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Measurement of ambient aerosols by single particle mass spectrometry in the Yangtze River Delta, China: Seasonal variations, mixing state and meteorological effects

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ABSTRACT

Continuous measurements of ambient aerosols were performed with a single-particle aerosol mass spectrometer in Nanjing during all four seasons of 2015. Ambient particles were clustered into 11 classes, which included elemental carbon (EC) mainly with sulfate (EC-S); EC with nitrate and sulfate (EC-SN); EC with obvious organic signals (ECOC); organic carbon (OC); biomass/biofuel burning particles (Biomass); Ammonium; particles with obvious Na, K (NaK) and sulfate (NaK-S), NaK with nitrate and sulfate (NaK-SN); iron-containing particles (Fe-rich); miscellaneous metal-containing particles (MiscsMetals) and Dust. Seasonal local sources, dominated air masses and distinct atmospheric processes all affected the concentrations of various particles and caused different diurnal changes. EC-SN during summer slowly increased in the afternoon and NaK-SN had a peak at noon during winter. Differences in size distribution of each particle type between seasons were discussed. All types of particles showed unimodal number size distributions, their peak radius ranked as follows: fall < spring < summer ≤ winter. OC during fall had higher number fractions of between 0.2 and 0.5 μm (> 20%) as a result from the decrease in temperature and increase in relative humidity (RH). The distributions of ECOC varied with seasons and were obviously influenced by EC and OC particles. Mixing states showed seasonal variations. In general, the fractions of particles mixed with secondary species were the highest/lowest in winter/fall. The effects of meteorological conditions on particles were investigated. With the increase of RH, the fractions of EC increased, and most particles mixed with more NH_4^+ and less $C_2H_3O^+$. Characteristics of precipitation, such as duration and total rainfall amount, influenced particles. Enhanced secondary organic/inorganic species were found in particles during long-/short-term precipitation with intensities < 1 mm. Less NH_4^+, $C_2H_3O^+$ and HSO_4^- were found during precipitation compared with non-precipitation days.

1. Introduction

Atmospheric visibility, air quality, public health and global climate are closely related to the characteristics of aerosol particles, and thus, relevant studies are appearing worldwide (Bäumer et al., 2008; Langridge et al., 2012; Lohmann and Feichter, 2005; Poschl, 2005; Tang, 2010). The Yangtze River Delta (YRD) is the largest estuary delta and one of the most developed and densely populated regions; rapid industrialization and urbanization has resulted in numerous pollutants in the air, which has facilitated serious air pollution (Fu et al., 2014; Wang et al., 2014). Nanjing is one of the largest cities in the YRD, which is also a comprehensive industrial base in eastern China. Due to various sources and meteorological conditions, the particle matter (PM) level in Nanjing still is high and haze pollutions appear frequently, especially during winter (Fu et al., 2013; Kang et al., 2013; Li et al., 2015). Considering that meteorological conditions differ dramatically between seasons, the seasonal variations in the chemical components, size distributions and mixing states of aerosol particles are notable and worth investigation.

The most intuitive, seasonality of ambient chemical components was varied. Results in urban Nanjing showed a high secondary organic carbon/organic carbon (SOC/OC) ratio during summer, which was attributed to stronger oxidation, and the OC and elemental carbon (EC) had the highest levels during winter due to the stable weather (Li et al., 2015). As shown in the research of Zhuang et al. (2014), concentrations of black carbon aerosol (BC) in urban Nanjing were high in spring and autumn and low in summer. Observations at the four sites in the YRD region exhibited clear seasonal trends in the concentrations of fine

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particles and ambient trace metals, which showed higher concentrations during winter and lower concentrations during summer (Ming et al., 2017).

Numerous previous studies also showed that the number size distributions of aerosols exhibited distinct seasonal variations and were significantly affected by meteorological factors (Zhang et al., 2013; Zhu et al., 2013). Zhu et al. (2013) presented the variations in number concentrations of particles in different size ranges in Nanjing, particles in the nuclei mode and accumulation mode had the lowest and the highest concentrations in autumn, respectively because of accumulation processes in the persistent air pollution. Yu et al. (2011) observed bimodal logarithm normal structures of aerosol volume size distributions during long-term measurement in the YRD; the fine modes had a larger peak radius in summer, whereas the coarse modes had a larger peak radius in winter.

Mixing states could influence optical properties, hygroscopicity and atmospheric lifetime of aerosols (Cahill et al., 2012), thus complicate their impact on visibility. Wang et al. (2015) observed enhanced sulfate and nitrate in carbonaceous particles during haze days in Nanjing. Due to the energy structures of the YRD, particles from local sources mixed with more chloride and nitrate, while others from long-range transportation mixed with more sulfate (Hu et al., 2018). Also the authors suggested aerosols mixed with more organics and nitrate in short-term rainfall which were different from that in long-term rainfall. Compared with rainy spring in Guangzhou, enhanced sulfate and oxidized organics were found in carbon-containing particles during the fall (Zhang et al., 2013). Wintertime submicron aerosols in Beijing showed more enhanced organics and chloride than aerosols in summer (Sun et al., 2013).

