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Seasonal and diurnal variations of ultrafine particle concentration in urban Gwangju, Korea: Observation of ultrafine particle events

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Abstract

Ultrafine particle concentration (3–100 nm) was continuously measured in summer (6/7/2006–17/8/2006), fall (1/10/2006–31/10/2006), winter (2/2/2007–7/3/2007), and spring (7/4/2007–7/5/2007) in urban Gwangju, Korea. By considering the size range with elevated concentration and hypothesizing the source or formation pathways, we classified ultrafine particle events into: (1) "10–100 nm traffic event," (2) "50–100 nm residential heating event," and (3) "10–30 nm photochemical event." Coincidence of NO_x, CO, O_3, and solar radiation with ultrafine particle concentration was used as an indicator for the traffic, residential heating, and photochemical contributions. We showed that particles due to traffic and residential heating led to enhanced ultrafine particle concentration in winter, while in summer particles formed by photochemical activity led to increased ultrafine particle concentration. The average ultrafine particle number concentrations were 8.8×10^3, 7.4×10^3, and $7.9 \times 10^3\,cm^{-3}$ with geometric mean diameters (GMDs) of 25, 48, and 53 nm in the photochemical, traffic, and residential heating events, respectively. Our ultrafine particle concentrations and other gas concentrations (NO_x and CO) were found to be lower than observations in Atlanta and in Fresno, probably due to lower source strength such as traffic and residential heating in current site. We occasionally observed particle growth after formation of particles in the photochemical event with growth rates of 2.2–4.7 $nm\,h^{-1}$. Morphological and elemental analysis for size-selected ultrafine particles showed that mixtures of sulfate and metals with the presence of semi-transparent part inside the particle were observed in the photochemical event (49 over 200 particles), while in the traffic event agglomerated carbonaceous particles were observed (66 over 130 particles), which were rarely detected in the photochemical event.

Keywords: Ultrafine particle events; Particle concentration; Photochemical event; Growth rate; Particle morphology

1. Introduction

Fine (<2.5 μm) and ultrafine (<100 nm) particles in the ambient atmosphere are of current interest due to their possible adverse health effects (Dockery and Pope, 1994), potential to grow into cloud condensation nuclei affecting earth climate indirectly, and

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their direct effect on the earth's radiation budget (Intergovernmental Panel on Climate Change, 2002). Additionally, ultrafine particles (<100 nm) may have higher reactivity and toxicity due to their enhanced surface area-to-volume ratio (Oberdörster, 2000; Peters et al., 1997). These particles are emitted directly from various sources or formed in the ambient atmosphere by gas-to-particle conversion processes. Continuous measurements of physical and chemical properties of ultrafine particles are essential to better understand their sources, their formation and growth mechanism, and their effects on the ambient atmosphere and human health. Recent studies based on continuous size distribution measurements reported increased ultrafine particle concentrations in specific event days in urban areas (Dunn et al., 2004; Kulmala et al., 2002, 2004; McMurry et al., 2000, 2005; Qian et al., 2007; Stanier et al., 2004a, b; Watson et al., 2006; Woo et al., 2001). By observing the size range with high ultrafine particle concentration and hypothesizing the source production or formation pathways, several distinct types of ultrafine particle events were reported. Woo et al. (2001) observed three types of ultrafine particle events (3–10, 10–35, and 35–45 nm events) at the Atlanta Supersite (Woo et al., 2001) and showed that the elevated ultrafine particle number concentration was correlated well with SO_2 concentration. Dunn et al. (2004) showed that similar nucleation events, which frequently occurred during daylight hours, were consistent with increased concentration of SO_2 in Mexico City (Mexico). Stanier et al. (2004b) showed a good correlation between nanoparticle formation (nucleation) and H_2SO_4 production and ultraviolet (UV) intensity at the Pittsburg Supersite (USA), suggesting that nucleation is associated with photochemical H_2SO_4 production. Watson et al. (2006) reported four types of ultrafine particle events at the Fresno Supersite (USA): (1) "3–10 nm nucleation event," (2) "10–30 nm photochemical event," (3) "10–30 nm traffic event," and (4) "50–84 nm residential wood combustion event. They also observed that nucleation events occurred with a low SO_2 concentration at the ground level. Qian et al. (2007) investigated regional nucleation events in St. Louis (USA). They reported that the nucleation events occurred more frequently in summer than in winter but that a clear association of new particle formation rates with SO_2 concentration was not observed. Previous results thus suggest that sources and formation mechanisms for ultrafine particles vary with time and place.

In this paper, continuous measurements of particle number concentrations in the range of 3–600 nm are reported for all four seasons in urban Gwangju, Korea. Furthermore, PM_{10}, nitrogen oxides (NO_x), carbon monoxide (CO), sulfur dioxide (SO_2), ozone (O_3), and meteorological data were measured simultaneously at the same place. Several distinct types of "ultrafine particle events" (i.e., short time periods during which ultrafine particle concentration increases significantly) are reported here, and seasonal and diurnal variations of ultrafine particle concentration are investigated. Elemental and morphological analyses of size-resolved ultrafine particles during ultrafine particle events were also carried out off-line to identify types of ultrafine particles and to find their possible sources or formation mechanisms.

2. Experimental

The sampling site is located ~7.6 km north of the downtown Gwangju city hall and ~4.2 km from Hanam industrial complex, influenced by traffic from a nearby highway (~1.5 km from the site), residential heating from residential/commercial areas (~0.6 km from the site), and biomass burning from agricultural areas (~0.8 km from the site). A map of the sampling site including possible local sources of emissions is shown in Fig. 1.

The $PM_{2.5}$ sampling inlet was placed on the roof of a four-story building located on the campus of Gwangju Institute of Science and Technology. All samples go through a $PM_{2.5}$ inlet and are dried out by a Nafion drier (Nafion MD-110) before entering the instruments. Particle size distributions were continuously measured during summer (6/7/2006–17/8/2006), fall (1/10/2006–31/10/2006), winter (2/2/2007–7/3/2007), and spring (7/4/2007–7/5/2007). In the size range 3–80 nm the measurements were made with the nano scanning mobility particle sizer (Nano SMPS, DMA: TSI 3085, UCPC: TSI 3776), and in the range from 20 to 600 nm with the regular SMPS (DMA: TSI 3081, CPC: TSI 3022A). For morphological and elemental analyses of ultrafine particles, particles selected by the differential mobility analyzer (DMA) or nano-DMA were collected on TEM grids using a nano-aerosol sampler (TSI 3089). These samples were analyzed by transmission electron microscopy (TEM, JEOL JEM-2100) and energy dispersive spectroscopy (EDS, OXFORD INCAx-sight). In the winter and spring, PM_{10} mass concentration was measured