Important role of ammonia on haze formation in Shanghai

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Abstract

A haze episode occurred on 12 September 2009 in Shanghai, when the mass ratio of PM$_{1.0}$/PM$_{2.5}$ (PM: particulate matter) reached 0.8. A similar variation of hygroscopic growth factor distribution was observed for Aitken mode particles and accumulation mode particles, implying that the enhancement of fine particles was caused by local atmospheric processing. The hygroscopicity measurements in combination with chemical analysis provided strong support for the significant contribution of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ to the haze episode. The molar ratio of $[\text{NH}_4^+] / ([\text{NO}_3^-] + 2[\text{SO}_4^{2-}])$ rose up to 0.96, coincident with the large increase in NH$_3$ concentration, suggesting that the available NH$_3$ played a vital role in the enhancement of particulate sulfate and nitrate during the haze episode.

Keywords: fine particle pollution, hygroscopicity, ammonia, atmospheric aerosol

1. Introduction

In the past 20 years, China has undergone rapid industrialization and urbanization. Due to the economic development dominantly powered by coal-based energy, China has been the biggest emitter of SO$_2$ in the world. Also, in contrast to substantial reductions in some areas of Europe and the USA, NO$_x$ emission in East Central China has accelerated since 2000 [1]. Geng et al [2] found that both SO$_2$ and NO$_x$ emissions over the Yangtze river delta (YRD) region mostly originated from coal combustion. In 2005, the industrial source accounted for 73% of the 5.13 × 10$^5$ tons of the total SO$_2$ emissions in Shanghai [3]. The emission intensity of SO$_2$ in Shanghai reached 81 tons km$^{-2}$, at least six times higher than that of other provinces in the YRD. On the other hand, the emission of NO$_x$ from power plants and industry reached 3 × 10$^5$ tons in Shanghai in 2005, accounting for about 60% of the total emission [4]. The large emissions of SO$_2$ and NO$_x$ caused severe air pollution problems. For example, haze has occurred much more often in the past several years. However, the mechanism of haze formation is still not clear. A better understanding of the relation between secondary aerosol formation and haze pollution in Shanghai is key to the control of urban air quality.

Several studies regarding secondary inorganic species in Shanghai have been reported. Wang et al [5] suggested that heterogeneous reactions played a main role in the formation of SO$_4^{2-}$ in the entire year whereas NO$_3^-$ was largely from gas-phase photochemical reactions in the cold season. The high equivalent ratio of $\text{NH}_4^+ / \text{SO}_4^{2-}$ from their results indicated that the aerosol was from neutral to slightly acidic. Fu et al [6] suggested that the transformation of SO$_2$ and NO$_x$ contributed much to the high concentrations of secondary aerosols during the heaviest pollution episode in Shanghai. They attributed the air pollution mass to long-range transport from the northern part of the YRD. However, Pathak et al [7] found that the molar ratio of $\text{NH}_4^+ / \text{SO}_4^{2-}$ was often below 1.5 in PM$_{2.5}$ samples collected in Taicang, which is 44 km to the northwest of Shanghai. They supposed that the high concentration of nitrate in particulate phase was formed by the hydrolysis of N$_2$O$_5$ on the surface of the pre-existing moist and acidic aerosols.

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In a laboratory study, Tursic et al. [8] found that the rate of SO2 conversion in the presence of NH3 increased by a factor of about 20 in comparison with that in the absence of NH3. It was reported that China had consumed over one-third of the world’s chemical nitrogen fertilizer [9, 10]. Streets et al. [11] estimated that the agriculture sector contributed 88% to the total emissions of NH3 in China. However, the role of atmospheric NH3 concentration on the haze formation was barely noticed.

The current work was performed in the framework of Mirage (Megacities Impact on Regional and Global Environment), Shanghai 2009–2012, as organized by the National Center for Atmospheric Research and the Shanghai Meteorological Bureau. Focusing on the formation of ozone and aerosols, the first field campaign was deployed in September 2009. This was the period with the best air quality in a year, because the prevailing wind direction in Shanghai was mainly from southeast to southwest in the summer while northerly advection brought polluted air from Jiangsu province in the winter. As shown in figure 1, the supersite measurement station was located in the Pudong Meteorological Bureau (PD, 121.55°E, 31.22°N), while NH3 concentration was measured at Dongtan beach (DT, 121.92°E, 31.52°N), the background site located in the east of Shanghai. The purpose of our work was to investigate the chemical mechanism of haze formation in Shanghai. The hygroscopicity and ion chemistry of fine particles are reported.

