

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/5853937>

# Chemical Closure Study on Hygroscopic Properties of Urban Aerosol Particles in Sapporo, Japan

ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · NOVEMBER 2007

Impact Factor: 5.33 · DOI: 10.1021/es063092m · Source: PubMed

---

CITATIONS

18

---

READS

34

## 4 AUTHORS, INCLUDING:



**Shankar G. Aggarwal**

National Physical Laboratory - India

57 PUBLICATIONS 669 CITATIONS

SEE PROFILE



**Michihiro Mochida**

Nagoya University

65 PUBLICATIONS 1,807 CITATIONS

SEE PROFILE



**Yasuyuki Kitamori**

Hokkaido University

6 PUBLICATIONS 245 CITATIONS

SEE PROFILE

# Chemical Closure Study on Hygroscopic Properties of Urban Aerosol Particles in Sapporo, Japan

SHANKAR GOPALA AGGARWAL,<sup>\*,†</sup>  
MICHIO MOCHIDA,<sup>†,‡</sup>  
YASUYUKI KITAMORI,<sup>†</sup> AND  
KIMITAKA KAWAMURA<sup>†</sup>

*Institute of Low Temperature Science, Hokkaido University,  
Kita 19, Nishi 8, Kita-ku, Sapporo 060-0819, Japan, and  
Institute for Advanced Research, Nagoya University, Furo-cho,  
Chikusa-ku, Nagoya 464-8601, Japan*

To assess the link between hygroscopicity of atmospheric particles and the chemical composition, we performed a chemical closure study on the hygroscopicity of organic–inorganic mixed particles nebulized from water extracts of ambient aerosols collected in Sapporo, Japan during summer 2005. The hygroscopicity of 100 nm particles was measured using a hygroscopicity tandem differential mobility analyzer (HTDMA) at 5–95% relative humidity. The chemical analyses of the extracts showed that inorganic salts accounted for 32–84% of the water-soluble fraction and that the remaining was water-soluble organic matter (WSOM). The liquid water content (LWC) of particles was primarily governed by the relative abundance of inorganic salts in particles. The chemical closure with a thermodynamic model did not indicate a significant perturbation of LWC by WSOM at 85% RH with the consideration of the uncertainties estimated. However, a positive perturbation by WSOM was suggested at 50% RH. Individual oxygenated compounds identified using gas chromatography were not abundant enough to substantially increase the LWC at 85% RH.

## Introduction

Aerosol particles affect the regional and global climate by participating in various atmospheric processes. Their hygroscopic response with the changes in relative humidity (RH) is critically important for their cloud condensation nuclei (CCN) activity, atmospheric residence time, optical property, and chemical reactivity. Many of previous laboratory studies used authentic standards or mixtures of some inorganic and organic compounds (1–7) to assess the link between the particle hygroscopicity and chemical composition. Although these studies are important to assess fundamental theories, the model particles do not necessarily represent ambient particles whose organic composition is extremely complex.

The organics in atmospheric aerosol particles affect the particle hygroscopicity. Recent field studies suggest that organic-rich particles are generally less hygroscopic than particles abundant in water-soluble inorganics (8–10). An important question is whether or not the presence of organics perturbs the liquid water content (LWC) of particles, com-

pared to the hypothetical case that organics are not present. Some field studies (11–14) suggest that organic components are inert with respect to water uptake. However, Dick et al. (15) and Pósfai et al. (16) suggested that water uptake by organics is responsible for the aerosol water content at low RH. Saxena et al. (17) suggested that organics alter LWC both positively and negatively. Gysel et al. (18) reported a positive contribution of organics to LWC up to ~90% RH.

To assess the possible perturbation of LWC by organics in ambient aerosols, we performed a chemical closure for particles generated from the water extracts of urban aerosol samples collected in Sapporo, Japan, in a manner similar to a previous work performed by Gysel et al. (18) for European rural aerosols. Although, in the offline method, some characteristics of atmospheric particles such as the external mixing state and the presence of insoluble fractions are lost, this technique has an advantage that the chemical composition and hygroscopicity can be compared using same aqueous samples. This is in contrast to online measurements in which the composition and hygroscopicity are obtained from different aerosol fractions (8, 15, 17, 19), which inherently accompanies large uncertainties. Using a thermodynamic model with the measured particle composition, we assessed the potential role of organics in LWC. A sensitivity study for the variables used in the chemical closure has also been performed.

## Experimental Section

**Aerosol Sampling.** Twenty aerosol samples were collected on precombusted quartz filters (25 × 20 cm) using a high-volume air sampler (~600 L min<sup>-1</sup>) on the rooftop of our institute building (~15 m agl) at Hokkaido University, Sapporo, Japan (43°3'56" N and 141°21'27" E) during May–July 2005. The samples were collected on a 24 h (*n* = 8), daytime (*n* = 6), and nighttime (*n* = 6) basis. The air quality is likely influenced by both local emissions in Sapporo (population: 1.9 million) and aged air masses from East Asia and the surrounding seas. The filter sample was placed into a glass jar and conditioned in a desiccator. The jars were then capped and stored at –20 °C.

