

Alteration of the mixing state of urban aerosols by the formation of secondary organics

Michihiro Mochida[1]; Takuma Miyakawa[2]; Nobuyuki Takegawa[3]; Kimitaka Kawamura[4]; Yutaka Kondo[5]

[1] IAR, Nagoya Univ.; [2] Earth and Planetary Sci., Univ. of Tokyo; [3] RCAST, Univ of Tokyo; [4] Inst. Low Temp. Sci., Hokkaido Univ.; [5] RCAST, Univ. of Tokyo

1. Introduction

Mixing state of atmospheric aerosol particles is tightly linked to various atmospheric processes including cloud formation. Recently, a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) has been demonstrated as a powerful tool to observe the external mixing state of particles with same dry diameters. This hygroscopicity mixing state is primarily governed by the chemical composition of particles, and is controlled by a number of processes in the atmosphere. In this study, we investigated the alteration of the mixing state of urban aerosol particles by photochemical formation of secondary organics, based on the hygroscopicity measurement using a HTDMA.

2. Experiments

Semi-continuous hygroscopicity measurement was performed using a HTDMA in Komaba, Tokyo from August 3 to 8, 2004. Hygroscopic growth factor g of particles whose dry mobility diameter ($d_{m,dry}$) was 100 nm was semi-continuously measured at fixed RH (85%), according to the equation $g = d_{m,85}/d_{m,dry}$, where $d_{m,85}$ is the particle mobility diameters at 85% RH. An aerosol mass spectrometer (AMS, Aerodyne Research) was operated in parallel to the HTDMA to obtain the size-segregated chemical composition data. Chemical compositions at vacuum aerodynamic diameter (d_{va}) ranging from 50 to 200 nm were used as estimates of the composition at $d_{m,dry} = 100$ nm.

3. Results and Discussion

The number distributions of 100 nm particles as a function of g show either uni- or bi-modal distributions depending on the time period. Although sulfate is the major inorganic salt detected throughout the period, particles having hygroscopic growth factor of ammoniated sulfate (1.55-1.6) are negligible except for on August 8. Most of sulfate may therefore be internally-mixed with organics that can retain no- or less water. A large abundance of organics detected by the AMS support this explanation. High positive correlation ($r = 0.76$) between moderately-hygroscopic particles to oxygenated organics suggests that the formation of secondary organics in the atmosphere is responsible for the occasional appearance of moderately hygroscopic particles.

The formation of moderately hygroscopic particles is assessed from the time evolution of the particle hygroscopicity during the photochemical event on August 6. The growth factor distribution was bimodal at 0800 LT, and then the peak diameters of the second mode decreased from 1.39 to 1.18 in 6 hours. Based on an insoluble-core/soluble shell model with $(\text{NH}_4)_2\text{SO}_4$ as a soluble shell, the mode hygroscopic growth factor g of 1.18 at 1400 LT, August 6 was calculated to be equivalent to 23% volume fraction of inorganic salts. The remaining fraction (70-80%) of particles whose growth factor g is around 1.2 is therefore composed of non-inorganic salt components, most likely secondary organics. This is also supported by the increase in the organic fraction from 55% to 70% in 6 hours. The increase is mainly caused by that of oxygenated organics (from 16% to 32%), which are presumably formed secondary in the urban air.

4. Conclusions

The results suggest that photochemical processes in the urban air is responsible for the changes in hygroscopicity mixing state of aerosol particles. The observed change may further affect the evolution of particles after they are transported out of the urban area. While the measurements of particle size distributions themselves provide limited information on the particle evolution processes, the hygroscopicity mixing state provide additional information on the processes as demonstrated in this study.