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Evolution of secondary inorganic and organic aerosols during transport: A case study at a regional receptor site☆

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ABSTRACT

Understanding the evolution of aerosols in the atmosphere is of great importance for improving air quality and reducing aerosol-related uncertainties in global climate simulations. Here, a unique haze episode at a regional receptor site near the East China Sea was examined as a case study of the aging process of atmospheric aerosols during transport. An increase in photochemical age from 5 h to more than 25 h and a progressive increase in the fitted mean particle diameter from 70 nm to approximately 300 nm were observed. According to the pollution features and meteorology conditions involved, pollution accumulation (PA), sea breeze (SB), and land breeze (LB) periods were identified. Concentrations of black carbon (BC), hydrocarbon-like organic aerosols (HOA), semi-volatile oxidized organic aerosols (SV-OOA), and nitrate increased by 7-fold up to 39-fold when the air masses passed through Taizhou, a nearby city. In addition, nitrate and SV-OOA dominated the aerosol composition in the urban outflow plumes (52% and 18%, respectively), yet they gradually decreased in concentration during transport. In contrast, sulfate and the low-volatile oxidized organic aerosols (LV-OOA) exhibited more regional footprints and potentially have similar formation mechanisms. The atomic oxygen-to-carbon (O/C) ratio also increased from 0.45 to 0.9, thereby suggesting that rapid formation of highly oxidized secondary organic aerosols (SOA) occurred during transport. Overall, these results provide valuable insight into the evolution of the chemical and physical features of aerosol pollution during transport and also highlight the need for regulatory controls of nitrogen oxides, sulfur dioxide, and VOCs to improve air quality on different scales.

1. Introduction

Atmospheric aerosols contribute to reduced visibility, adverse effects on human health, and mediate effects on direct and indirect radiative forcing (Dockery et al., 1993; IPCC, 2013; Bond et al., 2013). Thus, submicron atmospheric aerosols represent a major environmental problem. Aerosols are directly emitted from many sources, including combustion, road or wind-blown dust, and plants. Aerosols can also form through secondary formation processes, including nucleation and growth by multiphase chemical processes (Zhang et al., 2012; George and Abbatt, 2010). Both primary and secondary aerosols undergo chemical and physical aging processes in the atmosphere (Jimenez et al., 2009). Secondary formation mechanisms, diffusion, as well as mass loadings and the oxidation state of ambient organic aerosols (OA), can be affected by these aging processes (Cubison et al., 2011; Jimenez et al., 2009). Recent studies of severe haze episodes in the urban environments of China have demonstrated that the frequency of aerosol pollution mainly

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arises due to the aging process of ambient aerosols (Peng et al., 2016; Guo et al., 2014; Huang et al., 2014). However, to date, few ambient measurements have been made to investigate the aerosol-aging process and to quantify related changes in chemical composition. A major challenge in conducting these studies is the ability to track air masses under constantly varying ambient conditions (Peng et al., 2016).

The Yangtze River Delta (YRD) region is located in the eastern region of China and it encompasses the largest city cluster in China with a population of over 20 million. Over the past 30 years, this region has undergone extremely rapid economic development. As a result, the YRD region has become one of the most economically dynamic regions in the world. However, it has also experienced severe deterioration of its air quality on both urban and regional scales (Huang et al., 2013). Significant health risks associated with air quality have been identified in this region and have been attributed to exposure to atmospheric aerosols (Zhao et al., 2011). Previous studies conducted in the YRD region have mostly focused on aerosol pollution features in urban environments (Huang et al., 2012; Leng et al., 2014). However, only a few of these studies have provided insight into the aging process and the transformations of aerosols that occur during their transport to a receptor site (Zhang et al., 2015b). In order to improve regional air quality, a better understanding of aerosol aging during transport in the atmosphere is pivotal to assessing the roles of primary emissions, as well as secondary emissions, on the formation on ambient particular matter (PM) pollution.

Here, we present a case study of a severe haze episode that occurred at the Wenling receptor site in the YRD region. This coastal site is located downwind of the YRD region and is generally not exposed to local emissions. Thus, the haze episode that is described provided a unique opportunity to study aerosol transport from a polluted region to an unpolluted region. Both backward trajectory analysis and local meteorology conditions were used to investigate the origins of the air mass and to categorize the pollution types present. In addition, the influence of urban emissions on the chemical composition of the atmospheric aerosols was investigated. Evolution of particle size distribution, cloud condensation nuclei (CCN) concentration, and inorganic and organic aerosol chemical composition during transport were also examined and are quantified.