**Hygroscopic Growth Measurement.** Hygroscopicity of particles generated from the water extracts of aerosol filter samples was measured using a hygroscopicity tandem differential mobility analyzer (HTDMA) (20) at 293–298 K. First, a filter cut containing 4–16 mg of aerosol mass was extracted with Milli-Q water (>18 MΩ cm, 12–15 mL in total) under ultrasonication (10 min × 3). The extract was filtered by quartz wool and a membrane (Millex-GV, 0.22 μm, Millipore). Aerosol particles were generated from water extracts (~4 mL) using a nebulizer (20). The aerosol was dried (<5% RH) in two diffusion dryers and was introduced to the HTDMA. The HTDMA consists of an <sup>241</sup>Am neutralizer, two differential mobility analyzers (DMA, TSI model 3081), an optional prehumidifier and an aerosol humidity conditioner with Nafion tubes, and a condensation particle counter (CPC, TSI model 3010). Particles of 100 nm in mobility diameter at <5% RH (*d*<sub>m,dry</sub>) were classified in the first DMA. They were introduced to the RH-controlled humidity conditioner in humidification experiments or to the prehumidifier (95% RH) in advance in dehumidification experiments. The resulting particle size was measured using the second DMA and the CPC. More details on the RH control are presented elsewhere (20).

The hygroscopic growth factor, *g*(RH), was calculated from the mobility diameters, *d*<sub>m</sub>(RH), as

\* Corresponding author phone: +81-11-706-6883; fax +81-11-706-7142; e-mail: aggarwal@pop.lowtem.hokudai.ac.jp.

<sup>†</sup> Hokkaido University.

<sup>‡</sup> Nagoya University.

$$g(\text{RH}) = \frac{d_{\text{m}}(\text{RH})}{d_{\text{m,dry}}} \quad (1)$$

The relative standard deviation (RSD) of  $g(\text{RH})$  in the duplicate measurements for three water extract samples were 0.69% and 1.3% at 50% and 85% RH, respectively. The  $g(\text{RH})$  value of pure  $(\text{NH}_4)_2\text{SO}_4$  particles generated from the aqueous solution was  $1.53 \pm 0.03$  (mean  $\pm 1\sigma$ ,  $n = 3$ ) at 85% RH, which agrees within an experimental uncertainty ( $\leq 4\%$ ) to the  $g(\text{RH}) = 1.56$  predicted using the Aerosols Inorganic Model (AIM) (21). The predicted  $g(\text{RH})$  was calculated with the consideration of the Kelvin effect and with the density of  $1.76 \text{ g cm}^{-3}$  and the dynamic shape factor ( $\chi_{\text{dry}}$ ) of unity for dry particles.

**Analysis of Chemical Species.** Water-soluble organic carbon (WSOC) and inorganic ions in the water extracts were quantified. For the WSOC analysis, 0.1 mL of HCl (20%, v/v) was added to 5 mL water extracts, and after 10 min of bubbling, the solution was injected into a TOC analyzer (Shimadzu, TOC-5000A) (22). Inorganic ions ( $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) in the extracts were determined using a Dionex-500 ion chromatograph (22).

Water-soluble dicarboxylic acids, ketoacids, and dicarbonyls were determined by the methods described elsewhere (23, 24). Briefly, a filter aliquot of 8–24  $\text{cm}^2$  was cut in pieces, and the acids and carbonyls were extracted with Milli-Q water, derivatized with  $\text{BF}_3/\text{n-butanol}$ , and determined using a GC-FID. Similarly, sugars on a filter aliquot of 3–10  $\text{cm}^2$  were extracted with a dichloromethane and methanol mixture (2:1), derivatized with  $N,O$ -bis(trimethylsilyl)trifluoroacetamide (BSTFA), and determined using a GC-MS (25).

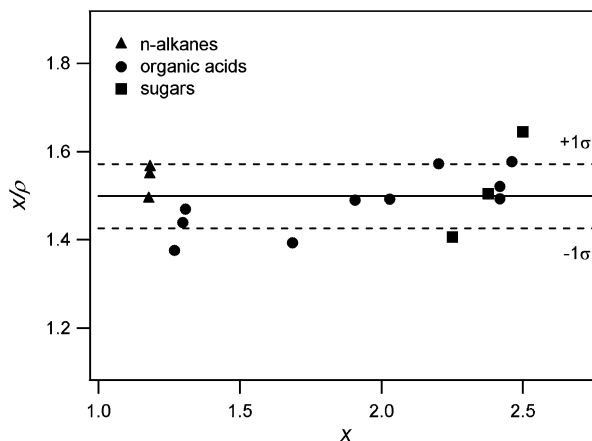
The concentrations of WSOC, inorganic ions, and individual organics reported in this paper are blank corrected. The blanks were not corrected for the chemical closure because of the negligible levels.

**Chemical Closure of Particle Hygroscopicity.** LWC of a particle is calculated using HTDMA and is compared to that predicted from the chemical composition. Here LWC is expressed by the water volume in a single particle ( $V_{\text{w}}$ ) relative to the dry particle volume ( $V_{\text{dry}}$ ), on the assumption that the volumes of water and solute are additive. The  $V_{\text{w}}/V_{\text{dry}}$  ratio (i.e., LWC) is calculated from the HTDMA data as

$$\frac{V_{\text{w}}}{V_{\text{dry}}} \approx \{\chi_{\text{dry}} g(\text{RH})\}^3 - 1 \quad (2)$$

We assumed that wet particles are spherical and that the amount of water associated with a particle at  $<5\%$  RH is negligibly small. We compared the measured  $g(\text{RH})$  of pure  $(\text{NH}_4)_2\text{SO}_4$  particles to that predicted using the AIM and determined the apparent  $\chi_{\text{dry}}$  to be 1.02. Because organic–inorganic mixed particles (generated from water extracts) are generally more spherical (26), their  $\chi_{\text{dry}}$  values should be in the range from 1.00 to 1.02.

