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Seasonal characteristics of submicrometer organic aerosols in urban Gwangju, Korea using an aerosol mass spectrometer

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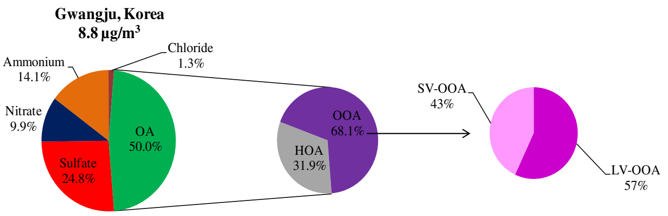
HIGHLIGHTS

- Organic aerosols were characterized using an aerosol mass spectrometer.
- A distinct seasonal and diurnal pattern of organics aerosols were found.
- Long-range transported aerosols significantly contributed to OA in winter.
- Summer organic aerosols experienced significant aging.
- SSA increased in the afternoon along with the LV-OOA.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemical characterization of organic aerosol (OA) was conducted using an aerosol mass spectrometer (AMS) in urban Gwangju, Korea, during the fall (8/30/2011–9/19/2011), winter (12/19/2011–12/30/2011), spring (5/15/2012–5/24/2012), and summer (7/23/2012–8/6/2012). OA was found to be the most dominant component of non-refractory submicrometer particles, with an average concentration of 4.39 μg m^{-3}. The oxygenated organic aerosol (OOA) content was higher than the hydrocarbon-like organic aerosol (HOA) content (68.1% versus 31.9%), and the less volatile-OOA (LV-OOA) content was higher than the semi-volatile OOA (SV-OOA) content (57.0% versus 43.0%). The seasonal data showed that both HOA and LV-OOA were abundant in winter due to the enhancement of the local OA source strength under strong temperature inversion and the frequent long-range transportation of aged air masses from polluted areas. The OA more than doubled when a northwest air mass occurred compared to the other air masses in winter, suggesting that the long-range transported organic species constitute more than 50% of the OA. Changes in the mixing height (i.e., dilution) and the strength of the HOA sources led to a pronounced diurnal pattern for the HOA in winter. A clear transition for the OA components was observed from winter to summer. In summer, LV-OOA became the most dominant component and increased in the afternoon in contrast to the HOA and SV-OOA. A bimodal size distribution of the OA was observed in all seasons due to multiple OA sources and aging. Optical properties of $PM_{2.5}$ measured in the spring showed that the single scattering albedo (SSA) at 532 nm increased in the afternoon along with the LV-OOA. The HOA was better correlated with the light absorption coefficient than the light scattering coefficient, suggesting that the HOA included a significant amount of light absorbing organics and/or were produced at the same time as the light absorbing black carbon.

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1. Introduction

Fine (<2.5 um) and ultrafine particles (<100 nm) in the ambient atmosphere are of current interest due to their effects on the earth's radiation balance via scatting or absorbing incoming solar light (Solomon et al., 2007), cloud formation via acting as cloud condensation nuclei (CCN) (Solomon et al., 2007), visibility (Chow et al., 2002; Deng et al., 2008; Chang et al., 2009), atmospheric chemistry (Reid and Sayer, 2002), and human health (Dockery and Pope, 1994; Peters et al., 1997; Oberdörster, 2000). These particles are directly emitted from anthropogenic and natural sources such as vehicles, industrial factories, burning of biomass, oceans, and deserts (primary aerosols) and are indirectly produced by gas-to-particle conversion processes (secondary aerosols) (Andreae, 2007, 2009). Due to their multiple sources and various aging processes after formation (e.g., condensation, coagulation, oxidation, and cloud processing), they exist in various states of mixing with multiple chemical constituents making it difficult to understand effects of aerosols on climate change. In urban areas, primary and secondary aerosols produced from various local and regional sources over a short time scale (from several hours to days) and long-range transported aerosols affect the air quality and human health. Thus, it is essential to determine the chemical characteristics of aerosols in real time to determine their sources, to establish an appropriate control strategy for ambient aerosols, and to reduce uncertainties in effects of aerosols on climate change.

It has been reported that organic aerosol (OA) constitutes a substantial fraction of the submicrometer particles in urban areas (Kanakidou et al., 2005; Murphy et al., 2006; Zhang et al., 2007). Because OA consists of thousands of chemical species (Ulbrich et al., 2009), their formation and aging mechanisms are not completely understood. It has been suggested that combustion, vehicular exhaust, a variety of industrial emissions, the burning of biomass, and secondary formation contribute to urban OA (Hildemann et al., 1991a,b; Rogge et al., 1993). For example, levoglucosan (from the burning of biomass), hopanes (from vehicle emissions), carboxylic acid (from secondary formation), and polycyclic aromatic hydrocarbons (PAHs) (from combustion) were reported as important components in the OAs observed at urban sites (Bae et al., 2009; Stone et al., 2011).