2. Materials and methods

2.1. Measurement site

This case study was conducted in November 2011 at the Wenling receptor site that is located on a small peninsula in the Zhejiang province, southeast China (Fig. 1). This coastal sampling site is approximately 2 km from the East China Sea from northeast to south, and is surrounded by farmland (Peng et al., 2014). The city of Taizhou is located approximately 30 km away to the northwest of the site, while the YRD city cluster is approximately 200–300 km away to the north (Fig. 1). In autumn, the wind direction at the Wenling site ranges from north to southeast, thereby allowing a continental air mass and a maritime air mass to alternately dominate the site.

2.2. Instrumentation

A suite of state-of-the-art instruments were utilized to characterize gas- and particulate-phase pollutants (Table S1).

The mass concentrations and size distributions of submicron non-refractory species, including organic aerosols (OA), sulfate, nitrate, ammonium, and chloride, were measured with a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) every 5 min. A nafion dryer (Perma Pure Inc.) was used in the inlet lines to keep the relative humidity (RH) of the sampled air streams below 30%. This AMS system has previously been described (Hu et al., 2013; Huang et al., 2010). Positive matrix factorization (PMF) analysis was applied to the high-resolution (HR) mass spectra obtained (mass-to-charge ratio, 12–196) to investigate the factors or sources that contributed to the organic mass loadings (Ulbrich et al., 2009). Four OA components with distinct mass spectral profiles and temporal variations were identified at the Wenling site from the AMS spectra. These included hydrocarbon-like OA (HOA), semi-volatile oxygenated OA (SV-OOA), low-volatility oxygenated OA (LVOOA), and a biomass burning OA (BBOA) (Fig. S1).

A Scanning Mobility Particle Sizer (SMPS) system (TSI Inc.) that included a differential mobility analyzer (DMA) and a condensation particle counter (CPC) was utilized to obtain particle number distributions in the range of 15–600 nm at the Wenling site. A silica diffusion dryer within the inlet lines was used to keep the RH of the air samples below 40%. All of the data were corrected by size-dependent particle loss correction parameters inside the instruments, as well as in the sampling tubes (Willeke and Baron, 1993).

A custom-built gas and aerosol collector (GAC) combined with two ion chromatography was used to measure the concentrations of water soluble inorganic ions with a diameter less than 2.5 μm (e.g., SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+, K^+, Ca^{2+}, etc.), as well as certain gas-phase pollutants (e.g., HONO, SO_2, NH_4, and HNO_3) (Dong et al., 2012). Measurements were collected every 30 min. A custom-built, on-line gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID) with a time-resolution of 1 h was used to measure multiple volatile organic compounds (VOCs) (Yuan et al., 2012, 2013). Black carbon (BC) in $PM_{2.5}$ was measured with a multi-angle absorption photometer (MAAP, Thermo Fisher Inc.) with a time-resolution of 5 min. Concentrations of CO, NOx, SO_2, and O_3 were measured with a suite of gas analyzers (Thermo Fisher Inc.).

2.3. Parameterization

To quantify particle diameter growth, particle number distributions were parameterized by a multiple log-normal distribution function. Each mode is described by the following function (Seinfeld and Pandis, 1998):

$$\frac{dN_i}{d\log D_p} = \frac{N_i}{\sqrt{2\pi}\log\sigma_i} exp\left[-\frac{(\log D_p - \log \mu_i)^2}{2(\log \sigma_i)^2}\right] \quad (1)$$

where N_i, μ_i, and σ_i are the total number concentration, mean diameter, and geometric mean standard deviation of the distribution of mode i, respectively. The task of the fitting program is to minimize the residual part, Q, which is described as:

$$Q = \int_{15}^{600} \frac{|dN/d\log D_p - \sum_i dN_i/d\log D_p|}{dN/d\log D_p} d\log D_p \quad (2)$$

Aerosol evolution during transport in the atmosphere is characterized by a photochemical-age-based parameterization method. Photochemical age can be calculated based on the ratios of two hydrocarbons that react at different rates with an OH radical (de Gouw et al., 2005). Considering that the transport of urban emissions was the dominant VOC source in the focused episode in this study, photochemical age was calculated from the measured

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