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Review

A review of single aerosol particle studies in the atmosphere of East Asia: morphology, mixing state, source, and heterogeneous reactions

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ABSTRACT

Emissions of anthropogenic air pollutants in East Asia significantly influence the regional climate, cause environmental deterioration and threaten public health. Single particle analyses have been widely applied to study aerosol particles collected on the ground and at elevated altitudes at mountains and by flights. Here we review current understanding on physicochemical properties, mixing state, heterogeneous chemical reactivity of individual particles in East Asia based on electron microscopy and mass spectrometry. We summarize the techniques of single particle analysis and discuss their advantages and disadvantages. Morphology and composition of the major particle types in East Asia obtained by these techniques are briefly introduced and are further used to identify particle sources. The diversity, heterogeneity, and variable size of ambient particles make it challenging to understand how the precise single particle analyses are efficient in studying particle optical properties, hygroscopic behavior, related heterogeneous reactions and potential health evaluations. We highlight the combinations of laboratory and field studies, single and bulk analytical methods, and the integration of different single particle technologies that may be very powerful to obtain a more complete picture of single particles. These research results can improve our knowledge on the fundamental physical chemistry of aerosol particles and be further extended to study their environment and climate effects as well as health risk.

1. Introduction

East Asia including China, South Korea, and Japan is thought to be one of the largest and strongest emission source areas of aerosols and trace gases on Earth. Large amounts of aerosols and trace gases from the Asian continent can be transported to the North Pacific Ocean during winter and spring monsoons. On a large timescale, long-range transport of pollutants from China may affect North America, the Pacific Ocean and the Arctic, making Chinese air pollution a truly global problem (Heald et al., 2006; Lin et al., 2014; Seinfeld et al., 2004). Fine particles (<2.5 μm) ($PM_{2.5}$) represent a major atmospheric environmental problem, deteriorate visibility, adversely affect human health, and directly and indirectly impact weather and climate (Cao et al., 2012; Kan et al., 2012; Li et al., 2011e; Ramana et al., 2010; Shao et al., 2006; Zhang et al., 2012b). In recent years, the number of haze days has been increasing, the extent of the haze area has been spreading, and the duration of a single haze event has been lengthening (Zhang et al., 2012b).

As a particular example, China experienced extremely severe and persistent haze pollution during January 2013, affecting more than 1.3 million km^2 and 800 million people (Huang et al., 2014).

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Abbreviation

AFM	atomic force microscopy
AMS	aerosol mass spectrometer
ATOFMS	aerosol-time-of-flight mass spectrometer
ATR-FTIR	attenuated total reflectance fourier transform infrared spectroscopy
BC	black carbon
BrC	brown carbon
CCN	cloud condensation nuclei
DDA	discrete dipole approximation
DRH	deliquescence relative humidity
EDX	energy dispersive X-ray spectrometry
EELS	electron energy-lossspectrometry
EPMA	electron probe X-ray microanalysis
GC–MS	gas chromatography–mass spectrometer
HR-MS	High-resolution mass spectrometry
HTDMA	Hygroscopic Tandem Differential Mobility Analyzer
IC	ion chromatograph
ICP-MS	inductively coupled plasma mass spectrometer
Nano-DESI	nanospray desorption electrospray ionisation
NanoSIMS	nanometer-scale secondary ion mass spectrometer
NEXAFS	near-edge X-ray absorption fine-structure spectroscopy
OM	organic matter
POA	primary organic aerosol
RMS	Roman microspectrometry
SAED	selected-area electron diffraction
SEM	scanning electron microscopy
SOA	secondary organic aerosol
SPAMS	single particle aerosol mass spectrometer
STXM	scanning transmission X-ray microscopy
TEM	transmission electron microscopy
TOF-SIMS	time of flight secondary ion mass spectrometer
VOCs	volatile organic compounds

