Atmospheric Research 169 (2016) 160–170

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

Comparison of aerosol hygroscopicity and mixing state between winter and summer seasons in Pearl River Delta region, China

Rongxin Jiang [a], Haobo Tan [a,b,*], Lili Tang [a,c,**], Mingfu Cai [d], Yan Yin [a], Fei Li [c], Li Liu [d], Hanbing Xu [d], P.W. Chan [e], Xuejiao Deng [b], Dui Wu [b]

[a] Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China
[b] Key Laboratory of Regional Numerical Weather Prediction, Institute of Tropical and Marine Meteorology, China Meteorological Administration, Guangzhou, Guangdong 510080, China
[c] Jiangsu Environmental Monitoring Center, Nanjing 210036, China
[d] Department of Environmental Science and Technology, Sun Yat-sen University, Guangzhou 510275, China
[e] Hong Kong Observatory, Hong Kong, China

ARTICLE INFO

Article history:
Received 29 January 2015
Received in revised form 3 August 2015
Accepted 28 September 2015
Available online 13 October 2015

Keywords:
Aerosol hygroscopicity
Mixing state
H-TDMA
PRD

ABSTRACT

Hygroscopic properties of aerosol particles are important for determining aerosol size distributions, and thus determining scattering and absorption coefficients at ambient atmospheric conditions. In this study, hygroscopic properties of aerosol particles at an urban site in Guangzhou, China, were measured using a Hygroscopic Tandem Differential Mobility Analyzer (H-TDMA) system during the winter and the summer. The results show that the urban aerosols were composed of more-hygroscopic, less-hygroscopic and non-hygroscopic particles. For less-hygroscopic particles of 40–200 nm in diameter, the hygroscopic parameter κ_{LH} was around 0.15. For more-hygroscopic particles, the κ_{MH} was from 0.290 to 0.339 with a particle size from 40 to 200 nm. For non-hygroscopic particles, the κ_{NH} was about 0.015. It was found that the number fraction of less-hygroscopic particles (NF_{LH}) was correlated with the atmospheric oxidation which can be presented by OC/EC. This paper attributed the larger NF_{LH} in winter to the higher value of OC/EC (3.0). Such conditions may lead to more formation of less-hygroscopic particles. Backward trajectories cluster analysis shows that there is a certain link between air mass origin and aerosol hygroscopicity, but it seems to be independent of the level of pollution. The difference of NF_{NH} indicates that the mixing state of aerosol particles can also be affected by air mass origin. Diurnal variations in aerosol hygroscopic parameters in both seasons show that during daytime, aerosol particles tend to have a low degree of external mixing or quasi-internal mixing, resulting in a higher NF_{MH} and a larger κ_{mean}; during nighttime and early mornings, they tend to be mixed externally, resulting in a lower NF_{MH} and a smaller κ_{mean}. This can be attributed to atmospheric aging effect and evolution of mixing layer height and implies that soot (non-hygroscopic) particles present to a large extent as internal mixtures by the time they leave the urban environment. Hence, only assuming a constant mixing state of soot particles, such as pure external or internal for the regional climate model and air quality model is still not realistic and may lead to uncertainties for the Pearl River Delta (PRD) region which is one of the three major economic regions in China. Comparing the diurnal variation of NF_{NH} in both seasons, it seems that such a diurnal cycle was mainly related to the differences in evolution of mixing layer between two seasons. Such quantitative hygroscopic properties of sub-micro particles are essential in assessing their impact on weather–climate effect and atmospheric visibility.

