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Particle number concentration, size distribution and chemical composition during haze and photochemical smog episodes in Shanghai

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ABSTRACT

The aerosol number concentration and size distribution as well as size-resolved particle chemical composition were measured during haze and photochemical smog episodes in Shanghai in 2009. The number of haze days accounted for 43%, of which 30% was severe (visibility < 2 km) and moderate (2 km ≤ visibility < 3 km) haze, mainly distributed in winter and spring. The mean particle number concentration was about 17,000 /cm^3 in haze, more than 2 times that in clean days. The greatest increase of particle number concentration was in 0.5–1 μm and 1–10 μm size fractions during haze events, about 17.78 times and 8.78 times those of clean days. The largest increase of particle number concentration was within 50–100 nm and 100–200 nm fractions during photochemical smog episodes, about 5.89 times and 4.29 times those of clean days. The particle volume concentration and surface concentration in haze, photochemical smog and clean days were 102, 49, 15 μm^3/cm^3 and 949, 649, 206 μm^2/cm^3, respectively. As haze events got more severe, the number concentration of particles smaller than 50 nm decreased, but the particles of 50–200 nm and 0.5–1 μm increased. The diurnal variation of particle number concentration showed a bimodal pattern in haze days. All soluble ions were increased during haze events, of which NH_4^+, SO_4^{2-} and NO_3^- increased greatly, followed by Na^+, K^+, Ca^{2+} and Cl^-. These ions were very different in size-resolved particles during haze and photochemical smog episodes.

Introduction

High concentrations of particles can affect light absorption and scattering, thus impacting regional visibility and climate. They can also degrade air quality and pose a threat to human health. In recent years, haze events caused by fine particle pollution in megacities have occurred more and more frequently. Impaired visibility has become a hot topic in atmospheric research. In 2010, the industry standard for the observation and forecasting levels of haze (QX/T 113-2010) was promulgated and implemented by

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the China Meteorological Administration. In 2012, the new air quality standard was put in place in China, in which the standard for $PM_{2.5}$ daily average concentration was set at 75 μg/m^3. In addition, regulatory monitoring networks for $PM_{2.5}$ were built in different cities across the country (Yuan et al., 2012).

So far, most haze studies in China have been in the North China Plain, in which Beijing is located (Tao et al., 2012; T. Yang et al., 2012; Li et al., 2009, 2010, 2011; Guo et al., 2012a; Duan et al., 2012; Ma et al., 2010; Wang et al., 2006; Z.T. Wang et al., 2012; Sun et al., 2006; Yu et al., 2011), and the Pearl River Delta region, where Guangzhou is situated (Wu et al., 2007; Tan et al., 2009, 2011; Chen et al., 2009; Guo et al., 2012b; X.M. Wang et al., 2012; Lu et al., 2009; Andreae et al., 2008; Xu et al., 2008). Most of these studies involve particle mass concentration, composition and optical properties in haze, while very few studies (Quan et al., 2011; Chen et al., 2012a) have looked at the particle number concentration and size distribution. In the study by Quan et al. (2011), the number concentration of dry aerosols (relative humidity (RH) < 40%) in the size range of 10–662 nm was as high as 24,000 /cm^3 during the period of dense haze mixed with fog on the North China Plain from November 5th to 8th, 2009. The formation of fog was increased with the large amount of particles serving as nuclei, leading to extremely low visibility of less than 100 m. Chen et al. (2012a,b) found that the average number concentration and volume concentration of dry particles (RH < 30%) in the size range of 3 nm–10 μm were 17,200 /cm^3 and 70.9 μm^3/cm^3, respectively, during another haze event on the North China Plain from July 13th to August 14th, 2009. They found that when RH < 90%, high particle volume concentration contributed more to visibility impairment than the increase of RH. However, they did not measure the size distribution. Although Shanghai is the largest megacity in the Yangtze River Delta region (YRD), there have been a few studies on haze here (Fu et al., 2008; Chen et al., 2012b; F. Yang et al., 2012; Huang et al., 2012; Du et al., 2011; Ye et al., 2011; Hou et al., 2011), mainly on chemical composition. Few results have been reported on particle number concentration, chemical composition and size distribution in haze in Shanghai, and studies focused on both haze and air oxidation have been rare.