2. Experimental section

The compositions of bulk particles were monitored online with a Monitor for Aerosols and Gases in Ambient Air (MARGA, Model ADI 2080, Metrohm Applikon BV) described previously [12]. Briefly, atmospheric aerosol (with a cutoff of 2.5 µm using a PM2.5 cyclone impactor) passed through a steam jet aerosol collector where the soluble components were captured and dissolved into the supersaturated steam. Subsequently, the mass concentrations of NH4+, Na+, K+, Ca2+, Mg2+, SO42-, NO3−, and Cl− were analyzed with an ion chromatograph.

The aerosol hygroscopicity was measured at 26 °C with a custom-built hygroscopic tandem differential mobility analyzer (HTDMA) described previously [13]. Briefly, the system was operated alternately in DMA and TDMA modes through which the particle size distribution and size-resolved hygroscopicity of submicrometer ambient aerosols were measured, respectively. The sample stream was dried to approximately 10% relative humidity (RH) and neutralized to charge equilibrium before entering the first DMA (Model 3081L, TSI Inc.). The hygroscopic growth was measured at RH = 20–91% (only results at 68% RH are reported here) and quantitatively expressed as hygroscopic growth factor (GF), defined as relative increase in particle size due to water uptake at a certain RH. The particle size distributions were determined by online DMA inversion, while hygroscopic growth factor distributions were obtained through TDMAinv inversion [14]. The number fraction of any particle mode was obtained by integrating the related segment of the normalized growth factor distribution.

Both the local meteorological data and air quality parameters including the daily average concentrations of ambient particulate matter, NH3, O3, and NO2, were provided by the Shanghai Meteorological Bureau.

3. Results and discussion

There was no precipitation during our observation. The average temperature and dew point over the observation were 26.1 ± 2.3 and 20.8 ± 2.6 °C, respectively. The prevailing wind was from the northeast, so air parcels arriving in Shanghai were mainly from the East China Sea. Figure 2 shows the daily average concentrations of particulate pollutants in Shanghai from 2–14 September. The daily average concentrations of PM10 (PM: particulate matter) were below the Grade I criteria of the National Ambient Air Quality Standard of China (50 mg m−3), except that the concentration reached 86 mg m−3 on 12th September when air parcels from Jiangsu Province arrived in Shanghai. The average concentration of PM10 during the observation was 39 mg m−3, significantly lower than the annual average concentration in 2009, i.e. 79 mg m−3 [15]. The daily concentration of PM2.5 on 12 September was 56.9 mg m−3, much higher than the 25 mg m−3 of the World.
92% of the theoretical GF of NH4NO3 regardless of the average GFs of the more-deliquesced group were about the deliquesced group hygroscopic growth factor distribution split into the less-deliquesced group, making a minor contribution to the haze formation. It is evident that the fine particles from long-range transport into urban areas were mostly influenced by local sources. Aitken mode particles in urban areas were generally hydrophobic while secondary inorganic aerosols from ammonia transformation were hygroscopic in nature. Some particles of diameter 50 nm significantly deliquesced at 68% RH, indicating that gas-to-particle phase conversion and subsequent condensation contributed to the Aitken mode particles significantly. A similar variation of hygroscopic growth mode was observed for particles in the whole size range, indicating that both Aitken mode and accumulation mode particles during the haze episode had undergone the same atmospheric processing. Because Aitken mode particles in urban areas were mostly influenced by local sources, it is evident that the fine particles from long-range transport made a minor contribution to the haze formation. The hygroscopic growth factor distribution split into the less-deliquesced group (GF < 1.1) and more-deliquesced group (GF > 1.1) during the period from 21:00 on 11 September to 19:00 on 12 September (local time). The presence of a more-deliquesced group at 68% RH suggested that NH4NO3 or NH4HSO4 was a significant aerosol constituent, because they were typical components in PM2.5 with deliquescence RH below 68%. Compared to theoretical calculation according to the hygroscopic growth calculator described previously, the average GFs of the more-deliquesced group were about 92% of the theoretical GF of NH4NO3 regardless of the particle size. The number fraction of the more-deliquesced groups displayed a feature of size dependence during the haze episode, with a larger fraction for bigger particles. This feature indicated that the atmospheric process was dominated by the deposition of hygroscopic materials.