The LWC is predicted using the AIM ( $V_{\text{w,inorg}}/V_{\text{dry}}$ ), on the assumptions that only inorganic salts contribute to LWC and that organics are inert. The possible difference between HTDMA-derived  $V_{\text{w}}/V_{\text{dry}}$  and the predicted  $V_{\text{w,inorg}}/V_{\text{dry}}$  thereby suggests the perturbation of LWC by the organics. In the prediction of  $V_{\text{w,inorg}}/V_{\text{dry}}$ , the amounts of water associated with individual inorganic salts are assumed to be additive (i.e., Zdanovskii-Stokes-Robinson (ZSR) approach (27)). A  $\sim 1\%$  difference between RH and water activity ( $a_{\text{w}}$ ) due to Kelvin effect is considered with the surface tension of pure water. The dry particle is assumed to be composed of  $(\text{NH}_4)_2\text{SO}_4$  (AS),  $\text{NH}_4\text{NO}_3$  (AN),  $\text{NH}_4\text{Cl}$  (AC),  $\text{NaCl}$  (SC),  $\text{NaNO}_3$  (SN), water-soluble organic matter (WSOM), and water-insoluble matter (WIM).  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  are neglected because of the low abundances. WSOM fraction possibly contains some



**FIGURE 1.** The  $x/\rho$  versus  $x$  for major organic compounds detected in ambient aerosol particles, where  $x$  is the organic mass to organic carbon mass ratio, and  $\rho$  is the density. Selected compounds ( $\geq \text{C}_4$ ) are organic acids (succinic, glutaric, adipic, pimelic, maleic, fumaric, cebacic, oleic, linoleic, and arachidonic), sugars (levoglucosan, sucrose, and glucose), and n-alkanes ( $\text{C}_{13}$ ,  $\text{C}_{14}$ , and  $\text{C}_{20}$ ).

colloidal insoluble organics if they are too small and can pass through the filters. Similarly, WIM possibly exists in the extracts. In the AIM, we used measured masses of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$  and predicted  $\text{NH}_4^+$  to balance the charge.  $\text{H}^+$  is neglected because the measured  $\text{NH}_4^+$  accounts for nearly 100% ( $99 \pm 24\%$ , mean and  $1\sigma$ ) of the predicted  $\text{NH}_4^+$ .

The mass of water associated with the inorganics at varying RH ( $a_{\text{w}}$ ) is calculated using the AIM as

$$m_{\text{W}}^{\text{ext}} = f_{\text{AIM}}(m_{\text{AS}}^{\text{ext}}, m_{\text{AN}}^{\text{ext}}, m_{\text{AC}}^{\text{ext}}, m_{\text{SC}}^{\text{ext}}, m_{\text{SN}}^{\text{ext}}) \quad (3)$$

where  $m_{\text{AS}}^{\text{ext}}$ ,  $m_{\text{AN}}^{\text{ext}}$ ,  $m_{\text{AC}}^{\text{ext}}$ ,  $m_{\text{SC}}^{\text{ext}}$ , and  $m_{\text{SN}}^{\text{ext}}$  are the masses of AS, AN, AC, SC, and SN in a unit volume of the water extracts, respectively. In an ideal case that WIM is not present in the particles, the  $V_{\text{w,inorg}}/V_{\text{dry}}$  ratio is predicted by

$$\left(\frac{V_{\text{w,inorg}}}{V_{\text{dry}}}\right)_{\text{uncorr}} = \left(\frac{m_{\text{W}}^{\text{ext}}}{\rho_{\text{W}}}\right) / \left(\frac{m_{\text{AS}}^{\text{ext}}}{\rho_{\text{AS}}} + \frac{m_{\text{AN}}^{\text{ext}}}{\rho_{\text{AN}}} + \frac{m_{\text{AC}}^{\text{ext}}}{\rho_{\text{AC}}} + \frac{m_{\text{SN}}^{\text{ext}}}{\rho_{\text{SN}}} + \frac{m_{\text{SC}}^{\text{ext}}}{\rho_{\text{SC}}} + \frac{m_{\text{WSOM}}^{\text{ext}} x}{\rho_{\text{WSOM}}}\right) \quad (4)$$

where  $\rho$  is the density, and  $m_{\text{WSOM}}^{\text{ext}}$  is the mass concentration of WSOC in a unit volume of the water extracts. For the estimation of WSOM from WSOC, the  $x/\rho_{\text{WSOM}}$  ratio (where  $x$  is the organic mass to organic carbon mass ratio) is important than those of independent values of  $x$  and  $\rho_{\text{WSOM}}$ . Figure 1 presents the  $x/\rho_{\text{WSOM}}$  ratios of typical organic compounds in atmospheric particles ( $\leq \text{C}_3$  compounds are excluded because these highly oxygenated compounds have much larger  $x/\rho_{\text{WSOM}}$  values). As seen in Figure 1, the  $x/\rho_{\text{WSOM}}$  ratios are in a narrow range (RSD = 4.9%) despite the large variability in  $x$  and in  $\rho_{\text{WSOM}}$ . We adapted  $x/\rho_{\text{WSOM}}$  of 1.5 for eq 4. This value is consistent with the considerations that  $x = 2.1$  (as derived by Kiss et al. (28)) and  $\rho_{\text{WSOM}} = 1.4$  (suggested by Dick et al. (15)) for typical water-soluble organics in aerosol particles.