The evident seasonal activities could lead to substantial changes in ambient aerosols. Using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) in Nanjing, Zhang et al. (2015) suggested that high PM pollution appeared during harvest seasons (summer and autumn). Observation focused on biomass burning in Nanjing also showed high levels of BC (Zhuang et al., 2014) and close link between OC and estimated K^+ (Li et al., 2015). Moreover, fireworks burning was identified to be an important source of polycyclic aromatic hydrocarbons in Nanjing during the Chinese Spring Festival with reduced traffic, industrial and construction activities (Kong et al., 2015). In addition, coal combustion was the largest primary source during the heating season in Beijing (Sun et al., 2013).

Meteorological conditions such as the origin of air masses, temperature, relative humidity (RH), precipitation, turbulent mixing, wind speeds and direction are mainly reflected in the formation, diffusion/accumulation and deposition processes of aerosols. All of the referenced researches above have more or less mentioned the impacts of meteorological conditions on ambient particles. Here are more examples, freshly pure BC particles were observed to age rapidly from photochemical processes (Ma et al., 2017). Particles mixed with substantial sulfate and OC during afternoon were results from photochemical reactions, meantime, nitrate was correlated well with aerosols during the night because of heterogeneous hydrolysis of N_2O_5, low temperature and high RH (Zhang et al., 2017). Liang et al. (2017) pointed that stable conditions are essential for the variations of aerosol chemical components, and the aqueous-phase reaction is important for the formation of $PM_{2.5}$ at high RH (Zhang et al., 2018).

Above all, it is obvious that most studies have concentrated on summer and winter, and thus, there has been a lack of comprehensive research on seasonal contrasts, as well as carbonaceous particles (which basically referred to EC and OC) have been the main focus, which does not represent all air conditions. Moreover, mixing states have been discussed in many special conditions, such as polluted periods and rainfall processes. Although seasonal differences also exist in mixed states, there are fewer relevant reports. Relevant seasonal studies also were limited by instruments. Traditional observations could not provide real-time single particle results, which prevented us from detailed learning about the interactions between various particles, as well as the dependence of aerosols on meteorological conditions. Furthermore, accurate observations would provide new insights into the atmospheric processes experienced by particles after emission and their seasonal differences. Although considering the results from Xu et al. (2017) and Sultana et al. (2017), there are some issues need to be fixed and we will explore those in depth in the following work.

The observation site is surrounded by commercial areas, residential areas and industrial; thus, the sampled particles were influenced by numerous sources. We conducted continuous measurements of ambient aerosols using real-time single particle aerosol mass spectrometer (SPAMS), and comprehensively analyzed seasonal variations in single particles in this paper. Furthermore, we discussed the correlations between ambient particles and meteorological conditions with the sincere hope these results would provide a more scientific basis for understanding the atmospheric processes of aerosols and air pollution mitigation.

2. Experimental methods

2.1. Sampling

Single particle measurements were obtained over nearly a year in 2015 using SPAMS (Guangzhou Hexin Analytical Instrument Co., Ltd., China); winter (between 1 and 31 January 2015), spring (from 29 March to 20 April 2015), summer (from 16 June to 15 July 2015) and fall (between 1 and 31 October 2015) periods were chosen to investigate the characteristics of particles during different seasons. Influenced by Changjiang-Huaihe Meiyu, the total rainfall duration (amount) during summer in Nanjing was 166-h (489.6 mm), which was 3.0 (15.6), 2.7 (5.4) and 3.3 (5.8) times larger than that during winter, spring and fall, respectively.

The observation site is located on the top of the meteorological building, which is approximately 40 m from the ground and 62 m above sea level, on the campus of Nanjing University of Information Science and Technology (NUIST, 32.21°N, 118.72°E). Within 1 km of the eastern observation site, there are some iron and steel plants and cogeneration plants. The Nanjing Chemical Industry Park and Yangzi Petrochemical are located to the north of the site. In addition, to the west of the site were villages and agricultural fields, which included agricultural product factories, ecological parks and vineyards. Additionally, there are many roads around the observation point, such as Jiangbei Avenue Expressway in the east and G40 Hushan Expressway in the west.

2.2. Instruments and data analysis

The d_{va} (vacuum aerodynamic diameter) and chemical components of single particles were analyzed using SPAMS, which has been described in detail in previous studies (e.g., Li et al. (2011)). Briefly, aerosol particles are introduced into SPAMS using an aerodynamic lens, and then those particles are detected and aerodynamically sized by two continuous wave 532-nm green lasers. The particle chemical composition is subsequently detected through a desorption/ionization process using a pulsed laser (266 nm), and then, mass to charge ratios (m/z) for individual ions are analyzed. Particle size and mass calibrations for this instrument were carried out using standard polystyrene latex particles (PSL) and metallic solution.

The size distribution and chemical composition of particles were analyzed by YAADA software (www.yaada.org), which is used for processing the single particle mass spectral data with a MATLAB-based software toolkit. Single particle mass spectra were grouped using an adaptive resonance theory neural network, ART-2a (Song et al., 1999). During all seasons, the most abundant (96%) particles with d_{va} of 0.2–2.0 μm were analyzed. We used a learning rate of 0.05, vigilance factor of 0.7, and 19 iterations in this experiment for ART-2a. Further