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Title: Hygroscopic properties of newly formed ultrafine particles at an urban site surrounded by deciduous forest (Sapporo, northern Japan) during the summer of 2011

Authors: Jinsang Jung, Kimitaka Kawamura

Responses to the reviewer's specific comments and questions;

Reviewer #1 (Comments):

There are a number of shortcomings in the paper. My biggest concern is that the authors attempt to conclude on the compositions of the particles based on HTDMA measurements. I appreciate the difficulty in analyzing the compositions of these nanoparticles but the tone used throughout the manuscript is not appropriate. At best, we can use the HTDMA measurements to infer the compositions or the HTDMA measurements can be explained by some proposed compositions. There are a number of places that I feel the authors have stretched too much in the implications/conclusions from their measurements.

Specific comments

1. Abstract is a bit focused too much on reporting the observations without enough science. The conclusion that "the hygroscopic property of large Aitken and small accumulation mode particles is highly influenced by the long range atmospheric transport of particles and their precursors" is of no surprise and is hardly an advancement of our understanding of atmospheric aerosols.

Response: We agree to the reviewer's comment. Discussions related to the hygroscopic properties of large Aitken and accumulation mode particles were deleted from the abstract. Instead, the hygroscopic property of nucleated particles that has grown to Aitken mode sizes has been added in the abstract. Please see the revised abstract.

2. Pg 8259, line 20…: "the hygroscopic growth factor of nucleated particles can be used to estimate their chemical compositions." I can understand that the authors perhaps used "estimate" to soften their tone but in my opinion, it is still an assertion that is not well substantiated. This is too strong a statement for field measurements.

Response: We agree to the reviewer's comment. The term "estimate" has been changed to "infer" to soften the tone of a statement throughout the manuscript. Please see line 67 in the

revised MS.

3. The authors need to define the term nucleated particles more clearly especially when freshly nucleated particles and grown Aitken mode particles were discussed too. It is not clear if the discussions of "nucleated particles" of Ehn et al. and Ristovski et al. mean freshly nucleated particles or grown nucleated particles.

Response: We agree to the reviewer's comment. The sentence starting "Ehn et al. (2007)…" in P8259, L22-23 in the original MS has been modified as follows. Please see lines 67-69 in the revised MS.

"Ehn et al. (2007) measured the g(RH) of freshly nucleated particles and the particle subsequently grown to Aitken mode sizes in a boreal forest in southern Finland."

The sentence starting "Ristovski et al. (2010)…" in P8259, L25-27 in the original MS has been modified as follows. Please see lines 72-74 in the revised MS.

"Ristovski et al. (2010) simultaneously measured the hygroscopicity and volatility of freshly nucleated particles in a eucalypt forest in Australia."

4. Page 8262, line 14: I cannot understand the sentence "Since a mode peak diameter of the Gaussian curve fit was used in this study, broadening effects caused by a transfer function between he first and second DMAs are negligible". The broadening effects are related to the spread of the measurements. It is not clear to me how the fitting would reduce or eliminate the broadening. Do you mean that broadening is not an issue since you are only concerned with the mode diameter?

Response: We agreed to the reviewer's comment. Because the sentence starting "Since a mode peak…" in P8262, L12-14 in the original MS is confusing as pointed by two reviewers, we decided to delete it.

5. Page 8264, line 2-4: "Increases in the number concentrations of humidified particles at dry Dp = 40nm were consistent with those at dry Dp = 20nm with and without a time gap". Pls rewrite this sentence. Meaning is not clear.

Response: The sentence starting "Increases in the number…" in P8264, L2-4 in the original MS was modified as follows. Please lines 201-203 in the revised MS.

"Increases in the number concentrations of humidified particles at a dry D_p of 40 nm were observed after the burst of humidified particles at a dry D_p of 20 nm occurred."

6. Page 8264, line 15: would some estimates of growth rates be useful to see if the increase in larger particle concentrations is due to condensation or inflow of different air mass?

Response: Thank you for the valuable comment. Variation of Mode D_p, which is indicative of particle growth rate, was used to investigate if the increase in larger particle concentrations is caused by condensation or inflow of different air mass in section 3.5 and Fig. 7 in the revised MS.

7. The paper calculates equivalent g(85%) at dry Dp=100nm to correct for the Kelvin effect. Kelvin effect depends on surface tension, which in turn depends on chemical compositions. The authors discussed the variation of compositions (as inferred from GF trends) of particles of different sizes, e.g. freshly nucleated particles and grown Aitken particles. Has this size dependence of surface tension been incorporated in the calculation? Would the uncertainty of the different surface tension be sufficiently large to affect the conclusion of the difference in GF of 20nm and 40nm particles and their inferred compositions?

Response: Thank you for the valuable comments. Following sentences have been added in lines 231-242 in the revised MS to discuss the effect of surface tension on the Kelvin effect.

