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Mixing state of atmospheric particles over the North China Plain

S.L. Zhang[a,c,d], N. Ma[d,*], S. Kecorius[d], P.C. Wang[a], M. Hu[b], Z.B. Wang[d,e], J. Größ[d], Z.J. Wu[b], A. Wiedensohler[d]

[a] Key Laboratory of Middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, 100029, China
[b] College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China
[c] Chengdu University of Information Technology, Chengdu, 610225, China
[d] Leibniz Institute for Tropospheric Research, Leipzig, 04318, Germany
[e] Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz, 55128, Germany

HIGHLIGHTS

- A HTDMA and a VTDMA were used together in a unique field study in China.
- A certain fraction of hydrophobic particles is volatile.
- Minor difference was found between the mixing states for different air mass types.
- Submicron particles in North China Plain are external mixture of two major groups.

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ABSTRACT

In this unique processing study, the mixing state of ambient submicron aerosol particles in terms of hygroscopicity and volatility was investigated with a Hygroscopicity Tandem Differential Mobility Analyzer and a Volatility Tandem Differential Mobility Analyzer. The measurements were conducted at a regional atmospheric observational site in the North China Plain (NCP) from 8 July to 9 August, 2013. Multimodal patterns were observed in the probability density functions of the hygroscopicity parameter κ and the shrink factor, indicating that ambient particles are mostly an external mixture of particles with different hygroscopicity and volatility. Linear relationships were found between the number fraction of hydrophobic and non-volatile populations, reflecting the dominance of soot in hydrophobic and non-volatile particles. The number fraction of non-volatile particles is lower than that of hydrophobic particles in most cases, indicating that a certain fraction of hydrophobic particles is volatile. Distinct diurnal patterns were found for the number fraction of the hydrophobic and non-volatile particles, with a higher level at nighttime and a lower level during the daytime. The result of air mass classification shows that aerosol particles in air masses coming from north with high moving speed have a high number fraction of hydrophobic/non-volatile population, and are more externally mixed. Only minor differences can be found between the measured aerosol properties for the rest of the air masses. With abundant precursor in the NCP, no matter where the air mass originates, as far as it stays in the NCP for a certain time, aerosol particles may get aged and mixed with newly emitted particles in a short time.

1. Introduction

The mixing state of atmospheric particles is a key feature for understanding their role in the atmosphere (Jacobson et al., 2000; Riemer et al., 2009; Oshima et al., 2009). It determines climate-relevant aerosol physical properties such as cloud condensation nuclei activity (Furutani et al., 2008; Zelenyuk et al., 2010; Wu et al., 2013b), hygroscopicity (Johnson et al., 2005; Herich et al., 2009; Liu et al., 2011) and optical properties (Jacobson, 2001; Moffet and Prather, 2009; Zaveri et al., 2010). Moreover, information on the aerosol mixing state is also necessary for accurate assessment of environmental problems (Laborde et al., 2013; Healy et al., 2014; Kamilli et al., 2014) and health effects (Schnelle-Kreis et al., 2009;

* Corresponding author.
E-mail address: ma@tropos.de (N. Ma).

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Londahl et al., 2010; Yang et al., 2014), and reducing uncertainties in global and regional aerosol models (Cappa et al., 2012; Reddington et al., 2013; Riemer et al., 2009).

The use of tandem differential mobility analyzers (TDMA) has been proven to be an effective way to determine particle mixing state and give indirect insights on chemical composition of particles (Swietlicki et al., 2008). A Volatility Tandem Differential Mobility Analyzer (VTDMA) in conjunction with a Differential Mobility Particle Sizer (DMPS) was used to determine the number and mass concentration of externally mixed less-volatile particles in urban background air (Frey et al., 2008). It was shown that the mass concentration of less-volatile particles agrees well with measured black carbon mass concentration. Wehner (Wehner et al., 2009), Rose (Rose et al., 2011) and Cheng (Cheng et al., 2012) estimated the mixing state of soot particle based on the fraction of low-volatile group from VTDMA measurements at Yufa, China in Aug. – Sep. 2006. Wehner (Wehner et al., 2009) indicated that the fraction of externally mixed soot particles decreased from about 37% during clean periods to 18% during heavily polluted periods. Tiitta (Tiitta et al., 2010) used a VTDMA system together with hygroscopic and organic TDMAs to study the composition of ultrafine particles near the major roads in Kuopio, Finland. In a laboratory study by Hossain (Hossain et al., 2012), VTDMA system was used to investigate the mixing state of size-selected ultrafine aerosol particles emitted from different biomass burning sources. The mixing state of aerosol particles from rice straw, oak and pine burning under different conditions including smoldering combustion, flaming combustion and open burning were analyzed. The VTDMA was also successfully applied in combustion engine exhaust studies in dynamometers by Burtscher (Burtscher et al., 2001).

