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A preliminary analysis of the surface chemistry of atmospheric aerosol particles in a typical urban area of Beijing

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ABSTRACT

Atmospheric aerosol particle samples were collected using an Ambient Eight Stage (Non-Viable) Cascade Impactor Sampler in a typical urban area of Beijing from 27th Sep. to 5th Oct., 2009. The surface chemistry of these aerosol particles was analyzed using Static Time of Flight-Secondary Ion Mass Spectrometry (Static TOF-SIMS). The factors influencing surface compositions were evaluated in conjunction with the air pollution levels, meteorological factors, and air mass transport for the sampling period. The results show that a variety of organic ion groups and inorganic ions/ion groups were accumulated on the surfaces of aerosol particles in urban areas of Beijing; and hydrophobic organic compounds with short- or middle-chain alkyl as well as hydrophilic secondary inorganic compounds were observed. All these compounds have the potential to affect the atmospheric behavior of urban aerosol particles. $PM_{1.1–2.1}$ and $PM_{3.3–4.7}$ had similar elements on their surfaces, but some molecules and ionic groups demonstrated differences in Time of Flight-Secondary Ion Mass Spectrometry spectra. This suggests that the quantities of elements varied between $PM_{1.1–2.1}$ and $PM_{3.3–4.7}$. In particular, more intense research efforts into fluoride pollution are required, because the fluorides on aerosol surfaces have the potential to harm human health. The levels of air pollution had the most significant influence on the surface compositions of aerosol particles in our study. Hence, heavier air pollution was associated with more complex surface compositions on aerosol particles. In addition, wind, rainfall, and air masses from the south also greatly influenced the surface compositions of these urban aerosol particles.

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Introduction

Surface physicochemical processes determine material conversion (Rita et al., 2006), energy transfer, and chemical conversion on the surfaces of aerosol particles (Peterson et al., 2006; Chan et al., 1997). Such transformations in aerosol particles affect both the environment and human health (Wang et al., 2011; Tang et al., 2006; Wei et al., 2009). In the context of their close relationship to aerosol surface area, morphology, surface chemical composition, structure and other surface characteristics (Zhu et al., 2010; Lazzeri et al., 2003; Xu, 2006; Li et al., 2007; Li et al., 2010; Wu et al., 2009; Lu et al., 2013; Bluhm and Siegmann, 2009; Sobanska et al., 2014), study of the surface physicochemical characteristics of aerosol particles has become an important aspect of aerosol particle research.

The main techniques for surface chemical and imaging analysis include Scanning Electron-Energy Dispersive X-ray Spectrometry (SEM-EDX), Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS or EDCA), Atomic Force Microscopy (AFM), and Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS) (Li et al., 2015). Compared with other surface analysis techniques, TOF-SIMS can distinguish ions of elements with low atomic numbers ($Z < 11$, Z = atomic number) as well as their isotopes, with high sensitivity and fine transverse and depth resolution (such as lateral resolution <50 nm, depth resolution <1 nm, organic matters, monolayer $<10^{-6}$) (Benninghoven and Cha, 2002; Zhou et al., 2004). The technique has two working modes, which are Static TOF-SIMS and Dynamic TOF-SIMS. Static TOF-SIMS can be used for surface mass spectrometry and imaging; while Dynamic TOF-SIMS is mainly used for in-depth analysis (Benninghoven and Cha, 2002; Stephan, 2001). TOF-SIMS has been widely used in microelectronics, materials science, nanotechnology, life sciences, space technology, and environmental science (Suzuki et al., 2006; Ni et al., 2012; Li et al., 2015).

In recent years, TOF-SIMS has been applied to many aspects of aerosol science studies, such as surface chemical composition, depth analysis of surface chemical composition, surface chemical reaction, surface toxicity and characteristics and identification of aerosol particle sources. Peterson and Tyler (2002, 2003) studied the surface inorganic and organic composition of particles from a Montana forest fire and Hawaiian sea salt, and discussed their interaction by combining the technique of Static TOF-SIMS and other surface techniques, such as XRF and SEM–EDX. Tervahattu et al. (2002) analyzed the surface composition of oceanic aerosol particles by using both Static TOF-SIMS and Dynamic-TOF-SIMS, and found some evidence for the existence of a surfactant layer on the aerosol surface. Palma et al. (2007) obtained the surface depth profile and 3D imaging of aerosol particles by Dynamic TOF-SIMS. Rita et al. (2006) studied the chemical reaction process of aerosol particles by using Static TOF-SIMS. Tomiyasu et al. (2004) studied the surface composition of diesel engine exhaust particles and iron particles, and discussed their health effects by combining the techniques of Dynamic TOF-SIMS, FE-SEM and EPMA (Electron Probe Microanalysis). Mayama et al. (2012) analyzed the surface composition of aerosol particles and identified their sources by using Dynamic TOF-SIMS and EPMA. These works helped to improve our knowledge about the surface characteristics of aerosol particles and the mechanism of surface chemical reactions on the aerosol particles.

However, based on the available literature, the application of TOF-SIMS techniques in the field of aerosol science is rare in China so far. Yu et al. (2000) studied the PAHs on individual particles in Beijing and got some "fingerprints" for identification of particle sources. Liang et al. (2001) analyzed PAHs on individual particles and provided a rapid method for qualitative analysis of PAHs and oxygenated-PAHs on aerosol particles. Mei et al. (2002) resolved the surface organic components of aerosol particles stemming from tobacco smoke and found that these particles contained N-containing heterocyclic compounds and PAHs using TOF-SIMS. Li et al. (2010) analyzed the surface inorganic compositions of fine and coarse aerosol particles, and found that atmospheric secondary hydrophilic inorganic compounds were present on the aerosol particles using the static TOF-SIMS technique. These publications concern either inorganic components or organic structure, but not the identification of qualitative organic species on the surface of aerosol particles.

With the development of the economy and society, air pollution has become an important environmental issue in Beijing. Heavy haze events have occurred frequently in Beijing in recent years (Bai et al., 2006; Zhu et al., 2010; Wu, 2012), which may have had adverse effects on the exposed population. In order to develop effective air pollution control measures, it is important to clarify the formation mechanisms of aerosol particles in the ambient air of Beijing. Among these mechanisms, heterogeneous reaction processes and mechanisms are the least understood, due to the lack of knowledge on the surface chemical composition and structure of aerosol particles (Wu, 2012; He et al., 2013). Therefore, it is necessary to carry out studies on the characterization of the inorganic and organic composition and structure of aerosol particles in Beijing. In our study, the surface chemical composition of aerosol particles from a typical urban area of Beijing was measured using Static TOF-SIMS. We determined the compositional characteristics of fine and coarse mode aerosol particles and correlated these with levels of air pollution, meteorological factors, and air mass transport.

1. Materials and experimental methods

1.1. Sample collection

Aerosol samples were collected on the roof of the Atmospheric Research Building of the Chinese Research Academy of Environmental Sciences (CRAES) in the Chaoyang District, Beijing (40°02′N, 116°25′E). The site is 15 m above the ground. It is in a residential and commercial area, adjacent to residential buildings to the east and north, 100 m from Chunhua Road to the south, and 450 m from Lishuiqiao South subway station to the west. There is no industrial pollution source within 500 m or any other notable local pollution source around the sampling site. It is representative of a typical urban area within Beijing.

The samples were collected using an Ambient Eight Stage (Non-Viable) Cascade Impactor Sampler (TISCH Environmental Inc., OH, USA), with aluminum substrates (d = 81 mm) and glass fiber substrates (d = 81 mm, only used in layer F). It consists of