"The surface tension of pure water was used to correct for the Kelvin effect on ultrafine particles. The surface tension of water mixed with $(NH_4)_2SO_4$ increases to approximately 12% higher than that of pure water (Lee and Hildemann, 2013), whereas that of water mixed with organic aerosols such as HULIS (humic-like substance) decreases by about 30% when compared with that of pure water (Salma et al., 2006). Using these two extreme cases to correct for the Kelvin effect on the g(RH) of ultrafine particles, the average Equiv. g(85%) of dry D_p = 20 nm (Table 1) was calculated to be 1.21 to 1.24, whereas that of dry D_p = 40 nm was 1.28 to 1.3, which is comparable with that of dry D_p = 20 nm (1.23) and 40 nm (1.3) calculated using the surface tension of pure water. As the uncertainty associated with the different values of surface tension is negligible, the surface tension of pure water was used in this study."

Two references were added in the reference section.

"Salma, I, Ocskay, R., Varga, I, and Maenhaut, W.: Surface tension of atmospheric humic-like substances in connection with relaxation, dilution, and solution pH, J. Geophys, Res., 111, D23205, doi:10.1029/2005JD007015, 2006.

Lee, J. Y. and Hildemann, L. M.: Surface tension of solutions containing dicarboxylic acids with ammonium sulfate, D-glucose, or humic acid, J. Aerosol Sci., 64, 94-102, 2013."

8. Page 8265, line 3: "Water soluble organic aerosols are assumed in the conversion to obtain Equivalent g at dry Dp=100nm using the Kohler equation." This does not seem to be consistent with the compositions of particles as discussed later in the ms. For example, see the quoted sentence below.

Response: Thank you for the valuable comment. We agree to the reviewer's comment. Inhomogeneity of particles is important for the calculation of Equiv. g(85%) at dry D_p = 100nm. Because Equiv. g(85%) at dry D_p = 100 nm was calculated using geometric mean g(RH) of particles in most figures and discussions in this study, we think that the uncertainty of Equiv. g(85%) at dry D_p = 100nm caused by inhomogeneity of particles is negligible.

9. Page 8265, line 26: "These results imply that water-insoluble particles emitted from traffic may contribute a large portion of particles at the dry Dp range of 40–120nm during the NPF event periods compared to the non-NPF periods." By reading Figures 3a and 3b, the difference is really not that great, less than 0.1 in g(85%), especially that the data for non –NPF (Figure 3b) fluctuate much more than those in Figure 3a. The oscillations of the data in Figure 3b are likely noise, probably because of lower particle concentrations. Hence the conclusion in the quoted sentence is a bit far-fetched to me.

Response: We agree to the reviewer's comment. We think the comparison of hygroscopic growth factor between the NPF and non-NPF episodes is not important. Thus, we decided to delete Figs. 3b and d from the original MS.

The sentences from P8265, L14 to P8266, L2 has been modified as follows. Please see lines 254-262 in the revised MS.

"The median g(85%) values at the dry D_p range of 20–120 nm gradually decreased during the period 4:00–8:00 LT as NO concentration increased (Fig. 4). The decrease in g(85%) values, accompanied by an increase in NO concentrations in the morning, suggest that the decrease in g(85%) values during Phase A can be attributed to increased emissions of water-insoluble ultrafine particles, probably from traffic. As seen in Fig. 5, g(85%) decreases with an increase in the number concentration of particles in each size bin between 4:00 and 8:00 LT. Thus, water-insoluble particles from traffic are important to the hygroscopic properties of particles within the dry D_p range of 40–120 nm prior to the burst of nucleation mode particles."

To clearly show the dependence between g(85%) and increased emission of water-insoluble particles from traffic, following sentences have been added in lines 258-260 in the revised MS.

"As seen in Fig. 5, g(85%) decreases with an increase in the number concentration of particles in each size bin between 4:00 and 8:00 LT."

Following figures have added in Fig. 5 in the revised MS.

"

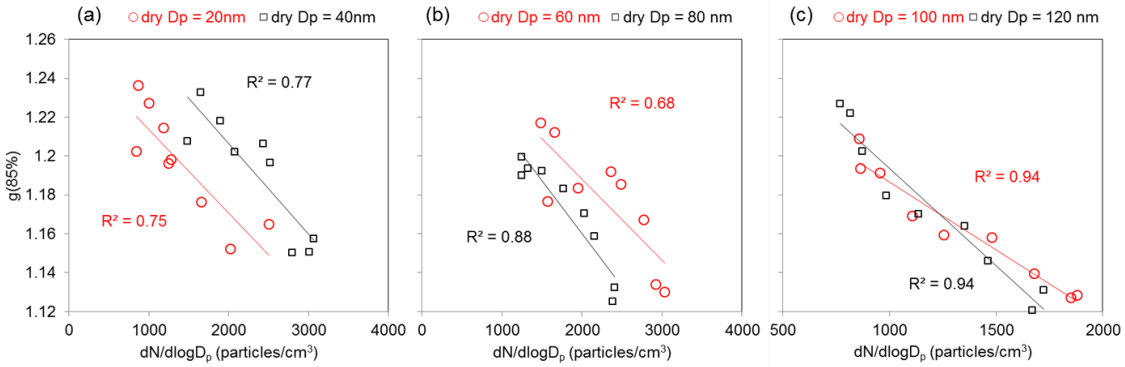

Fig. 5 Scatter plots of g(85%) versus particle number concentrations in each size bin during the NPF events. (a) Dry D_p = 20 nm and 40 nm, (b) Dry D_p = 60 nm and 80 nm, (c) Dry D_p = 100 nm and 120 nm. The data points are 30-min averaged g(85%) values and particle number concentrations from 4:00 to 8:00 LT are marked (A) in Fig. 4a and c."