Aerosol mass spectrometer (AMS) has been a powerful tool to determine the OA in submicrometer atmospheric aerosol in real time, and various types of AMS have been developed (Suess and Prather, 1999; Jayne et al., 2000; Noble and Prather, 2000; Takegawa et al., 2005; DeCarlo et al., 2006; Nash et al., 2006; Canagaratna et al., 2007). In particular, the Aerodyne AMS (Aerodyne Research Inc., USA), hereafter referred to as AMS, determines the chemical composition (organics, sulfate, nitrate, ammonium, and chloride) of particles in several minutes by using a particle vaporization and electron impact ionization method, in which the non-refractory particles are vaporized at 600 °C under high vacuum and the generated vapors are immediately ionized via electron impact with the subsequent ion analyses by a quadruple or time-of-flight mass spectrometer (Jayne et al., 2000). The mass spectra of organics obtained from the AMS can be further analyzed, providing useful insights into OA components such as hydrocarbon-like organic aerosol (HOA), biomass burning OA (BBOA), and oxygenated OA (OOA) (Ng et al., 2011a). The OOA can be further separated into semi-volatile OOA (SV-OOA) and less-volatile OOA (LV-OOA) (Ng et al., 2011a).

Determination of aerosol light scattering and absorption is essential to better understand impacts of aerosols on radiation balance. OA and inorganic aerosols typically scatter light in the visible wavelength leading to have a cool effect on climate while black carbon aerosols strongly absorb light from near IR to UV having a warming effect on climate (Andreae et al., 2002). Some OA was also known to absorb light particularly at short wavelengths (UV). Thus, simultaneous measurements of OA components and aerosol light scattering and absorption can provide useful insights into radiative impacts of the OA.

In this study, the AMS was applied to determine the OA characteristics in an urban area of Gwangju, Korea, during four seasons (fall 2011, winter 2012, spring 2012, and summer 2012). The seasonal and diurnal variations of the OA and their components were investigated along with their size distributions, and the effects of the air mass on the OA characteristics were examined. The OA characteristics were also compared with those of other urban and/or rural areas in East Asia. In the spring, the optical properties such as the light absorption coefficient (B_{abs}), the light scattering coefficient (B_{scat}), and the single scattering albedo (SSA) of $PM_{2.5}$ were measured to relate these properties to the OA components.

2. Experimental

The AMS was continuously operated in urban Gwangju (35:09N, 125:54E), Korea, during the fall (8/30/2011–9/19/2011), winter (12/19/2011–12/30/2011), spring (5/15/2012–5/24/2012), and summer (7/23/2012–8/6/2012). Gwangju is the 5th largest city in Korea and has a population of ~1,400,000, and the sampling site was located ~7.6 km north of the downtown Gwangju city hall, influenced by the traffic from a nearby highway (~1.5 km west from the site), residential heating from residential/commercial areas (~0.6 km south from the site), industrial complex (~4.2 km west from the site), and burning of biomass from agricultural areas (~0.8 km north from the site) (Park et al., 2008, 2012). The major industrial areas in Korea near the site are a petrochemical industrial complex and steel works located ~90 km southeast from the site and ~230 km northeast from the site, respectively. The air mass often passed over an industrial area in China, located ~1000 km northwest from the site, before arriving at the sampling site.

The operation of the AMS was described thoroughly in our previous paper (Park et al., 2012). Briefly, the ambient air was sampled at 6 m above ground level at a flow rate of 25 lpm through a $PM_{2.5}$ cyclone inlet (URG-2000, USA) and was dried using a Nafion drier (Nafion MD-110) before entering the AMS. The sample flow was split into the AMS (0.07 lpm) and an additional pump (24.63 lpm). Isokinetic sampling was achieved for the AMS by controlling the size of the sampling lines and flow rates. To determine the relative ionization efficiency, size-selected ammonium nitrate particles were used (Jayne et al., 2000). Because the particle collection efficiency (CE) for the AMS system was often reported to be ~0.5 for inorganic and organic compounds under dry conditions (Takegawa et al., 2009a), a CE of 0.5 was used in this study.

Positive Matrix Factorization (PMF) analysis for OA was conducted by using PMF2 software to deconvolve AMS organic data (Paatero and Tapper, 1994; Paatero, 1997). The PMF2 program was performed in robust mode to analyze mass spectra of organic aerosols with $m/z < 150$ (these m/z account for ~98% of the total organic mass) measured with the QAMS. Individual extraordinarily high data points (i.e., spikes) in the time series of the mass spectra were excluded. An initial error matrix was calculated using the algorithm developed by Allan et al. (2003) in the QMAS data analysis software (Igor Pro 6.22A) (Wavemetrics, Lake Oswego, OR). The error matrix was further modified following the protocol suggested by Ulbrich et al. (2009). Briefly, a minimum error of 1 ion and 3-point box smoothing were applied for the error matrix. Bad ions with the signal-to-noise ratio (SNR) less than 0.2 were removed from mass spectral and error matrices, whereas weak ions with SNR between 0.2 and 2 were downweighted by a factor of 2.5. Then, CO_2^+ (m/z 44) ions and its associated ions such as H_2O^+ (m/z 18), HO^+ (m/z 17), and O^+ (m/z 16) were also downweighted by a