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Mixing state of ambient aerosols during different fog-haze pollution episodes in the Yangtze River Delta, China

Rui Hu[a], Honglei Wang[a,*], Yan Yin[a,**], Kui Chen[a], Bin Zhu[a], Zefeng Zhang[a], Hui Kang[a], Lijuan Shen[a,b]

[a] *Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters, Key Laboratory for Aerosol-Cloud-Precipitation of China Meteorological Administration, Nanjing University of Information Science &Technology, Nanjing 210044, China*
[b] *Jiaxing Environmental Monitoring Station, Jiaxing 314000, China*

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ABSTRACT

The mixing state of aerosol particles were investigated using a single particle aerosol mass spectrometer (SPAMS) during a regional fog-haze episode in the Yangtze River Delta (YRD) on 16–28 Dec., 2015. The aerosols were analyzed and clustered into 12 classes: aged elemental carbon (Aged-EC), internally mixed organics and elemental carbon (ECOC), organic carbon (OC), Biomass, Amine, Ammonium, Na-K, V-rich, Pb-rich, Cu-rich, Fe-rich and Dust. Results showed that particles in short-term rainfalls mixed with more nitrate and oxidized organics, while they mixed with more ammonium and sulfate in long-term rainfall. Due to anthropogenic activities, stronger winds and solar radiation, the particle counts increased and the size ranges of particles broadened in haze. Carbonaceous particles and Na-K mixed with enhanced secondary species during haze, and obviously were more acidic, especially for the ones with a size range of 0.6–1.2 μm. For local and long-range transported pollution, OC had distinct size distributions while the changes of ECOC were uniform. The secondary formation of ECOC contributed significantly in local pollution and affected much smaller particles (as small as 0.5 μm) in long-range transported pollution. And long-range transported pollution was more helpful for the growth of OC. Particles mixed with more chloride and nitrate/sulfate in local/long-range transported pollution.

1. Introduction

Atmospheric visibility, air quality, public health and global climate are closely related to the size distribution, chemical composition and mixing state of aerosol particles (Bäumer et al., 2008; Chang et al., 2014; Langridge et al., 2012; Lohmann and Feichter, 2005; Poschl, 2005). The YRD is the largest estuary delta and one of the most developed and densely populated regions in the world, and rapid industrialization and urbanization have resulted in numerous pollutants in the air and facilitated serious air pollution (Fu et al., 2014; Wang et al., 2014), there were many studies indicated that high concentrations of particulate matter (Chan and Yao, 2008) and extremely low visibilities occurred in the YRD region (Fu et al., 2008; Gao et al., 2011).

Caused significant impacts on the local and/or regional air quality, the haze episodes are characterized by low visibility, high particle mass loading and aerosol optical depth (Hu et al., 2016; Wang et al., 2014; Zhang, 2015). And as an another important horizontal obscuration, fog could facilitate the accumulation of the pollution of $PM_{2.5}$ (particular matter with size less than 2.5 μm) and PM_{10} (particular matter with size less than 10 μm) near the ground layer and affect the size distributions of PM_{10} (Meng et al., 2015), meantime, fogs contribute an aqueous reaction medium to aerosol mass formation through gas scavenging and chemical reaction in the droplets (Dall'Osto et al., 2009b). Haze and fog events all could change particles' chemical composition and mixing state clearly, and result in most aerosols internally mixing with secondary species such as nitrate, sulfate, and ammonium. Their mixing states further influenced their optical properties, hygroscopicity and atmospheric lifetime (Cahill et al., 2012), thus complicate their impact on visibility. Due to the diurnal variation of relative humidity (RH), the fog and haze episodes could transform each other in one day. Numerous studies focused on the characteristics of fog and/or haze (e.g., Yuskiewicz et al. (1996), Zhang et al. (2013), Li (2015)), however, it is difficult to make a strict distinction between fog and haze, their conversion is fast. In this study, the time resolution of single results was improved with the help of SPAMS, like five minutes, to investigate the

* Corresponding author.
** Corresponding author.
E-mail addresses: hongleiwang@nuist.edu.cn (H. Wang), yinyan@nuist.edu.cn (Y. Yin).

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characteristics of ambient particles in this process. Because of the fast and frequent transformation, the regional pollution occurred in the YRD during 16–28 Dec., 2015 was referred to as a fog-haze episode. This event had a large range of influence, lasted quite a long time, had aroused widespread public concern, and was worthy to discuss.