To assess the presence of WIM, the amount of less-volatile species in 100 nm particles were quantified using a volatility tandem DMA (VTDMA) with a heated tube ( $\sim 400^\circ\text{C}$ ) placed between first and second DMA. Less-volatile particles, substantially larger in size, were detected when particles generated from sample extracts were introduced to the VTDMA, whereas they were absent in the case of the blank water extracts. The less-volatile components possibly include insoluble inorganics, elemental carbon and crustal materials,

**TABLE 1. Concentrations of Water-Soluble Components ( $\mu\text{g m}^{-3}$ ) in the Aerosol Samples ( $n = 20$ )**

component	min	max	mean	SD
<b>Water-Soluble Components</b>				
$\text{NH}_4^+$	0.53	4.5	2.5	0.97
$\text{Na}^+$	0.06	1.7	0.72	0.59
$\text{Cl}^-$	0.06	3.7	1.1	1.1
$\text{SO}_4^{2-}$	1.4	9.7	5.2	2.2
$\text{NO}_3^-$	0.28	5.4	1.7	1.3
WSOM <sup>a</sup>	1.7	17	6.6	3.8
<b>Identified Water-Soluble Organics</b>				
total diacids <sup>b</sup>	0.11	0.79	0.41	0.19
total ketoacids <sup>c</sup>	0.01	0.08	0.04	0.02
total $\alpha$ -dicarbonyls <sup>d</sup>	0.00	0.03	0.01	0.01
total sugars <sup>e</sup>	0.01	1.1	0.21	0.23

<sup>a</sup> WSOM = WSOC  $\times$  2.1. <sup>b</sup> Saturated  $\text{C}_2$ – $\text{C}_{12}$  straight-chain dicarboxylic acids and methylmalonic, methylsuccinic, 2-methylglutaric, maleic, fumaric, methylmaleic, phthalic, m-phthalic, p-phthalic, malic, ketomalonic, and 4-ketopimelic acids. <sup>c</sup> Pyruvic, glyoxylic, 3-oxopropanoic, 4-oxobutanoic, and 9-oxononanoic acids. <sup>d</sup> Glyoxal and methylglyoxal. <sup>e</sup> Levoglucosan, arabinol, fructose, glucose, mannitol, inositol, sucrose, and mycose.

and less-volatile inorganic salts ( $\text{NaCl}$  and  $\text{NaNO}_3$  (29)). In addition, there is a possibility that charred organics may be present as well, although they might be in a limited fraction (30). The volume fraction of WIM ( $v_{\text{WIM}}$ ) in 100 nm particles is estimated from those of SC ( $v_{\text{SC}}$ ) and SN ( $v_{\text{SN}}$ ) by

$$v_{\text{WIM}} \leq \left( \frac{d_{\text{m},400^\circ\text{C}}}{d_{\text{m},25^\circ\text{C}}} \right)^3 - v_{\text{SC}} - v_{\text{SN}} \quad (5)$$

where  $d_{\text{m},400^\circ\text{C}}$  (<100 nm) and  $d_{\text{m},25^\circ\text{C}}$  (=100 nm) are the mobility diameters of particles with and without heating in the VTDMA, respectively. The right side of eq 5 gives upper limits of  $v_{\text{WIM}}$  because residual particles are possibly non-spherical and contain charred organics. Here a possible change in the particle volume by the decomposition of  $\text{NaNO}_3$  to  $\text{NaNO}_2$  is neglected.

The  $V_{\text{w, inorg}}/V_{\text{dry}}$  ratio for a sample could be lowest in the case that the less volatile residual particles in the VTDMA are spherical and do not contain charred organics. In this case, the following relationship can be achieved

$$\left( \frac{m_{\text{AS}}^{\text{ext}}}{\rho_{\text{AS}}} + \frac{m_{\text{AN}}^{\text{ext}}}{\rho_{\text{AN}}} + \frac{m_{\text{AC}}^{\text{ext}}}{\rho_{\text{AC}}} + \frac{m_{\text{SC}}^{\text{ext}}}{\rho_{\text{SC}}} + \frac{m_{\text{SN}}^{\text{ext}}}{\rho_{\text{SN}}} + \frac{m_{\text{WSOC}}^{\text{ext}}}{\rho_{\text{WSOC}}} \right) / \left( \frac{m_{\text{AS}}^{\text{ext}}}{\rho_{\text{AS}}} + \frac{m_{\text{AN}}^{\text{ext}}}{\rho_{\text{AN}}} + \frac{m_{\text{AC}}^{\text{ext}}}{\rho_{\text{AC}}} + \frac{m_{\text{WSOC}}^{\text{ext}}}{\rho_{\text{WSOC}}} \right) = (1 - v_{\text{WIM}}) / \left[ 1 - \left( \frac{d_{\text{m},400^\circ\text{C}}}{d_{\text{m},25^\circ\text{C}}} \right)^3 \right] \quad (6)$$