1. Introduction

Aerosol hygroscopicity describes the uptake of water molecules by particles in response to increasing relative humidity (RH). The hygroscopicity describes the link between microphysical properties and ambient RH, and depends on the aerosol chemical composition. It plays an important role in atmospheric science because the hygroscopic growth of ambient aerosols changes both the particle size and the optical properties (Swietlicki et al., 1999), and thus affects the chemical composition and the heterogeneous reactions on particles. Upon hygroscopic growth, the scattering coefficients of ambient aerosols will increase by the enlarged cross-sectional area (Tang, 1996; Malm et al., 2003; Li et al., 2014) and hence cause a great threat to the atmospheric visibility (Liu et al., 2013). Furthermore, the hygroscopic behavior of atmospheric aerosol may affect its ability to play a role in the cloud

* Correspondence to: H. Tan, Key Laboratory of Regional Numerical Weather Prediction, Institute of Tropical and Marine Meteorology, China Meteorological Administration, Guangzhou, Guangdong 510080, China.
** Correspondence to: L. Tang, Jiangsu Environmental Monitoring Center, Nanjing 210036, China.
E-mail addresses: hbtan@grmc.gov.cn (H. Tan), lili3258@163.com (L. Tang).

http://dx.doi.org/10.1016/j.atmosres.2015.09.031
0169-8095/

condensation nuclei activation (Petters and Kreidenweis, 2007; Svenningsson et al., 2006), which is the key parameter for determining the indirect climate effect of aerosols.

Several techniques such as nephelometer (Carrico et al., 2000), electro-dynamic balance (Davis et al., 1990), and hygroscopic tandem differential mobility analyzer (H-TDMA) (Liu et al., 1978) have been used to measure the hygroscopic behavior of ambient aerosols. H-TDMA is commonly employed to measure ambient aerosol hygroscopicity because it is the only in-situ instrument that can determine aerosol liquid water uptake as well as to probe the mixing state of aerosol based on aerosol hygroscopicity.

There are various kinds of measurement locations such as ground-based H-TDMA measurements at marine, rural, and urban to free tropospheric measurement sites. Previous works using H-TDMA have been summarized by Swietlicki et al. (2008). Most of the measurements were conducted in Europe and North America (Baltensperger et al., 2002; Chen et al., 2003; Cocker et al., 2001; Massling et al., 2005; McMurry and Stolzenburg, 1989; Mochida et al., 2006; Adam et al., 2012; L. Štefancová et al., 2010). Different modes of hygroscopic growth of ambient aerosols are often observed. In China, several studies were conducted in recent years. Massling (Massling et al., 2009) presented that non-hygroscopic particles varied between 10 and 32% depending on dry particle size and season in Beijing, and showed a decreasing trend during heavily polluted times. Guo (Guo et al., 2014) also pointed out that there is a noticeable absence of the primary aerosol constituents from the H-TDMA and density measurement during the transition and polluted periods. Ye (Ye et al., 2011) reported the result obtained by H-TDMA in Shanghai, but also revealed that the addition of nitrate on the particles was initially promoted by sulfate condensation. Tan (Tan et al., 2013b) presented that the particles are more likely to have a homogeneous chemical composition during clean periods with air masses from the north.

The aerosol mixing state can be determined by H-TDMA from the measurement of different hygroscopic modes for a given selected diameter (Sjogren et al., 2008). The main component of non-hygroscopic submicron particles is freshly emitted soot. Soot particles usually undergo aging processes by condensation and coagulation, as well as oxidation and cloud processes (Riemer et al., 2004; Ivleva et al., 2007). The mixing state is a key parameter for soot particles, and uncertainty about which enables the assessment of its climatic impact (Xue et al., 2011). Comparing to individual soot particles, the light absorption capability of coated soot particles can be enhanced by a factor of 1.5–3.0 (Bond and Bergstrom, 2006; Lesins et al., 2002). The global mean direct radiative forcing of black carbon at the top of the atmosphere has been estimated with widely ranging values, depending on different treatments of the aerosol mixing state (Jacobson et al., 2000). From the probability distribution of particle growth factor, external mixture can be determined when multimodal distribution occurs, while internal mixture should be unimodal. Liu (Liu et al., 2011) reported that the number fraction of non-hygroscopic particles during the day was about 8%, while during nighttime it can reach up to 20% in Wuqing, indicating the mixing state in terms of hygroscopicity varied significantly during a day. Because both freshly emitted soot and water-insoluble organic compounds are nearly hydrophobic, the mixing state derived from H-TDMA based on aerosol hygroscopicity is not exactly the mixing state of soot, and may be different from the results obtained by other experimental approaches.

