Executive Summary

Aerosol particles in the atmosphere affect global climate directly by absorbing and scattering solar radiation and indirectly by acting as cloud condensation nuclei (CCN). One of the factors that determine the CCN activation of particles is hygroscopicity. The hygroscopicity of particles changes in the atmosphere, which results in the changes in the CCN activity. For example, hydrophobic particles composed of BC or HOA become hydrophilic and act as CCN after condensation of hygroscopic secondary particles (e.g., sulfate and nitrate) and oxidation, and other chemical transformation. In previous laboratory studies and atmospheric observation studies, CCN number concentrations (N_{CCN}) were predicted from a combination of hygroscopicity (or chemical composition) of particles and the number-size distributions, and were compared to those measured. Previous studies show that the predicted N_{CCN} agreed (~10%) or disagreed (>30%) to the measured and the degrees of disagreements were various. Urban areas have a large source of aerosol particles, in particular less hygroscopic particles containing organics. However, there are few studies in which the importance of hygroscopicity on CCN and cloud droplet formation were analyzed quantitatively based on the observed data of hygroscopicity. Forest areas have a large source of biogenic secondary organic aerosol (BSOA). Whereas some studies in the boreal forest sites in Northern Europe indicate the changes of hygroscopicity and chemical composition with new particle formation and the relationship to the CCN activity, there are only few reports about the changes for the forest sites in temperate zone in Asia. In this study, to better understand the CCN activity of particles and factors controlling the number concentrations of CCN and cloud droplets, atmospheric observations were performed at urban and forest sites. The size-resolved hygroscopicity and CCN activity of urban and forest aerosols were characterized. Further, hygroscopic parameter κ of the particles were derived from the hygroscopic growth factors (g) and CCN activation diameters (d_{act}). Then, the differences of particle hygroscopicity under sub- and super-saturated conditions and the hygroscopicity of organics were analyzed and discussed. The influences of the hygroscopicity of organics and variations of g with time and particle size on N_{CCN} were assessed.

From observation of urban aerosols over Nagoya in 2009, the g distributions at 85% relative humidity (RH) was on average bimodal with less and more hygroscopic modes. Organic-rich particles were dominant in the Aitken mode range. The κ of particles ranged of 0.17–0.33 at 24–359 nm; smaller particles were less hygroscopic and larger particles were more hygroscopic on average. The mean κ of organics (κ_{org}) was 0.11–0.19, suggesting that organics was moderately hygroscopic. The κ values calculated from CCN activation curves under super-

saturated conditions (RH: >100%) were 37% higher than those derived from g under sub-saturated conditions (RH: 85%). Possible reasons for the discrepancy were a reduction of surface tension, the presence of sparingly soluble materials, the dependence of the activity coefficient of water on the solution concentration, and particle asphericity. The 28% difference of the 37% difference is not explained by the difference of κ of inorganics under sub- and super-saturated conditions, suggesting a large contribution of organics to the difference. In the CCN closure, while the N_{CCN}/N_{CN} values predicted from the composition are underestimated largely if organics are assumed to be insoluble, they agree to the measured better if κ_{org} of 0.11 or 0.19 is applied. The N_{CCN}/N_{CN} values predicted from the hygroscopicity show fair agreement to the measured if a single averaged g is applied to all particles. The agreements improve if size- and time-resolved g or size- and time-resolved g distributions are used. The results demonstrate the importance of the hygroscopicity of organics and the dependence of g of particles with time and particle size for CCN number concentrations in the urban atmosphere.

From observation of aerosol particles over a forest site in Wakayama in 2010, the g distributions at 85% RH was on average broad and unimodal. The observation period was categorized to new particle formation (NPF) event days and non-event days, based on the analysis of number-size distributions. On non-event days, g distributions showed similar distributions throughout a day and the differences with time sections and particle size were not clear. The d_{act} and N_{CCN} were almost constant throughout a day. By contrast, on NPF event days, g distributions showed a clear diurnal pattern and the differences with time sections and particle size were large. In the daytime (0900-2100 JST), fine less-hygroscopic particles (κ~0.1) were dominant in the Aitken mode range and the mean g at 24–359 nm were ~30% lower than those on non-event days. The observed κ was similar to that of laboratory-generated pure BSOA, indicating that low hygroscopic particles in the Aitken mode range were newly-formed BSOA and they contributed significantly to the decrease of the hygroscopicity of pre-existing particles. On the other hand, in the nighttime (2100-0900 JST), large and more hygroscopic particles (κ~0.35) were dominant and the mean g at 24–359 nm were ~15% higher than those during non-event days. Possible reasons for the increase of particle hygroscopicity were the aging of particles, the production of water soluble organic matter, and the influence of the inflow of maritime aerosols at large diameter. The CCN activation of the aerosols in the daytime was characterized by the small activated fraction and the large d_{act} and those in the nighttime was characterized by the large activated fraction and the small d_{act} corresponding to the changes of particle hygroscopicity. The result suggests that formation of new particles with less hygroscopicity and their conversion to more hygroscopic particles by aging affect the CCN

activation behavior of the aerosols. The κ calculated for particles in the Aitken mode on NPF event days from g and d_{act} were 0.17 and 0.17, respectively, and κ of newly-formed BSOA was calculated to be 0.13. The calculated κ was similar to the reported κ values of laboratory-generated pure BSOA. The difference of κ values under sub- and super-saturated conditions was within 10% on average, suggesting that the contribution of organics or less hygroscopic particle to the increase of particle hygroscopicity under super-saturated conditions was small. The predicted N_{CCN}/N_{CN} using size- and time-averaged mean g during the observation period agreed well to the measured N_{CCN}/N_{CN}. The results suggest that locally-formed BSOA particles after aging and particles in the background aerosol contributed to the CCN number concentrations largely.

To understand the relationship of the hygroscopicity of particles and their CCN activity, and cloud droplet formation in detail, another aerosol observation was performed in Nagoya in 2010. Size-resolved measurements of the ratios of CCN to CN for particles with selected different g were performed, in addition to the measurements of g distributions at 85% RH. The obtained g distributions were bimodal with less and more hygroscopic modes on average, as the aerosols observed in 2009. The d_{act} were predicted from the respective g of particles and were compared to the measured. While the differences between the CCN activation diameters predicted from g ($d_{act,g85}$) and those measured ($d_{act,CCN}$) were within 12% for more hygroscopic particles (g: 1.25 and 1.4), the differences were larger (16%–41%) for less hygroscopic particles (g: 1.0 and 1.1). The result suggests that less hygroscopic particles contributed to the difference of hygroscopicity of particles under sub- and super-saturated conditions described above. The number concentrations of CCN and cloud droplets (N_{cd}), and the effective radius of cloud droplets (R_{eff}) were estimated from the g distributions using a cloud parcel model. With high updraft velocity (>1.0 ms^{-1}), the presence of less hygroscopic particles in addition to more hygroscopic particles ($0.8 \leq g \leq 2.2$) led to 27% and 18% increase of N_{CCN} and N_{cd}, respectively, and 5% decrease of R_{eff} as compared to the case that only more hygroscopic particles ($g \geq 1.25$) were present. These results suggested that the presence of less hygroscopic particles can contribute substantially to N_{CCN} and N_{cd} and can lead to smaller cloud droplets.