As shown in figure 3, the hourly concentrations of sulfate and nitrate in PM2.5 reached 0.285 and 3.45 µg m−3, equivalent to 27.4 and 21.4 μg m−3, respectively. These results suggested that the fine particle enhancement on 12 September should be attributed to secondary inorganic aerosol formation. The nitrate concentration varied in accordance with the number fraction of the more-deliquesced group, providing strong support for the significant contribution of NH4NO3 indicated by hygroscopicity. The more-deliquesced group disappeared when the molar ratio of sulfate to nitrate (S/N) was above 1.5. These results indicated a negligible contribution of NH4HSO4 to the haze formation.

Figure 4 illustrates the correlation between the daily average concentrations of ammonium, sulfate, and nitrate during the whole period. The linear fit to the equivalent concentration of the sum of sulfate and nitrate versus that of ammonium had a square correlation coefficient of 0.998 and a slope of 0.94. The measured slope was approximately 1.0, suggesting the important role of gaseous NH3 in the formation of particulate sulfate and nitrate. The high occurrence of slightly acidic aerosols, indicated by NH4+/NO3− < 1, was often limited by the availability of gaseous NH3. At NH4+/SO42− < 2, sulfate enhancement was coincident with the increase of ammonium concentration, while nitrate concentration was affected inconsiderably. The ratio of NH4+/([NO3−] + 2[SO42−]) was 0.96 on 12 September, indicating that the contribution of acidic sulfate to haze formation was negligible. The average NH4+/([NO3−] + 2[SO42−]) was 0.74 ± 0.10 during the whole period, indicating the high occurrence of slightly acidic aerosols.
The formation of NH$_4$NO$_3$ depended on the reaction dissociation constant and the product of the partial pressure of NH$_3$ and HNO$_3$. Under urban atmosphere, NH$_3$ was liable to react with acidic sulfate before HNO$_3$ could condense onto aerosols as ammonium nitrate. Thus, the formation of NH$_4$NO$_3$ was often suppressed in NH$_3$-deficient atmosphere. This was the typical case for our observation. The increase in NH$_3$ concentration was attributed to the change in wind direction. In contrast to the prevailing winds from the eastern direction during the observation, air parcels arriving in Shanghai on 12 September were from the northwest and had passed through Jiangsu Province. Although Shanghai is normally an ammonia-deficient city, Jiangsu Province to the north of Shanghai is one of the biggest NH$_3$ emitters in China [9]. The annual average concentration of NH$_3$ was consistent with the enhancement of particulate sulfate. This was the typical case for our observation. The increase in NH$_3$ concentration was attributed to the change in wind direction. In contrast to the prevailing winds from the eastern direction during the observation, air parcels arriving in Shanghai on 12 September were from the northwest and had passed through Jiangsu Province. Although Shanghai is normally an ammonia-deficient city, Jiangsu Province to the north of Shanghai is one of the biggest NH$_3$ emitters in China [9]. The annual average concentration of NH$_3$ in Huian (Jiangsu Province) in 2008 reached 14.1 ± 8.6 ppb, corresponding to 41.5 ± 25.3 µg m$^{-3}$ (NH$_4$)$_2$SO$_4$ or 50.3 ± 30.7 µg m$^{-3}$ NH$_4$NO$_3$. Particulate NH$_4$NO$_3$ was formed from the reaction between gaseous NH$_3$ and HNO$_3$ through a reversible process:

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\text{NH}_3(g) + \text{HNO}_3(g) = \text{NH}_4\text{NO}_3(s \text{ or aq}).
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