In China, with its rapid industrialization and urbanization, air pollution in Chinese megacities has become a common problem during the last decades. The Pearl River Delta (PRD) is one of the three major economic regions in China. It also suffers from a severe haze problem in China (Chan and Yao, 2008; Wu et al., 2005; Wu et al., 2007). Short-term in-situ measurements on the hygroscopic properties of aerosols have been performed in Beijing (Massling et al., 2009), Tianjin (Liu et al., 2011), Shanghai (Ye et al., 2011, 2013) and Guangzhou (Eichler et al., 2008; Tan et al., 2013b). However, there is still lack of systematic investigation of hygroscopic growth and the mixing state of sub-micrometer particles in the PRD.

This study focuses on the comparison of hygroscopicity and the mixing state of sub-micrometer aerosol particles in different seasons in PRD. The aerosol hygroscopicity at 90% RH was respectively measured by an H-TDMA system in two separate field campaigns (Dec 2012 up to Jan 2013, Jul to Sept 2013), covering the winter season and the summer season from 2012 to 2013. OC/EC and back-trajectories clusters analysis were performed to characterize the influence of chemical composition and air mass origins on aerosol hygroscopic properties respectively. The effect of mixed layer height and air mass origin on the mixing state of urban ambient aerosols is also discussed.

2. Experiment and data analysis

2.1. Measurement site

The campaign took place at the Chinese Meteorological Administration (CMA) Atmospheric Watch Network (CAWNET) Station in Panyu, Guangzhou, China. Two separate field campaigns were performed in Dec 2012, as well as Jan, Jul, Aug and Sep 2013, covering the winter and summer seasons, and were operated by the Institute of Tropical and Marine Meteorology (ITMM) of CMA. The Panyu station is located at the center of the PRD region and at the top of Dazhengang Mountain (23°00′N, 113°21′E) with an altitude of about 150 m (Fig. 1). It is about 120 m above the city average elevation and is surrounded by residential neighborhoods with no significant industrial pollution sources nearby.

2.2. Instrumentation

An H-TDMA was used to observe particle number size distribution, hygroscopic growth factor and mixing state of aerosol particles. A detailed description of the custom-built H-TDMA has been published (Tan et al., 2013a). Briefly, the system can be operated as a scanning mobility particle sizer (SMPS) and a TDMA, alternatively. During the experiment period, the aerosol sampling port was equipped with a $PM_{1.0}$ impactor inlet. Sample aerosol particles first passed through a Nafion dryer (Model PD-70T-24ss, Perma Pure Inc., USA) to achieve a RH of <10%. Then they flowed through a neutralizer (Kr85, TSI Inc.) and aerosol particles of a specific diameter were selected by a Differential Mobility Analyzer (DMA1, Model 3081L, TSI Inc.). Subsequently the monodisperse particles were introduced into a Nafion humidifier (Model PD-70T-24ss, Perma Pure Inc., USA) with residence time of 10 s, where they were exposed to water vapor and were humidified to 90% RH with a standard deviation of ±0.44%. A second differential mobility analyzer (DMA2) and a CPC (Model 3772, TSI Inc.) were used to measure the number size distribution of the humidified particles. Thus, growth factor (GF) of the particles can be calculated as:

$$GF = Dp/D_0 \quad (1)$$

Here, Dp refers to the particle diameter measured at 90% RH and D_0 to the selected diameter under dry conditions (RH < 10%). The H-TDMA measures GF for 5 selected dry diameters (40, 80, 110, 150 and 200 nm) continuously except during calibration periods. One GF data acquisition cycle for all dry particle sizes takes about 30 min. The calibration of H-TDMA was conducted every two weeks. Standard polystyrene latex spheres and ammonium sulfate were used to test the system's precision. The deviation of GF is within a scope of −0.02 to 0.03.

Hourly PM2.5 organic carbon (OC) and elemental carbon (EC) were measured by a semi-continuous thermal-optical transmittance (TOT) carbon analyzer (Model RT-4, Sunset Laboratory Inc., Tigard, Oregon, USA). Validation of Sunset field carbon analyzer can be found elsewhere (Bae et al., 2004; Bauer et al., 2009). Each measurement cycle contains