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Chemical characteristics and sources of PM_1 during the 2016 summer in Hangzhou☆

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ABSTRACT

During the 2016 Hangzhou G20 Summit, the chemical composition of submicron particles (PM_1) was measured by a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) along with a suite of collocated instruments. The campaign was undertaken between August 5 and September 23, 2016. The impacts of emission controls and meteorological conditions on PM_1 chemical composition, diurnal cycles, organic aerosol (OA) source apportionment, size distribution and elemental ratios were characterized in detail. Excluding rainy days, the mean PM_1 mass concentration during G20 was 30.3 μg/m^3, similar to that observed before G20 (28.6 μg/m^3), but much lower than that after G20 (42.7 μg/m^3). The aerosol chemistry during the three periods was substantially different. Before G20, high PM_1 loading mostly occurred at daytime, with OA accounting for 60.1% of PM_1, followed by sulfate (15.6%) and ammonium (9.1%). During G20, the OA fraction decreased from 60.1% to 44.6%, whereas secondary inorganic aerosol (SIA) increased from 31.8% to 49.5%. After G20, SIA dominated high PM_1 loading, especially at nighttime. Further analysis showed that the nighttime regional transport might play an unfavorable role in the slight increase of secondary PM_1 during G20, while the strict emissions controls were implemented. The OA (O/C = 0.58) during G20 was more aged, 48.7% and 13.7% higher than that before and after G20 respectively. Our study highlighted that the emission controls during G20 were of great success in lowering locally produced aerosol and pollutants, despite of co-existence of nighttime regional transport containing aerosol high in low-volatile organics and sulfate. It was implied that not only are emissions controls on both local and regional scale important, but that the transport of pollutants needs to be sufficiently well accounted for, to ensure the successful implementation of air pollution mitigation campaigns in China.

1. Introduction

Atmospheric haze pollution has become a major environmental problem in China, and has received much attention in recent years (Chen et al., 2017; Guo et al., 2014; Huang et al., 2014; Li et al., 2017a; Peng et al., 2016; Tong et al., 2017). A major component of this haze is fine particles, which have extinction effects on sunlight, leading to decreased visibility and haze formation (Huang et al., 2014; Li et al., 2017b; Peng et al., 2016). Particles with diameters between 0.4 and 1.0 μm have the highest extinction potential in the atmosphere, as the wavelength of visible light is between 0.4 and 0.7 μm (Madronich and Flocke, 1999; Zhuang et al., 2014). Therefore, measurements of submicron particles (PM_1) chemical composition are essential for elucidating the aerosol sources and reaction mechanisms, as well as the role of regional transport in haze formation.

The Aerodyne Aerosol Mass Spectrometer (AMS) is a robust and highly sensitive instrument which provides real-time characterization and composition of size-resolved non-refractory submicron aerosol (NR-PM_1) (DeCarlo et al., 2006; Drewnick et al., 2005; Jimenez et al., 2009). Since the first deployment in China in 2006

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(Takegawa et al., 2009), it has been used to characterize aerosol at a number of different sites, including Beijing (Sun et al., 2010, 2016a), Shanghai (Huang et al., 2012), Lanzhou (Zhang et al., 2017), Hong Kong (Huang et al., 2015), as well as some cities in the Yangtze River Delta (YRD) region such as Nanjing (Wang et al., 2016a, 2016b; Zhang et al., 2015), Yangzhou (Ge et al., 2017) and Changzhou (Ye et al., 2017a, 2017b). Li et al. (2017c) has summarized the AMS field studies in China, and it has been widely recognized that frequent haze pollution events are caused by a combination of large amounts of primary particle emissions, rapid secondary aerosol formation and typically stagnant meteorological conditions (Sun et al., 2014, 2016b). Despite the many studies undertaken to determine the sources and formation mechanisms of severe haze pollution in China, the responses of aerosol chemistry to meteorology and emissions remain poorly understood.

In recent years, the Chinese government has implemented the "Atmospheric Pollution Prevention and Control Action Plan", aiming to reduce $PM_{2.5}$ in the Beijing-Tianjin-Hebei region, the Yangtze River Delta, and the Pearl River Delta by at least 25%, 20% and 15% by 2017 respectively, compared to 2012 levels. However, the sources and complex formation mechanisms of aerosol, as well as the changing meteorology, make targeted mitigation of air pollution sources in megacities a considerable challenge. Several major events in China, such as the 2008 Beijing Olympic, 2014 APEC and 2015 Parade, have employed strict regional emissions control to improve local air quality during the events. Aerosol characterization studies undertaken during these events shown that the aerosol chemical composition changes significantly due to emissions control, and have shown the success of regional emissions control in decreasing both primary and secondary aerosol (Huang et al., 2010; Li et al., 2016; Sun et al., 2016c; Xu et al., 2015; Zhao et al., 2017). These special emissions control periods are an unique and essential tool for understanding the response of aerosol formation and chemistry to emissions controls, and ultimately determining sources of aerosol pollution.

