods, indicating different contribution from transported sources.



## 1. Introduction

Soot is produced from incomplete combustion of fossil fuel and biomass burning (Kondo et al., 2006). Once emitted into the atmosphere, soot particles gradually become internally mixed with a variety of chemical components through several atmospheric aging processes

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(Gong et al., 2016; Qiu et al., 2012; Riemer et al., 2004; Zuberi et al., 2005). After aging processes such as condensation, coagulation, oxidation, and cloud processing, the structure and mixing state of the soot particles are changed significantly (Chen et al., 2016; Ghazi and Olfert, 2013; Zhang et al., 2008).

Consisting mainly of black carbon and possibly coating with a thin layer of organic carbon, Soot particles are generally regarded as the most efficient light absorbing component of atmospheric aerosols (Bond and Bergstrom, 2006; Bond et al., 2013; Fierce et al., 2016; Rosen et al., 1978). After atmospheric aging with sulfate, nitrate, or organic carbon, the light absorbing capacity of internally mixed soot particles is quite distinct from the freshly emitted external mixture (Bond and Bergstrom, 2006). A nearly 2-fold enhancement on light absorption was observed after coating soot particles with sulfuric acid and subsequent hygroscopic growth at 80% RH (Zhang et al., 2008). It was suggested that soot was the second most important component of global warming after $CO_2$ in terms of direct forcing (Jacobson, 2001). Besides influence on their climate effects, the mixing state of soot particles also exists strong impact on atmospheric visibility. In urban area, traffic source is the major contribution of externally mixed soot particles whereas long-range transported soot particles are internally mixed with other particles or volatile compounds (Wehner et al., 2009). However, fresh soot particles are possibly modified to internally mixed in a very short time under the background of highly pollution (Gong et al., 2016).

To determine the mixing state of soot particles, V-TDMA was extensively employed both in laboratory research and field observations (Cheung et al., 2016; Sakurai et al., 2003; Wang et al., 2017; Wehner et al., 2009). After the pioneering work of Rader and McMurry (1986), Wehner et al. (2004) developed a V-TDMA that was capable of distinguishing volatile and non-volatile particles in the urban environment. On the basis of residual particle size distribution at temperature up to 300 °C, the V-TDMA can not only estimate the nonvolatile particle fraction of a selected monodisperse aerosol but also detect the thickness of volatile coating for the particles aged with a large amount of volatile substances.

Over the past 30 years, rapid industrialization and urbanization in China is accompanied with the increasing consumption of fossil-fuel such as coal, oil, and natural gas. A large amount of carbonaceous aerosols were emitted from power plant, daily traffic, industrial activities, and biomass burning, causing a significant impact on visibility, climate, and human health in China (Butt et al., 2016; Chen et al., 2017; Zhang et al., 2015). In this study, measurements of size-resolved aerosol volatility were conducted using a custom-built V-TDMA in the urban area of Shanghai during wintertime in January 2014. We present time-series of nonvolatile size distribution for 50–400 nm particles. Characteristics of aerosol volatility in clean and haze periods are discussed in detail. Also, the relations between nonvolatile mode particles and the concentrations of $SO_2$ and $NO_x$ are investigated by comparing their temporal variations.

## 2. Experimental

### 2.1. Sampling site

The observation was deployed at the main campus of Fudan University (31.30°N, 121.5°E). There are many residential quarters and commercial blocks in the surrounding area. At 400 m south and 1000 m west of the measurement site, there are the Middle Ring Line and the Yixian Elevated Road, respectively, two of the busiest main roads in the city. Influenced with mixing pollutants emitted from traffic, residential, and industrial sources, the measurement site is a good representative of urban area in Shanghai.

### 2.2. Volatility measurements

The volatility measurement was conducted from January 1 to 20, 2014 in the Environmental Building in the school using the custom-built V-TDMA. The ambient aerosol was pumped into the laboratory at 10 l $min^{-1}$ through a main sampling tube with an inner diameter of 1/2 in. The inlet of the sampling tube was about 1 m above the roof of the building. A 0.4 l $min^{-1}$ aerosol sample was bypassed at the end of the main sampling tube and introduced into the V-TDMA through a 1.5 m long Swagelok® stainless steel tube with a 1/4 in diameter.

The V-TDMA was upgraded from our custom-built hygroscopic-TDMA described previously in detail (Ye et al., 2009). In the V-TDMA (Fig. 1), the heat denuder is located between the upstream and downstream DMAs (Model 3081 L, TSI Inc.) instead of the humidifier in the hygroscopic TDMA. Briefly, the aerosol sample was dried at RH < 20% (determined by the RH sensor before the Condensation Particle Counter (CPC, Model 3771, TSI Inc.)) before charging and subsequently entering the upstream DMA1. The V-TDMA was operated alternatively in SMPS mode and then V-TDMA mode. In the SMPS mode, particle size distribution in the range of 14–600 nm dry diameter was determined. In the V-TDMA mode, the monodisperse aerosols with dry mobility diameters of 50, 100, 200, 300, and 400 nm were selected and then sent to the heat denuder at 300 °C in turn. The residence time of the selected aerosols in the heating zone of the denuder is about 1.5 s. Finally, the residual aerosols after evaporation at 300 °C were screened by the downstream DMA2 to obtain the nonvolatile size distribution. The volatility shrink factor (VSF) is defined as relative decrease in mobility diameter of dry particles due to evaporation at a certain temperature:

$$VSF = \frac{D_T}{D_0}$$

where $D_T$ is the mobility diameter of residual particles after heating at a specific temperature T, and $D_0$ is the initial dry particle mobility diameter of the selected monodisperse aerosol.

### 2.3. Measurements of air quality index and meteorological parameters

The meteorological parameters (e. g., ambient temperature, relative humidity, wind direction and speed, and precipitation) were continuously measured by an automatic meteorological station (Model CAWS600, Huayun Inc., China) equipped with a Model HMP155 temperature and RH sensor. The data about air pollutants (e. g. the hourly concentrations of $PM_{2.5}$, $SO_2$, and $NO_x$) were provided by the Pudong Area Monitoring Station of the Shanghai Environmental Monitoring Center, a distance of ~8 km to the main campus of Fudan University.

## 3. Results and discussion

### 3.1. Overviews of meteorological conditions

Located at the estuary of the Yangtze River, Shanghai has a subtropical monsoon climate with the prevailing wind directions typically from northwest to northeast in the winter and from southeast to southwest in the summer (Chan and Yao, 2008). Fig. 2 shows the main meteorological parameters during the observation. The ambient temperature (T) and relative humidity (RH) displayed obvious diurnal cycle patterns,

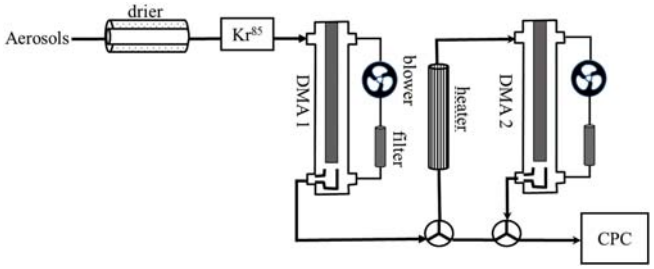


**Fig. 1.** A schematic plot of the custom-built Volatility-TDMA system.