MEASUREMENT OF AEROSOL HYGROSCOPICITY AND CLOUD CONDENSATION NUCLEI AT A REMOTE NORTHEAST ASIAN COASTAL SITE IN GOSAN, KOREA IN SUMMER 2006 AND SPRING 2007

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1. INTRODUCTION

Hygroscopicity of aerosols affect radiation energy reaching the surface both by altering aerosol optical depth in the atmosphere. Aerosols that can experience large hygroscopic growth at a relatively small supersaturation (S) can act as cloud condensation nuclei (CCN), which is a key parameter in the assessment of indirect aerosol effects..

The hygroscopicity of submicron aerosol and CCN concentration (N_{CCN}) were measured at a remote northeast Asian coastal site in Gosan, Korea in summer 2006 and spring 2007. The site is strategically located at the western tip of Jeju Island, south of the Korean Peninsula and provides a unique opportunity to monitor aerosols from Asian continental outflow.

2. EXPERIMENT SETUP

During the Gosan campaign (August 16 ~ September 1, 2006), N_{CCN} at 0.2, 0.4, 0.6, 0.8 and 1.0% S were measured using a DMT CCN counter every 30 minute. Aerosol concentrations for diameter, d, larger than 10 nm (N_{CN10}) were measured every minute using a TSI CPC 3010. Submicron size distribution ranging between 10 and 300nm were measured with 95 size bins using an SMPS every 3 minute.

Hygroscopic growth factors (GF) for aerosols having diameter 50, 100, 150 and 200 nm were measured by a humidified tandem differential mobility analyzer (H-TDMA) at 85~95% relative humidity (RH). With a single SMPS available, this could only be done when the SMPS was not used for aerosol size distribution measurement. H-TDMA measurement produces GF values for controlled relative humidity (RH). Due to the temperature variation within the instrument shelter, the temperature within the DMA also varied from time to time, resulting in RH fluctuation. Therefore, only the samples with small fluctuation (standard deviation less than 0.2% RH, which is one-tenth of instrumental accuracy) during the 2-minute voltage scan were used for analysis.

Similar instruments were used in the 2006 autumn campaign in Seoul.

During April 16 ~ May 15, 2007, as a part of Pacific Dust Experiment (PACDEX), N_{CCN} and GF were measured at Gosan using the same instruments mentioned above, except that the measurement was continuously done this

time and 250 nm instead of 50 nm was selected along with the other three diameters. N_{CN10} and submicron size distribution were measured by other research groups but effort has not been made to incorporate all the data yet.

3. OVERALL HYGROSCOPICITY

Fig. 1 illustrates the relationship between measured GF and RH for 150 nm aerosols during the whole 2007 spring campaign. The embedded black curve represents the GF of $(NH_4)_2SO_4$. It is clearly shown that most of the aerosols were hygroscopic but not as hygroscopic as $(NH_4)_2SO_4$. There were also some hydrophobic aerosols having GF less than 1.1. The results for 100, 200 and 250 nm aerosols were also similar (not shown).

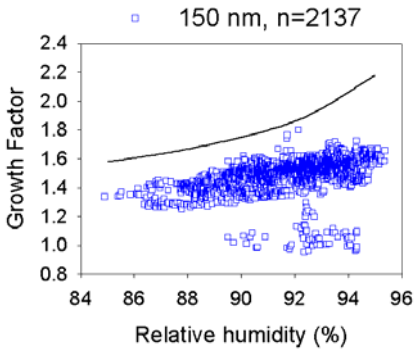

Fig. 1. GF as a function of RH during the 2007 spring campaign.

These GF values are similar to Massling et al.'s (2007) GF measurement at 90% RH in the marine region between Korea and Japan during ACE-Asia in spring 2001. The authors have attributed the reason for such aerosol hygroscopicities as pollution from Korea and Japan. They also found that the aerosols as hygroscopic as $(NH_4)_2SO_4$ were always present. Surprisingly, such aerosol was seldom measured throughout the whole PACDEX campaign.

Maria et al. (2003) reported that there were virtually no sea salts in the submicron sizes in this region based on filter measurement. Massling et al. (2007) also did not found any sea salts except for the case when the air mass had traveled over the ocean for 6 days with no contact with the land. These results agree well with the fact that the aerosols with growth factors significantly exceeding that of $(NH_4)_2SO_4$ were measured only in two occasions throughout the whole measurement period: one at 200 nm and another at 250 nm.

4. SOLUBLE FRACTION

GF can be converted to soluble fraction (ε), assuming that the soluble part of the aerosol volume consists of $(NH_4)_2SO_4$ by simple relation (Pitchford and McMurry, 1994):

$$\epsilon = \frac{GF_a^3 - 1}{GF_{ref}^3 - 1}$$

where GF_a and GF_{ref} stand for measured GF and the reference GF for $(NH_4)_2SO_4$, respectively. Although the exact chemical composition of aerosols may not be $(NH_4)_2SO_4$, such an assumption provides a convenient measure of comparing GFs.