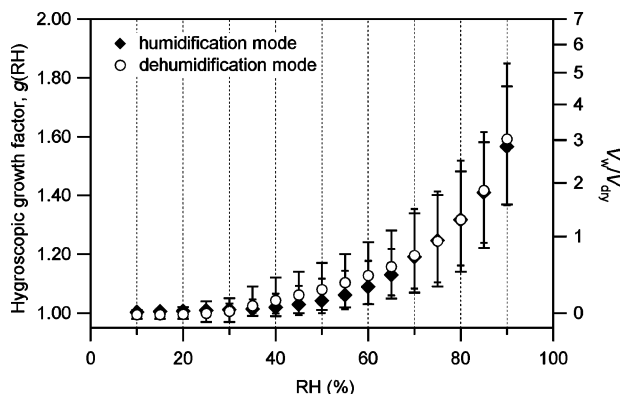
The  $V_{\text{w, inorg}}/V_{\text{dry}}$  ratio is then derived from eqs 4 and 7

$$\left( \frac{V_{\text{w, inorg}}}{V_{\text{dry}}} \right)_{\text{corr}} = (1 - v_{\text{WIM}}) \left( \frac{V_{\text{w, inorg}}}{V_{\text{dry}}} \right)_{\text{uncorr}} = \left[ \left( \frac{m_{\text{W}}^{\text{ext}}}{\rho_{\text{W}}} \right) \left\{ 1 - \left( \frac{d_{\text{m},400^\circ\text{C}}}{d_{\text{m},25^\circ\text{C}}} \right)^3 \right\} \right] / \left( \frac{m_{\text{AS}}^{\text{ext}}}{\rho_{\text{AS}}} + \frac{m_{\text{AN}}^{\text{ext}}}{\rho_{\text{AN}}} + \frac{m_{\text{AC}}^{\text{ext}}}{\rho_{\text{AC}}} + \frac{m_{\text{WSOC}}^{\text{ext}}}{\rho_{\text{WSOC}}} \right) \quad (7)$$

Because of the uncertainty in the actual volume fraction of  $v_{\text{WIM}}$ , the most appropriate  $V_{\text{w, inorg}}/V_{\text{dry}}$  value should be in the range from  $(V_{\text{w, inorg}}/V_{\text{dry}})_{\text{corr}}$  to  $(V_{\text{w, inorg}}/V_{\text{dry}})_{\text{uncorr}}$ .

## Results and Discussion

**Aerosol Chemical Composition.** The concentrations of inorganic salts and WSOM (=WSOC  $\times$  2.1, as discussed above in the prediction of the  $x/\rho_{\text{WSOM}}$  value for eq 4) are summarized in Table 1. WSOM accounts for 16–68% (mean: 35%) of water-soluble aerosol mass, i.e., water-soluble matter (WSM).



**FIGURE 2. The RH dependence of average hygroscopic growth factors  $g(\text{RH})$  for the humidification and dehumidification modes with the minimum and maximum. The  $g(\text{RH})$  from 5% to 90% RH with 5% increments were calculated for each sample by the interpolation at the nearest RH, and then they were averaged. The right axis presents the corresponding liquid water volume,  $V_{\text{w}}$ , normalized by the dry particle volume,  $V_{\text{dry}}$ .**

The sum of inorganic ions that is included in the AIM (Table 1) accounts for 87–100% (mean: 94%) of the total inorganic ion mass (not shown).

Dicarboxylic acids, ketoacids, and dicarbonyls, which are probably from secondary origin, comprise 1.1–4.1% (mean: 2.5%) of WSM and 4.2–12% (mean: 7.1%) of WSOM. Among these organics, oxalic acid was the most abundant followed by malonic acid. Sugar class compounds, which should be from primary origin, account for 0.12–4.6% (mean: 1.1%) of WSM and 0.76–7.3% (mean: 2.9%) of WSOM. The most abundant anhydro- and hydrosugars were levoglucosan and sucrose, respectively.

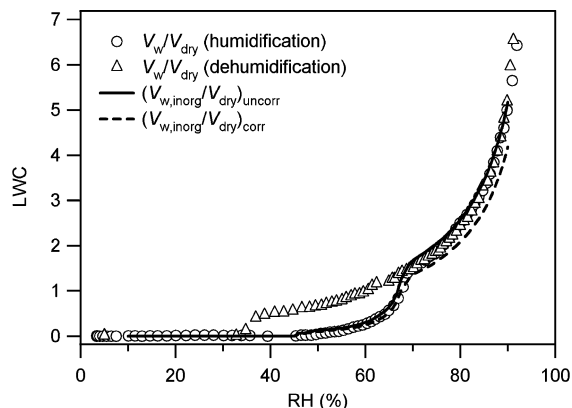
**Measured Hygroscopic Growth.** Figure 2 presents the RH dependence of the averaged  $g(\text{RH})$  on the humidification and dehumidification modes. At high RH (>70%),  $g(\text{RH})$  on both modes are very similar. On the humidification mode,  $g(\text{RH})$  at 85% RH are 1.24–1.62 (mean: 1.41). At lower RH,  $g(\text{RH})$  on the dehumidification mode is higher than that on the humidification mode, as a result of the hysteresis observed for most of the individual samples. However, even on the humidification mode,  $g(\text{RH})$  is equal to or higher than the unity, i.e., 1.00–1.12 (mean: 1.04) at 50% RH. Gysel et al. (18) suggests that dry particles in their experiment were not like packed spheres, because they observed substantial reduction (4–5%) in the particle mobility diameter at 20–40% RH. Such negative growth was negligible (Figure 2), supporting our assumption that dry particles are nearly spherical.