Massling (Massling et al., 2009) and Liu (Liu et al., 2011) carried out aerosol hygroscopicity experiments applying a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) in Beijing (Jun. – Jul. 2004, Jan. – Feb. 2005) and Wuqing (Jul. – Aug. 2009), respectively. Massling (Massling et al., 2009) reported the number fraction of freshly emitted soot to be 20–32% depending on dry particle sizes and seasons. Liu (Liu et al., 2011) found that the aerosol mixing state varied significantly during the day, and the number fraction of externally mixed hydrophobic particles was about 8% during daytime and 20% at night. Possible correlations between non-voylatile particles and hydrophobic particles were analyzed by Kuwata (Kuwata et al., 2007; Kuwata and Kondo, 2008) and Rose (Rose et al., 2011). Kuwata (Kuwata et al., 2007) showed that most of less hygroscopic particles were less volatile, while more hygroscopic particles were likely to be more volatile. Similar conclusion was found by Rose during a campaign near Guangzhou, China (Rose et al., 2011).

The North China Plain (NCP), including a group of megacities (Beijing and Tianjin), is an area with great industrial activity and dense population, consuming large amounts of fossil fuels like coal, gasoline, diesel and natural gas (Liu et al., 2009; Zong et al., 2015). As a consequence, large amounts of particulate and gaseous pollutants are emitted into the atmosphere causing severe air pollution (Tao et al., 2012; Liu et al., 2015). The widespread combustion of fossil fuels and biomass makes the NCP a significant source of light absorbing carbonaceous aerosol (LAC), which plays an important role in the global radiative balance (Cheng et al., 2009; Wehner et al., 2009). With high particle loading and abundant precursor in the NCP, the mixing state of aerosol particles might be complex, and its influence on aerosol climatic and environmental effects might also be specific. Recent assessments of aerosol radiative effects (Zhuang et al., 2013; Nordmann et al., 2014) have highlighted the importance of particle mixing state in reducing the uncertainties in climate models and in improving pollution control strategies. By applying parallel measurements of V- and HTDMA system in the NCP, we aim to have a better understanding of the impact of different aerosol sources and transformation processes on the particle mixing state in polluted areas. Tiitta (Tiitta et al., 2010) has demonstrated the advantages of using different TDMAs in parallel to investigate the properties of aerosol particles. V- and HTDMA system setup gives not only information on inorganic contribution but also on the temperature-dependent aerosol component which separates the contribution of black carbon. To our knowledge, such a setup was applied for the first time in the NCP.

In this study, an overview of the parallel measurements of VTDMA and HTDMA is presented. Then a comparison between the number fraction of non-volatile particles and hydrophobic particles was done. Diurnal variations of particle mixing state, as well as volatility and hygroscopicity were discussed. Air mass back trajectory analysis was carried out to investigate the impact of different aerosol sources and transportation processes on particle mixing state. At last, we parameterized the measured size-dependent particle mixing state to facilitate further applications.

2. Experiment

2.1. Measurement site

During the field campaign (8 July to 9 August, 2013), aerosol microphysical and optical properties were measured at Xianghe station (39.75 °N, 116.96 °E, 36 m a.s.l.), a regional site in the NCP about 70 km southeast from Beijing. The measurement site is located at the outskirts of a small village about 5 km west to the Xianghe town center. The surroundings are residential areas and farm land. Fig. 1 shows the average aerosol optical depth (AOD) distribution during summer from 2012 to 2014 over the NCP, monitored by the Ozone Monitoring Instrument (OMI) with a high

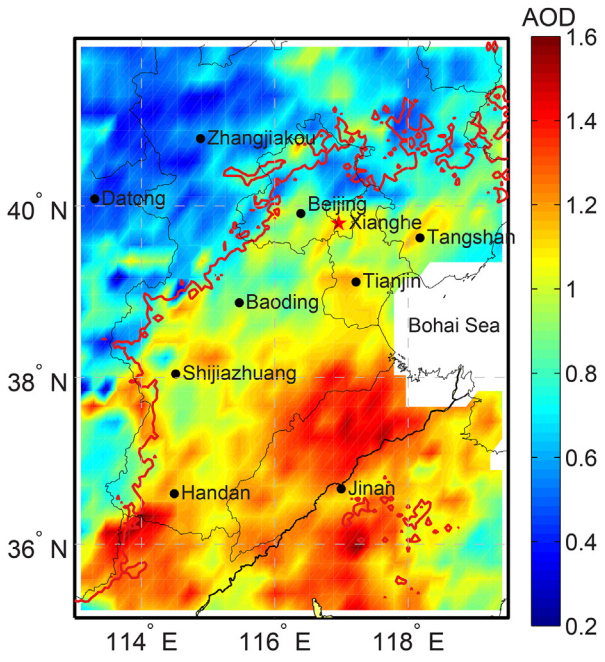

Fig. 1. Map of the North China Plain. The measurement site is marked with red star. Black dots show the major cities in the NCP. Contour plot shows the 3-year summer average OMI AOD distribution (2012–2014, 0.25° × 0.25° resolution). The red solid line denotes the 500 m contour line of elevation height, which can be considered as the boundary of the NCP.