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Changes in shape and composition of sea-salt particles upon aging in an urban atmosphere

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HIGHLIGHTS

- Na occurs in almost half of the analyzed particles.
- Sea-salt particles change compositions within several hours after emission.
- Sea-salt particles change their effects on climate as they age in urban air.

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ABSTRACT

Sea salt is one of the most abundant types of natural aerosol particles and significantly influences local and global climate. It is an important constituent of samples collected between June 10 and 15 in the Los Angeles area during the 2010 CalNex campaign. The sea-salt particles reacted with other species in the atmosphere and became Na-bearing aerosol (NaA) particles. Using transmission electron microscopy, we found that Na occurred in almost half of all analyzed particles (~3500), although commonly only in minor amounts. Almost all the NaA particles contained S but not Cl, suggesting that Cl was depleted through particle formation to sulfate, nitrate, or both in the urban atmosphere. We observed both rounded and euhedral NaA particles. The rounded ones consisted mainly of aged sea salt (>12 h) that had reacted extensively with sulfate, whereas the euhedral ones occurred in samples from relatively fresh marine air. The shapes and compositions of NaA particles changed within 3 h in the urban atmosphere. Moreover, our calculations indicate that light scattering from NaA particles depends on their shapes (e.g., roughly spherical, flat, or elongated). These compositions and shapes affect hygroscopicities and light scattering, respectively, both of which influence their climate effects.

1. Introduction

Sea salt is one of the most abundant aerosol types in the atmosphere (Pósfai and Buseck, 2010; Seinfeld and Pandis, 2006; Mahowald et al., 2006) and has important radiative effects (Murphy et al., 1998). Most sea-salt aerosol particles form through interaction between the ocean surface and wind, resulting in breaking waves and bursting bubbles (Lewis and Schwartz, 2004). Compositions of newly formed sea-salt particles are essentially the same as that of sea water, which contains Na, Cl, Mg, S, Ca, Br, and K as well as other minor elements (Ebert et al., 2000; Lewis and Schwartz, 2004; Seinfeld and Pandis, 2006). Na and Mg are convenient tracers of sea salt even if it has reacted with other materials. Sea-salt particles are hygroscopic and can contribute to cloud-condensation nuclei.

During transport through the atmosphere, sea-salt particles commonly react with gases and other types of aerosol particles and in the process change compositions. Chlorine is replaced by SO_4^{2-} and NO_3^-, resulting in emission of HCl and forming Na sulfate and nitrate (Gard et al., 1998; Pakkanen, 1996). The Cl from sea salt can interact with ozone as well as organic matter in the atmosphere (Finlayson-Pitts and Hemminger, 2000). In polluted atmospheres, many sea-salt particles become internally mixed with sulfate and nitrate (Buseck and Pósfai, 1999; Dall'Osto et al., 2004; DeBock et al., 2000; Hara et al., 2005; Laskin et al., 2002, 2012; Li et al., 2003; McInnes et al., 1994; Mouri et al., 1993; Pósfai et al., 1994, 1995; Ro et al., 2001).

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We used transmission electron microscopes (TEMs) to analyze the compositions, shapes, and abundances of Na-bearing aerosol (NaA) particles collected during the CalNex (California Research at the Nexus of Air Quality and Climate Change) campaign in 2010. Since these samples were collected from urban air near the Pacific Ocean (Pasadena, CA, 16 km northeast of downtown Los Angeles and 37 km east of the ocean), many particles were mixture of two or more types. Using the same CalNex samples, we reported TEM analyses of mixing states and shapes of nano-spherical soot (ns-soot) (Adachi and Buseck, 2013; Buseck et al., 2014). Using an environmental TEM, we also showed that the analyzed CalNex sea-salt particles deliquesce at ~80% relative humidity (RH) (Adachi et al., 2011).

Sea-salt particles are abundant in the LA area as well as in other coastal cities and have important effects on the atmospheric chemistry and climate. Hayes et al. (2013) reported that sea-salt particles were abundant in the area based on measurements made using X-ray fluorescence analysis (XRF) and particle analysis by laser mass spectrometry during the campaign. The abundances and distributions of sea salt depend on marine air and differ from those of ns-soot, sulfate, and organic aerosol particles. In the current study, we focus on the shapes and compositions of urban NaA particles. The goal is to understand the changes experienced by sea-salt particles in an urban atmosphere.