The regional pollution could form through the combination of local sources and long-range transport, which is prominent in megacity clusters, such as the YRD (Shao et al., 2006; Shen et al., 2015; Zhu and Zhao, 2011). While local and long-range pollution lead to distinct chemical composition, concentration (Skyllakou et al., 2014), and size distributions (Ding et al., 2017) of particles. Particles from regional or long-range transport are expected to become larger due to the formation of secondary species (such as sulfate and nitrate) during sufficient aging processes (Johnson et al., 2005; Roldin et al., 2011). Ault et al. (2009) noted that influenced by regional transport events, particle concentrations in San Diego region were 2–4 times higher than typical average concentrations from local sources. Ding et al. (2017) analyzed the PM results in the Shanghai, YRD and yielded similar conclusions. Using Aerosol Time-of-Flight Mass Spectrometry (ATOFMS), Dall'Osto et al. (2009a)analyzed the mixing state of local and regional nitrate particles which behaved differently. Particles came from various sources experienced different atmospheric reactions, it is essential to analyze particles under a high temporal resolution and at a single-particle scale, to provide more detailed information.

Considering the large-scale pollution, the diffusion of pollutants within megacity cluster was ignored, the YRD was taken as a whole to study the impacts of external transport (emissions are located outside the research region) and local sources (emissions within the research region are included) on the air quality of megacity cluster. The pollution was divided into local pollution and long-range transported pollution based on the length of back-trajectories. By using SPAMS, which can obtain the aerodynamic diameter and chemical composition of a single particle in real-time, and coupling with back-trajectories and $PM_{2.5}$, we expect to complete the knowledge of influences of local/long-range sources on different particles in a megacity cluster. Meanwhile, the impact of precipitation on air quality is closely related to rainfall intensity, duration and their types (Yuan, 2014). Weak short-term rainfall processes provide high relative humidity and liquid phase reaction interface that might contribute to the growth of certain types of particles and cannot mitigate the air pollution effectively. Two types of rainfall processes with different duration during sampling were observed, and it is interesting to investigate the differences of particles between short-term and long-term rainfall.

Nanjing is one of the most representative and largest cities in the YRD and is also a comprehensive industrial base in eastern China. The PM level in this region is high, and fog-haze pollution appears frequently, especially in winter (Fu et al., 2013; Kang et al., 2013; Li et al., 2015). Influenced by this regional pollution, half of the days in Nanjing was, and sometimes even exceeded, the moderately polluted level (Fig. S1). Combined with the meteorological conditions, by exploring the characteristics of $PM_{2.5}$ and ambient particles, we hope it will provide a more scientific basis for aerosol source apportionment and air pollution mitigation.

2. Experimental methods

2.1. Sampling

The size and chemical composition of single particles were analyzed during 16–28 Dec., 2015, using a SPAMS (Guangzhou Hexin Analytical Instrument Co., Ltd., China). 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, as well as Ningliu Road. The Nanjing Chemical Industry Area and Yangzi Petrochemical are located to the north of the site.

2.2. Instruments and data analysis

The 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 chemical composition of particles is subsequently detected through desorption/ionization process using a pulsed laser (266 nm) and mass to charge ratios (m/z) for individual ions are then analyzed. Particle size and mass calibrations for this instrument were carried out every three months 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 with an Adaptive Resonance Theory neural network, ART-2a (Song et al., 1999). Particles with the vacuum aerodynamic diameter of 0.2–2.0 μm were analyzed. We used a learning rate of 0.05, vigilance factor of 0.70, and 19 iterations in this experiment for ART-2a. Further manual classification was used to refine the aerosols into 12 chemical classes based on mass spectral similarity (Table 1).

Meanwhile, the hourly $PM_{2.5}$ was observed using a FH62C14 (Thermo Fisher Scientific Co., USA) with 30-min resolution. The hourly meteorological parameters (wind speed (WS) and direction (WD), temperature, RH, visibility, and precipitation) used in this observation were obtained from China Meteorological Administration observing, training and practice base (Nanjing) located on the campus of NUIST (http://web.nuist.edu.cn/gcjd/). The detailed analysis of meteorological conditions was placed in the Supplementary Material. The criterion of fog and haze process was defined by the Chinese Meteorological Administration and Hu et al. (2016): (1) for the fog process: visibility $<$ 10 km and RH $>$ 90%; (2) for the haze process: visibility $<$ 10 km and RH ≤ 90%.

3. Results and discussions

3.1. Mass spectral characteristics of particles

Particles were classified according to the characteristic peaks in their mass spectra (Table S1). As shown in Table 1, carbonaceous particles dominated over the sampling period, accounting for 68.8% of the total. From Fig. 1, aged elemental carbon (Aged-EC) particles had larger $C_n^{\pm}$ fragment peaks (e.g., $m/z \pm 24, \pm 36, \pm 48$) and fragments

Table 1
Summary of number counts and fractions of single-particle classes.

Single particles classes	Number count	Number fraction[a] (%)
Aged-EC	1,020,848	33.3
ECOC	250,244	8.2
OC	441,151	14.4
Biomass	397,259	12.9
Amine	11,871	0.4
Ammonium	57,306	1.9
Na-K	526,490	17.2
V-rich	34,210	1.1
Pb-rich	36,880	1.2
Cu-rich	11,479	0.4
Fe-rich	202,830	6.6
Dust	78,567	2.6

[a] Number fraction was calculated through dividing the number count of each particle classes by the total particle count.