The frequency distributions of soluble fraction are shown in Fig. 2. The soluble fraction of about three-fourth of the samples fall in the range 0.3~0.5. For the smallest diameter, 100 nm, the soluble fraction is

almost normally distributed, with a distinct peak at 0.4, while more evenly distributed shape is shown for the largest diameter, 250 nm. This suggests changes in aerosol chemical composition with size.

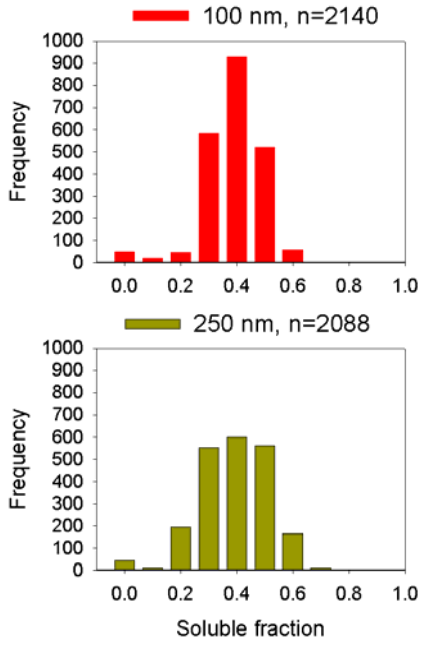

Fig. 2. Frequency of soluble fractions for two different dry sizes for 2007 spring campaign.

Daily variation of solubility frequency ratio is shown for the two diameter, 100 and 250 nm in Fig. 3. Here soluble fraction, <0.3, 0.3-0.6, and >0.6 are termed as hydrophobic, less hygroscopic and more hygroscopic, respectively. The frequency ratio varied much from day to day and from size to size. The wind was very strong on April 21 when the long tongue of more hygroscopic aerosols is found at sizes 150 nm and above, although there was no sign of sea salt. Heavily polluted air mass was reported on April 25~27, when there was a tendency to show greater hygroscopicity in all size ranges. It is not clear what caused a large increase in hydrophobic aerosols on May 10 for 100 nm and May 10~13 for 250 nm.

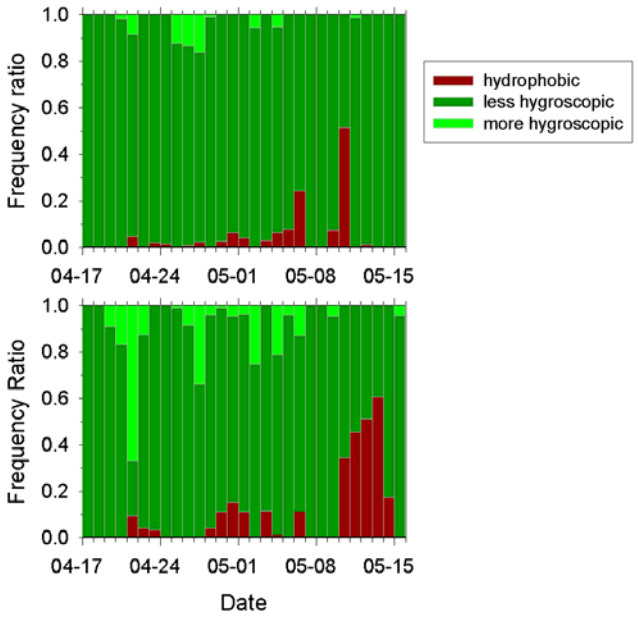

Fig. 3. Daily variation of solubility frequency ratio for (top) 100 nm and (bottom) 250 nm during 2007 spring campaign.

Similar analysis is made for the diurnal variation for 200 nm (Fig. 4). It is noted that hydrophobic aerosols were reduced in the afternoon hours.. Other sizes showed similar diurnal trend but with less significance.

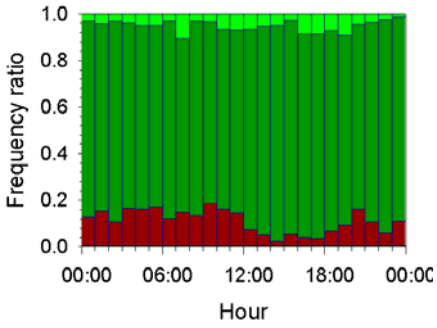

Fig. 4. Average diurnal variation of soluble fraction for 200 nm during 2007 spring campaign.

The aerosol nucleation and growth event

was frequently observed at Gosan. Fig. 5 is an example of such event during the 2006 summer campaign. The GF measurement was made before and after the event, during which the mode diameter grew from 10 nm to about 70 nm, with the average growth rate of 3.3 nm hr^{-1}. To note is that the soluble fraction for 50 nm increased from less than 0.4 before the event to greater than 0.6 after the event, suggesting that condensation of gaseous species during the growth enhanced the hygroscopicity. Similar hehavior was observed for 100 nm.