2. Materials and analyses

2.1. Sampling

Aerosol particles were collected directly onto TEM grids by using 3-stage impactor samplers (MPS-3, California Measurements, Inc.) under ambient conditions. The 50% cutoff aerodynamic diameters of the samplers were 2.0, 0.3, and 0.05 μm. We used samples collected on the smallest impactor stage (between 0.05 and 0.3 μm). Sampling times varied from 3 to 30 min depending on the atmospheric particle concentrations, and most were collected for ~5 min. Particles were collected onto lacey-carbon TEM substrates resembling spider webs, the fibers of which produce minimal overlap with the trapped particles (Adachi and Buseck, 2008). The samplers were placed on the roof of a building at the California Institute of Technology (CalTech) in Pasadena, CA (34.138 N, 118.124 W) between May 14 and June 15, 2010 (Adachi and Buseck, 2013). We manually collected samples daily and had eight intensive sampling periods (more than 20 samples per day). On average, 17 samples per day were collected. During the intensive sampling periods, samples were collected at least hourly during daytime and every two or 3 h during the night. A total of 460 TEM samples were collected throughout the campaign. Samples were stored under dry condition in a desiccator at room temperature. Most TEM analyses were done within one year after the sampling.

2.2. TEM analyses

A 200 kV Tecnai F20 TEM (FEI) and CM 200 TEM (Philips Corp.) were used for imaging and energy-dispersive X-ray spectrometer (EDS; EDAX Inc.) analyses, respectively (Buseck and Adachi, 2008; Adachi and Buseck, 2010, 2011). We also used a 120 kV JEM-1400 scanning transmission electron microscope (STEM) with EDS for determination of element distributions within particles of selected samples. For each grid sample, we took >20 TEM images and analyzed compositions of >10 particles per grid to test for the presence of Na in all 460 samples (Fig. 1). We also obtained EDS spectra of ~3500 particles from 63 TEM samples (~50 particles from 50 to 200 μm^2 per sample) collected between June 10 and 15 using 40-sec acquisition times.

EDS peak intensities were obtained by subtracting the background signals from net EDS intensities of targeted elements. We discuss the occurrences of elements when their peak intensities exceed their minimum mass fraction values (Lorimer, 1987) as calculated by the EDAX EDS software. No distinction was made between ammonium sulfate and mixtures of Na sulfate and nitrate since they contain the same elements.

3. Results and discussion

3.1. Compositions of sea-salt aerosol particles

The abundances and compositions of sea-salt particles change during mixing with anthropogenic particles and gases in the urban atmosphere. During the campaign, NaA particles dominated the aerosol particles on four occasions (Fig. 1). The abundances agree with the results of Hayes et al. (2013), who also showed four plumes having high sea-salt fractions between May 15 and 16, May 20 and 26, May 29 and June 4, and June 11 and 16 for particles with sizes between 1 and 2.5 μm. The consistency between their on-line particle analysis and our results confirms that our off-line TEM study produces results that are representative of the aerosol. These

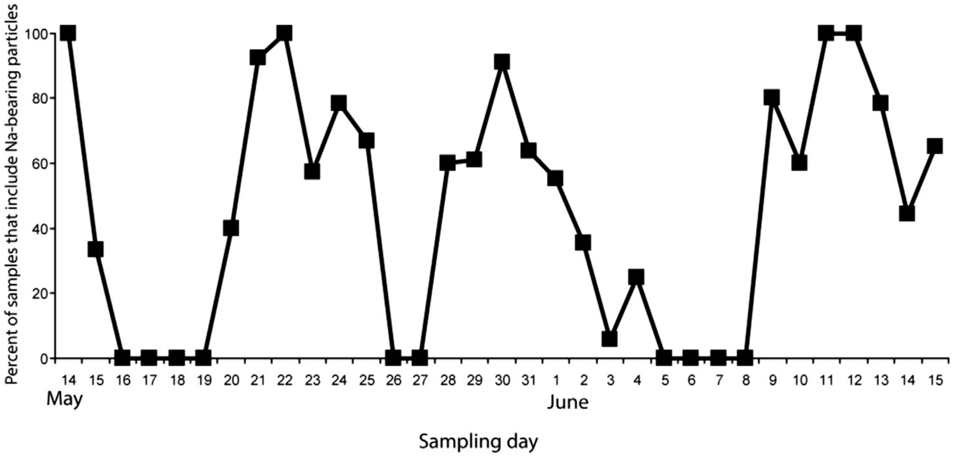

Fig. 1. Abundances of Na-bearing samples during the CalNex campaign. Percentages indicate the number of samples that included NaA particles divided by the number of all samples within a given day. We measured >10 particles per sample for this analysis.