Hangzhou, the second largest city in the Yangtze River Delta, has undergone rapid economic growth in recent years. The 2016 G20 summit was held in Hangzhou on 4–5 September. Strict emissions controls of air pollutants were implemented in Hangzhou and its surrounding municipalities and provinces (including Zhejiang, Shanghai, Jiangsu, and Anhui) between August 24 and September 6, which was to ensure good air quality during the G20 period. The temporary emissions control measures included restrictions on the number of vehicles, limited production or complete shut-down of industrial enterprises, and temporary cessation of construction activities. Since the previous emissions control campaigns in China have been mostly enforced in Beijing, the Hangzhou G20 summit serves as another important case study of the response of aerosol chemistry to emissions control, in a location with contrasting local emissions and meteorology compared to Beijing. Specifically, Hangzhou in August–September of 2016 had higher temperatures (~28 °C vs. ~23 °C) and higher humidity (~70% vs. ~62%) when compared to Beijing during August–September of 2015 (Zhao et al., 2017). Also, the routine circulation of mountain-valley breeze was found to play an important role in changing the diurnal cycles of aerosol species in Beijing (Xu et al., 2015), which was different than what was expected in Hangzhou. On the regional scale, the overall average $PM_{2.5}$ in the Yangtze River Delta was much lower than the North China Plain (42.8 μg/m^3 vs. 77.0 μg/m^3, June–August 2013), which indicated that the different polluted level and emission characteristics in the two regions (Hu et al., 2014).

In this study, PM_1 chemical composition was characterized in situ by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) along with a suite of collocated instruments, between August 5 and September 23 during the 2016 Hangzhou G20 summit period. The impacts of emissions controls and meteorological conditions on PM_1 mass concentration and chemical composition were characterized in detail. The diurnal cycles, sources apportionment of organic aerosol, size distributions and elemental composition of PM_1 were investigated further by comparing the aerosol chemistry before, during and after G20. In addition, the evolution process of aerosol composition, source apportionment, size distributions and back trajectories during G20 are investigated and elucidated with a comprehensive case study.

2. Method

2.1. Sampling site

The sampling site was located on the roof of an 8-floor building, adjacent to the Binjiang (BJ) national air quality monitoring station (30°12′29.6″N, 120°12′43.3″E), which was located in a typical urban location in Hangzhou, about 5 km southwest of the G20 main event hall (Fig. S1). The surroundings of this site were main roads, as well as residential and business areas.

2.2. Instrumentation and AMS operation

An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, shortened hereafter to AMS) was deployed in a temperature controlled (25 °C) sampling room to measure PM_1 components (including ammonium, nitrate, sulfate, chloride, and organic), typically referred as non-refractory PM_1 (NR-PM_1 (Canagaratna et al., 2007),). Measurements from collocated instruments included black carbon (BC) by a seven wavelength Aethalometer (AE33, Magee Scientific Corp.) at 880 nm, and particle number concentration (14–700 nm) by Scanning Mobility Particle Sizer (SMPS 3936, TSI), with a long-Differential Mobility Analyzer (DMA 3081, TSI) in combination with a butanol Condensation Particle Counter (CPC 3776, TSI).

The sampling inlet was installed on the roof of the sampling room, with a $PM_{2.5}$ cyclone (model URG-2000-30ED) used to remove coarse particles. The sample stream was dried (RH < 25%) via a Nafion tube (Dryer-50, Aerodyne Research Inc.) before entering the AMS and SMPS instruments. The sampling line (~ 2.5 m) was assembled using 3/8′stainless steel tubing (coated by sponge to prevent water condensation). The total air flow rate was controlled at 3 L/min, with 85 cc/min sampled into the AMS and 300 cc/min sampled into the SMPS.

The AMS was calibrated for inlet flow, ionization efficiency (IE), and particle size following standard protocols (Jayne et al., 2000; Jimenez et al., 2003). The IE calibrations were undertaken using size-selected (300 nm) pure ammonium nitrate particles (generated by an aerosol generator), and calibrated by CPC counts at different number concentrations. It should be noted that the PSL spheres were not available during this campaign, therefore the particle size was calibrated by using DMA selected pure ammonium nitrate alternatively, using a range of mobility diameters (60/80/100/150/200/250/300/350/400/500/600 nm). These calibrations were performed every fortnight to ensure accuracy. There were five IE calibration values during the whole campaign (Table S2). We have divided whole campaign into three periods with separate IE calibration values: 1.63×10^{-7} for Aug. 5~Aug. 21, 1.13×10^{-7} for Aug. 25~Sep. 5, and 9.0×10^{-8} for Sep. 6~Sep. 23, respectively.

A detailed description of typical AMS operation can be found in previous studies (DeCarlo et al., 2006; Drewnick et al., 2005), although a brief description is provided below. The AMS was operated by alternating every 5 min between the mass-sensitive V-mode and the high-mass-resolution W-mode. Under V-mode

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