An example of the RH dependence of the measured  $V_{\text{w}}/V_{\text{dry}}$  for a single sample is presented in Figure 3 with predicted  $(V_{\text{w, inorg}}/V_{\text{dry}})_{\text{uncorr}}$  and  $(V_{\text{w, inorg}}/V_{\text{dry}})_{\text{corr}}$  values. The increase in  $g(\text{RH})$  at 60–70% RH as a result of deliquescence of inorganic salts is well predicted. The difference between predicted- and measured  $g(\text{RH})$  on the dehumidification mode at low RH (35–70%) is due to the presence of a meta-stable aqueous phase, which is not modeled here. In Figure 3, the predicted values,  $(V_{\text{w, inorg}}/V_{\text{dry}})_{\text{uncorr}}$  and  $(V_{\text{w, inorg}}/V_{\text{dry}})_{\text{corr}}$ , are close to the measured  $V_{\text{w}}/V_{\text{dry}}$ , suggesting a limited perturbation of LWC by WSOM in the sample. This point is further discussed in the following section.

### Uncertainty in Input Variables for the Chemical Closure.

The uncertainty in the input variables for the chemical closure at 50% and 85% RH is determined to assess the significance of the difference between predicted and measured LWCs (Table 2). The random errors in the concentrations of inorganic salts and WSOM ( $C_{\text{IS}}$  and  $C_{\text{WSOM}}$ ) and in the  $x/\rho$  ratio cause the errors in  $V_{\text{w, inorg}}/V_{\text{dry}}$ , whereas the random





**FIGURE 3.** An example of the RH dependence of the measured- and predicted LWC. The aerosol sample was collected from 2100LT, June 29 to 0440LT, June 30, 2005.

**TABLE 2.** Sensitivity Analysis of the Measured and Predicted Liquid Water Content

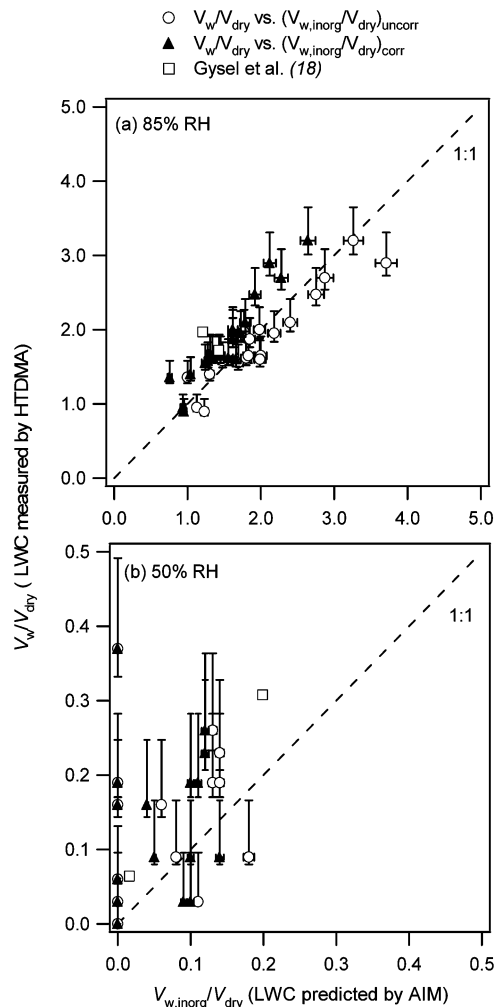
variables	errors	associated errors	
		$V_{w,inorg}/V_{dry}$ (AIM) (%)	$V_w/V_{dry}$ (HTDMA) (%)
85% RH			
Random Errors			
$C_{IS}, C_{WSOM}$	1.1%, 3.5%	2 <sup>c</sup>	
$x/\rho$	4.9%	2 <sup>c</sup>	
$g$	1.3%		6
total <sup>a</sup>		≤ 4	6
Systematic Errors <sup>b</sup>			
$\chi_{dry}$	1.02		8–13
$v_{WIM}$	0.08–0.43	–43 to –8	
50% RH			
Random Errors			
$C_{IS}, C_{WSOM}$	1.1%, 3.5%	2 <sup>c</sup>	
$x/\rho$	4.9%	2 <sup>c</sup>	
$g$	0.69%		10
total <sup>a</sup>		≤ 4	10
Systematic Errors <sup>b</sup>			
$\chi_{dry}$	1.02		23–210
$v_{WIM}$	0.08–0.43	–43 to –8	

<sup>a</sup> Total random errors. <sup>b</sup> Systematic errors show the upper limits. <sup>c</sup> Averaged values.

error in  $g(RH)$  causes the error in  $V_w/V_{dry}$ . Nonspherical particle shape ( $\chi_{dry}$ ) and the presence of WIM ( $v_{WIM}$ ) lead to systematic errors in  $V_w/V_{dry}$  and  $V_{w,inorg}/V_{dry}$ , respectively. We regarded  $\chi_{dry} = 1.00$  as a base case and presented the associated systematic error in  $V_w/V_{dry}$  at  $\chi_{dry} = 1.02$ . The difference between  $(V_{w,inorg}/V_{dry})_{corr}$  and  $(V_{w,inorg}/V_{dry})_{uncorr}$  is presented as the systematic error in  $V_{w,inorg}/V_{dry}$  originated from the uncertainty in  $v_{WIM}$ .

It should be noted that there might be some other potential errors that are not assessed in this study. For instance, WSOM is underestimated if the efficiency of pyrolysis in the TOC analyzer is not 100%, or if some WSOM were evaporated during the bubbling of the extracts. Evaporation of semivolatile components in the HTDMA possibly biases the closure, although no significant change in diameter was observed at <30% RH (see Figure 2).