However, photochemical smog, characterized by high ozone and other oxidant levels, has remained one of the severe environmental problems of the YRD (Ma et al., 2012). Frequent adverse effects of elevated ozone levels on the air quality were becoming a cause for concern from early summer to early autumn, even though no haze events appeared. Ozone pollution contributed to heart and respiratory disease, especially to susceptible groups (Zhang et al., 2006). Most days of high ozone concentration could easily be overlooked by the public when no haze was present.

To obtain a more complete picture on the characterization of haze and photochemical smog in this coastal megacity as well as the processes of their formation and removal, additional data were needed. In this study, we reported the occurrence frequency of different levels of haze and ozone concentration during the year, and measured the aerosol number concentration, size distribution and size-resolved particle chemical compositions at Fudan University, an urban site in Shanghai, during haze and photochemical smog episodes in 2009. The conclusions and suggestions provide reference data for decision making by air pollution treatment administrators.

1. Material and methods

1.1. Description of sampling sites

Sampling sites were located at the roof of a five-story building, about 20 m above ground, in the campus of Fudan University. The campus is in a commercial and residential area. The sampling inlet was set up according to standard air quality monitoring methods.

1.2. Sampling instruments and sample analysis

The Wide-Range Particle Spectrum 1000XP (MSP Company, Minneapolis, MN, USA) was used in this study. It could measure the number concentration of particles in size ranges from 10 nm to 10 μm, and the particle volume concentration and surface concentration could also be derived *via* predetermined algorithms. The instrument uses a Differential Mobility Analyzer (DMA) and Condensation Particle Counter (CPC) to measure particles between 10 nm and 0.5 μm and a Laser Particle Spectrometer (LPS) to measure particles between 0.35 and 10 μm. The instrument was calibrated with standard particle samples before and after sampling periods. It took about 3 min for one complete scan of the entire size range. More details on the instrument have been described elsewhere (Gao et al., 2009; Zhang et al., 2010).

Ozone was measured using a UV Photometric Ozone analyzer (Model 49i, Thermo Fisher Scientific Inc., Waltham, MA, USA), and was recorded each minute. Quality control checks were performed as per specifications including zero, precision and span checks. Filters were replaced every week, and calibration was carried out every three months.

An Andersen 1 ACFM Eight-stage Cascade Impactor (Thermo Fisher Scientific Inc., Waltham, MA, USA) was used for particle size-segregated sampling. The particle size ranges captured by the eight stages were 0.4–0.7, 0.7–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9.0 and 9.0–10 μm, respectively. Particles were collected with Whatman 41 fiber filters (GE Healthcare UK Ltd, Buckinghamshire, England), with a pore size of 0.2 μm. Filters were placed in a chamber with constant humidity (40 ± 1)% and temperature (20 ± 1)°C for 24 hr and then weighed with an electronic balance (accuracy = 10 μg), before and after sampling. Sampled filters were folded and wrapped with sulfuric acid paper and stored in sealed plastic bags refrigerated at −20°C for further analysis of chemical composition. Each sample and control was cut diagonally into 8 pieces before analysis. Two pieces were used to extract ions by ultrasound in 10 mL pure water (18 MΩ/cm^3) for 20 min. The liquid was filtered with a microporous membrane and analyzed by ion chromatography. Ions measured in the analysis included Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, NO_3^-, Cl^-, $HCOOH^-$, $C_2H_2OOH^-$, HNO_2^- and F^-.

1.3. Meteorological data

Meteorological parameters such as half-hour average visibility, RH and precipitation in 2009 were collected from www.wunderground.com.