These results are consistent with Buzorius et al. (2004) who measured GF during aerosol growth events at Gosan during ACE-ASIA for 25 nm aerosol and found that its growth was similar to that of $(NH_4)_2SO_4$. Hameri et al. (2001) also reported growth in GF during the growth event in Finland boreal forest.

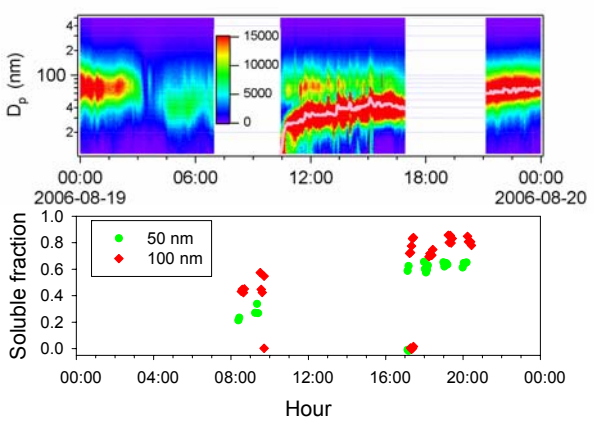

Fig. 5. Aerosol growth event and soluble fraction during 2006 summer campaign: (Top) Temporal variation of aerosol size distribution showing growth event with mode diameter marked as tracer, (Bottom) Temporal variation soluble fraction.

5. HYGROSCOPIC MEASUREMENT IN SEOUL

Shown in Fig. 6 is the measurement in Seoul, highly populated city wih many local sources. Seoul aerosols are comprised of two distinct types: one with extreme hydrophobicity (GF=1) and the other as soluble as, or even more hydroscopic than $(NH_4)_2SO_4$. Consistently, soluble fraction of zero has the highest frequency (Fig. 6)..

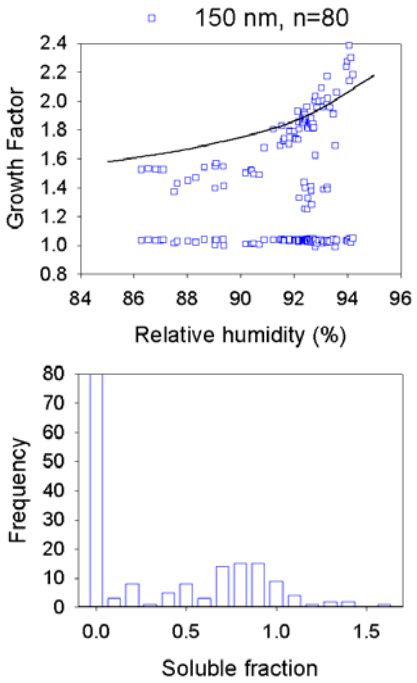

Fig. 6. (Top) GF as a function of RH, (Bottom) Frequency of soluble fractions for Seoul during the 2007 autumn.

6. HYGROSCOPICITY AND CCN

To investigate the effect of hygroscopicity on CCN activity, soluble fraction was compared with CCN number ratio (N_{CCN}/N_{CN}) on daily basis (Fig. 7). In order to account the fact that aerosols with larger diameter tends to act as CCN more easily under same S, samples with soluble fraction larger than 0.4

was selected for 200 and 250 nm while soluble fraction larger than 0.6 was selected for 100 and 150 nm.

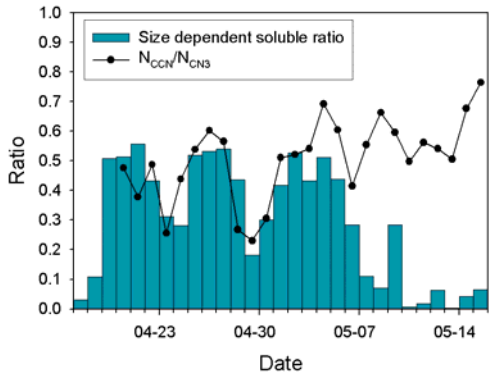

Fig. 7. Daily variations of N_{CCN}/N_{CN} and size-dependent soluble ratio during 2007 spring campaign. CCN was measured under 0.6% S.

The result shows that the two patterns tend to share their local maximum and local minimum until May 5th. The soluble fraction stayed low compared to CCN fraction, indicating that particles with less solubility also acted as CCN. Since May 6th, the CCN number ratio increases but the soluble fraction stays very low. Aerosols with diameter larger than 250 nm must have contributed during that period.

Yum et al. (2007) have reported that Gosan aerosols act almost like $(NH_4)_2SO_4$ as far as CCN activity is concerned. Their cut-off size was 300 nm which is comparable to 250 nm. However, this study shows that particles less soluble than $(NH_4)_2SO_4$ can also act as CCN.

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