Many international atmospheric scientists focused on the fine particles to understand how the regional haze episodes form in continental East Asia, what their impacts on human health might be, and how they directly and indirectly affect climate (Guo et al., 2014; Huang et al., 2014; Jung and Kim, 2011; Li et al., 2011d; Ma et al., 2012; Ramana et al., 2010; Seinfeld et al., 2004). These research results suggested that secondary particulate species – (e.g., sulfate, nitrate and secondary organic aerosol (SOA)), formed from trace gases such as SO_2, NO_x, and volatile organic compounds (VOCs) – were the most important aerosol components of regional haze (Guo et al., 2014). Organic matter in aerosol particles was dominant in these secondary aerosols (Huang et al., 2014). Most of these studies have applied various "bulk" techniques to understand the chemical and physical properties of aerosol particles collected during the regional haze episodes. These bulk methods mostly obtain mass concentrations of different aerosol species such as sulfate, nitrate, organic matter (OM), black carbon, metal element, dust, and the number concentration of size-resolved particles. Although these results were critically important to understand emission sources and haze formation and their possible impacts on health and climate, they cannot give details of the actual mixing state of individual particles in the atmosphere (Buseck and Posfai, 1999; Li and Shao, 2009b). Knowledge of mixing state of individual particles is crucial to understand the hygroscopic and optical properties of particles and to provide information about their atmospheric histories (aging and reactions), which is a bridge for combining the laboratory and field experiments (Posfai and Buseck, 2010).

During the regional haze episodes in East Asia, particles in the Aitken (20–100 nm) and accumulation modes (100–1000 nm) become dominant and normally have long lifetimes compared with nucleation (<20 nm) and coarse modes (>1000 nm) during long-range transport (Guo et al., 2014; Li et al., 2011d). There are not only high mass concentrations of $PM_{2.5}$ (100–772 μg m^{-3}) but also rather high number concentrations of particles (50,000–130,000 cm^{-3}) during the haze pollution (Guo et al., 2014; Huang et al., 2014; Li et al., 2011d). As a result, these studies well reflects the extremely high aerosol pollution occurring in East Asia. The online "bulk" methods such as Aerodyne aerosol mass spectrometer (AMS) can record mass concentrations of organics, sulfate, and nitrate (Guo et al., 2014; Huang et al., 2014) and quantify the dramatic increases of sulfate during the haze episodes (Sun et al., 2014). These results cannot be explained due to the absence of the information on mixing states of individual particles and to the lack of the consideration of the heterogeneous reactions on particle surfaces under low O_3 concentrations in winter haze (Wang et al., 2014). Beside non-refractory aerosols (e.g., sulfates, nitrates, and OM), there are nanosized refractory aerosols in a high particle number but with low mass concentration such as metal, fly ash, and soot particles, which are mostly internally mixed with non-refractory particles (Adachi and Buseck, 2010; Li et al., 2013a, 2011d). For example, sulfates from aqueous SO_2 (S(IV)) oxidation catalyzed by transition metals have been found to be an important atmospheric processes in aerosol particles (Alexander et al., 2009) and cloud processes in droplets during long-range transport (Harris et al., 2013). Therefore, single particle analysis can well provide direct microscopic information about the mixing state of these non-refractory particles and explain heterogeneous reactions on particle surfaces during air pollution episodes in East Asia (Adachi et al., 2014; Fu et al., 2012b; Geng et al., 2010; Li et al., 2013b; Li and Shao, 2009b; Niu et al., 2011; Shi et al., 2008b; Yang et al., 2012; Zhang et al., 2013). In addition, single particle analysis – through laboratory and field measurements and theoretical calculations – adequately revealed the optical properties of single particles, which depends on their aging properties or mixing states (Adachi et al., 2010; Moffet and Prather, 2009; Thompson et al., 2012). Moreover, special single particle analyses have been employed to observe hygroscopic growth of single particles, which can reveal their composition and mixing state (Ahn et al., 2010; Ebert et al., 2002; Freney et al., 2010; Hiranuma et al., 2008; Li et al., 2014a, 2014b; Liu et al., 2008; Semeniuk et al., 2007; Wise et al., 2005). These single particle analytical techniques significantly enhance the rigor of atmospheric chemistry.

In this review, research results from single particle analyses have been acknowledged in the literature and have been used to explain some atmospheric phenomena from case studies (e.g., chemical reaction mechanisms, hygroscopicity, and emission source identification) which cannot be answered easily by "bulk" sample analysis or be applied to climate models (Posfai and Buseck, 2010). In this review paper, we introduce the differences of the bulk and single particle sampling and analytical technologies for aerosol particles and focus on the major analytical technologies for single particle analyses. Single particle types from electron microscopy and mass spectroscopy and their sources were classified and