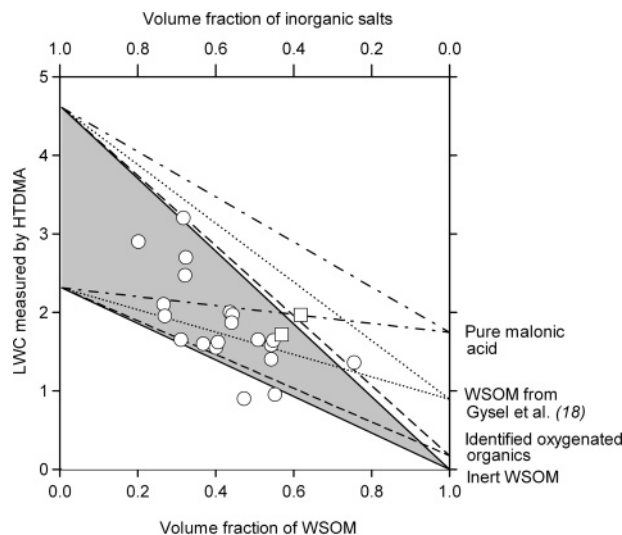
**Perturbation of Liquid Water Content by Water-Soluble Organics.** The measured  $V_w/V_{dry}$  on the humidification mode at 85% RH is compared to the predicted  $(V_{w,inorg}/V_{dry})_{uncorr}$  and  $(V_{w,inorg}/V_{dry})_{corr}$  values for all the samples (Figure 4a). The error bars include a possible range of the bias due to  $\chi_{dry} \neq 1.00$ , addition to the random errors in Table 2. The measured  $V_w/V_{dry}$  values are 0.90–3.20 (mean: 1.85) at 85% RH. The ratios of  $V_w/V_{dry}$  to  $(V_{w,inorg}/V_{dry})_{uncorr}$  and to  $(V_{w,inorg}/V_{dry})_{corr}$



**FIGURE 4.** Plots of  $V_w/V_{dry}$  against  $(V_{w,inorg}/V_{dry})_{uncorr}$  (open circles) and  $(V_{w,inorg}/V_{dry})_{corr}$  (solid triangles) at (a) 85% RH and (b) 50% RH. The error bars include systematic errors (due to  $\chi_{dry} \neq 1.00$ ) and total random errors (Table 2). Two data points (open squares) are adapted from ref 18, in which the samples are labeled as KP010112 and KP010726.

$V_{dry})_{corr}$  are 0.73–1.36 (mean: 0.95) and 0.95–1.78 (mean: 1.21), respectively. Since the modeled  $V_{w,inorg}/V_{dry}$  values have uncertainties ranging from  $(V_{w,inorg}/V_{dry})_{uncorr}$  to  $(V_{w,inorg}/V_{dry})_{corr}$ , the difference of  $V_w/V_{dry}$  from  $V_{w,inorg}/V_{dry}$  is not significant for most of the samples (17 out of 20). This indicates a minor systematic perturbation of LWC by WSOM, which is not detectable within the uncertainty in the closure. The correlation coefficients ( $r^2$ ) between measured  $V_w/V_{dry}$  with predicted  $(V_{w,inorg}/V_{dry})_{uncorr}$  and  $(V_{w,inorg}/V_{dry})_{corr}$  were 0.87 and 0.89, respectively, which are higher than those reported in previous closure studies (17, 19). Figure 4a also shows the measured and predicted LWC reported in ref 18, in which the chemical closure was performed for particles generated from water extracts of European rural aerosol samples. Most of the data points in this study are below or close to the 1:1 line than the points obtained from ref 18, suggesting that the hygroscopicity of WSOM reported in ref 18 roughly provides the upper limit for the WSOM studied.

The dependency of the organic composition on the magnitude and sign of the perturbation of LWC, which was suggested by Saxena et al. (17), is not evident. The  $(V_w/V_{dry})/(V_{w,inorg}/V_{dry})_{uncorr}$  and  $(V_w/V_{dry})/(V_{w,inorg}/V_{dry})_{corr}$  ratios do not correlate either with oxalic acid/WSOM ( $r^2 = 0.06$  and 0.002, respectively) or levoglucosan/WSOM ( $r^2 = 0.06$  and 0.04, respectively), where levoglucosan and oxalic acid are the



**FIGURE 5. Relationships between  $V_w/V_{dry}$  measured using HTDMA and inorganic salts/WSOM volume fractions (open circles). Two data points from ref 18 (open squares, originally labeled as KP010112 and KP010726) are derived with the assumed density of  $1.76 \text{ g cm}^{-3}$  for the inorganic salt fraction. Triangles show LWC in several hypothetical cases. Shaded triangle: liquid water is associated only with inorganic salts. Triangle with dotted-dashed lines: hygroscopicity of WSOM is the same as that of malonic acid (31). Triangle with dashed lines: among WSOM, only identified organics (acids, carbonyls, and sugars) contribute to the water contents. Hygroscopicities of acids+carbonyls and sugars are represented by that of malonic acid (31) and D-glucose (20), respectively, and the right axis point is calculated as [(LWC by malonic acid  $\times$  volume fraction of acids+carbonyls in WSOM) + (LWC by D-glucose  $\times$  volume fraction of sugars in WSOM)]. Triangle with dotted lines: hygroscopicity of WSM is taken from ref 18, and the right axis point is calculated as (LWC by WSM  $\times$  volume fraction of WSOM).**

markers for primary and secondary water-soluble organics, respectively. However, the RSD of  $(V_w/V_{dry}) / (V_{w,inorg}/V_{dry})_{uncorr}$  and  $(V_w/V_{dry}) / (V_{w,inorg}/V_{dry})_{corr}$  ratios (16% and 15%, respectively) is not fully explained by the expected RSD (7%) estimated from the random errors in  $V_w/V_{dry}$  and  $V_{w,inorg}/V_{dry}$ . Sample-to-sample variations in  $V_{w,inorg}/V_{dry}$  (between  $(V_{w,inorg}/V_{dry})_{uncorr}$  and  $(V_{w,inorg}/V_{dry})_{corr}$ ) and in  $\chi_{dry}$  ( $\neq 1.00$ ) are possible reasons, and more detailed investigations on these variables are required in future studies.