10. Page 8266, section 3.3, why a bimodal distribution is presented in a typical highly hygroscopic particle distribution? Was the less hygroscopic mode always observed when the highly hygroscopic fraction appeared? If so, was it due to merely mixing of different air mass?

Response: Thank you for the valuable comment on a bimodal distribution of a typical highly hygroscopic particle distribution. Following sentences have been added in lines 284-290 in the revised MS.

"The less-hygroscopic mode was frequently observed when elevated highly-hygroscopic mode distributions were observed as seen in Figs 3 and 6. This bimodal distribution can be explained by the mixing of locally emitted insoluble particles and a complex mixture of long-range transported water-soluble and water-insoluble particles within the Asian continental outflows (Seinfeld et al., 2004). Highly-hygroscopic particles within the Asian outflows are discussed in section 3.6."

A reference was added in the reference section.

"Seinfeld, J., Carmaichael, G., Arimoto, R., Conant, W., Brechtel, F., et al.: ACE-ASIA: Regional climatic and atmospheric chemical effects of Asian Dust and pollution, Bull. Amer. Meteor. Soc., 85, 367–380, 2004."

11. Page 8269, line 10-15, "The different behaviors of the hygroscopic properties indicate that different growth mechanisms for freshly formed nucleation mode particles may exist between the boreal coniferous forest in southern Finland and the present urban site adjacent to a deciduous forest in northern Japan." The authors argue that the growth mechanisms are different between this study and the Finland study show different trends. However, is it possible that the freshly nucleated particles are different but the growth mechanisms are the same, which

could also lead to different trends in terms of changes of hygroscopic properties between the nucleation and the Aitken mode particles?

Response: We agree to the reviewer's comment. The sentence in P8269, L11-14 in the original MS has been slightly modified as follows. Please see lines 365-369 in the revised MS.

"The contrast in the behavior of the hygroscopic properties reported here and by Ehn et al. (2007) indicates that differences may exist in the formation mechanisms of the freshly nucleated particles, or in their growth mechanisms, between the boreal coniferous forest in southern Finland and the Sapporo urban site adjacent to a deciduous forest in northern Japan."

12. Page 8269, line 20-25: "Increased number fractions of intermediately-hygroscopic particles at dry Dp = 20nm were observed when the burst of nucleation mode particles occurred (Fig. 5a and d), indicating that the hygroscopic property of freshly formed nucleation mode particles is intermediate." I notice that the number concentration shows a huge difference (5d) during NPF but the increases of the highly-hygroscopic fractions are moderate. I would imagine that if the nucleation mode particles were mainly highly hygroscopic particles, its fraction will overwhelm the rest. Figure 5a does not suggest that though.

Response: Thank you for the valuable comment on the hygroscopic property of newly formed particles. Because number fractions of freshly formed nucleation mode particles is dominated by intermediately-hygroscopic particles as shown in Fig. 3b and Fig. 7a in the revised MS, we decided to keep the original sentence in P8269, L20-25 in the original MS.

13. The authors put the discussions of different air masses and the diel variations of particle concentrations almost at the end of the paper. I would think that it is more logical to put it up front as an overall discussion and then focus on those observations that are due to NPF. As is, these discussions appear almost like an after-thought. I also noticed that these issues are discussed first in the beginning of the conclusion.

Response: We agree to the reviewer's comment. Discussion related to Fig. 6 in the original MS was moved to the beginning of section 3.1 and Fig. 6 in the original MS was moved to Fig. 2.

14. Related to the above, I found (Page 8270, line 10-13) "Thus, local wind direction was an important factor controlling the growth of newly formed particles and their hygroscopic properties" very strange. The discussion was on different air masses. I would agree that local wind direction affects the OBSERVED growth factor of the particles but I have strong reservations that there is evidence to show that they affect the growth of the newly formed particles their hygroscopic properties.

Response: We agree to the reviewer's comment. The sentences in P8270, L10-12 in the original

MS have been modified as follows. Please lines 392-394 in the revised MS.

"Thus, the hygroscopic growth factor of newly formed particles was perturbed by the local winds that delivered different air masses to the measurement site."

15. Page 8271, line 10-15: "Significantly higher g(85 %)_total values at dry Dp =120nm were obtained during the polluted periods (1.27±0.05) than the clean period (1.19±0.06)." I am curious what the PM compositions over the clean period are.

Response: Thank you for the valuable comments. Unfortunately, no chemical measurements of Aitken and accumulation mode particles had been conducted at the same site before. Thus, it is difficult to answer the reviewer's comment. Following sentence has been added in lines 410-412 in the revised MS.

"To better understand the hygroscopic properties of Aitken and accumulation mode particles, size-segregated chemical measurements will be required in a future study."