By contrast, the predicted- and measured LWCs on the humidification mode disagree at 50% RH (Figure 4b). The  $V_w/V_{dry}$  values as high as 0.37 (mean: 0.12) are not predicted by the AIM, suggesting a positive perturbation of LWC by the presence of organics at low RH. This is consistent with the suggestions by Dick et al. (15) and Pósfai et al. (16) and the  $V_w/V_{dry}$  values from ref 18 (Figure 4b). However, there is still a need for further investigation. For instance, if the amount of  $\text{NH}_4^+$  in the AIM is reduced to 75% ( $-1\sigma$  value of the difference between  $\text{NH}_4^+$  measured and that used in the AIM, see the Experimental Section), and the balance is replaced by  $\text{H}^+$ , the  $(V_w/V_{dry}) / (V_{w,inorg}/V_{dry})_{uncorr}$  and  $(V_w/V_{dry}) / (V_{w,inorg}/V_{dry})_{corr}$  ratios are on average less than unity ( $0.55 \pm 0.45$  and  $0.68 \pm 0.54$ , respectively, with  $1\sigma$ ). This is because LWC at 50% RH is very sensitive to the acidity of particles by means of the changes in the deliquescence RH of inorganic salts (note that, however, same tests at 85% RH result in only  $<2.5\%$  error in  $V_{w,inorg}/V_{dry}$ ).

**Mixing Lines between LWCs Associated with Inorganic Salts and WSOM.** The measured  $V_w/V_{dry}$  values at 85% RH are plotted as a function of the volume fraction of WSOM (Figure 5) to further assess the role of organics in LWC. A clear decreasing trend indicates the primary contribution of inorganic salts to LWC. In Figure 5, the upper and lower

bounds of the shaded triangle present the mixing lines of the particle hygroscopicity calculated using ZSR approach, on the assumption that the liquid water is associated only with inorganics. The bounds were calculated using the AIM by measured inorganic compositions with the highest and the lowest  $V_{w,inorg}/V_{inorg}$  (where,  $V_{inorg}$  is the volume of inorganics) values, respectively. The presence of WIM is not discussed here, although the estimated mixing lines could be 21% lower on average if  $\nu_{WIM}$  is considered.

Most of the data points, including those from ref 18, are in the shaded triangle area in Figure 5. The approximation of inert WSOM with respect to water uptake property thereby does not lead to a significant error in the prediction of LWC. By contrast, if the hygroscopicity of WSOM is assumed to be as high as that of malonic acid (i.e., 1.40 taken from ref 31), the expected LWC (dashed-dotted lines) is completely overestimated. Hence, the hygroscopicity of WSOM is substantially less than that of malonic acid, which is highly hygroscopic because of its small molecular weight and dissociation characteristic. By contrast, the quantified organic acids and sugars are not abundant enough to affect the LWC. The dashed lines (Figure 5) represent the areas of  $V_w/V_{dry}$  on the assumption that among WSOM, only identified organic species contribute to total aerosol water contents. The shift in the triangle area from the shaded area is negligibly small, if compares the variations in  $V_w/V_{dry}$  and to those in the WSOM fraction.

Gysel et al. (18) reported the mass fractions of inorganic salts and WSOM, and the estimated mass of water associated with these two components at 90%RH. If the densities of inorganic salts and WSOM in their reports are assumed to be  $1.76$  (i.e., that of  $(\text{NH}_4)_2\text{SO}_4$ ) and  $1.5 \text{ g cm}^{-3}$  (18), respectively, the amount of water associated with the unit volume of WSOM is  $0.19$ – $0.42$  (mean:  $0.32$ ) times of  $(\text{NH}_4)_2\text{SO}_4$ . Such modest hygroscopicity of WSOM (Figure 5) is not highly contradicted to our observation, given the uncertainty in the mixing lines due to  $\nu_{WIM}$ . In other words, in most cases the LWCs by particles studied are not highly sensitive to the hygroscopicity of WSOM up to the values in ref 18. More precise information on the hygroscopicity of WSOM is critically important, especially in the cases when WSOM fractions are larger (i.e.,  $>0.6$ ).

## Acknowledgments

This study is in part supported by the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) through grant-in-aid No. 17340166, 18651001, and 18684031; it was also supported by the Program for Improvement of Research Environment for Young Researchers from Special Coordination Funds for Promoting Science and Technology (SCF) by MEXT. S.G.A. thanks the Japanese Society for the Promotion of Science for a postdoctoral fellowship.

## Literature Cited

- Hansson, H.-C.; Rood, M. J.; Koloutsou-Vakakis, S.; Hämeri, K.; Orsini, D.; Wiedensohler, A. NaCl aerosol particle hygroscopicity dependence on mixing with organic compounds. *J. Atmos. Chem.* **1998**, *31* (3), 321–346.
- Cruz, C. N.; Pandis, S. N. Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol. *Environ. Sci. Technol.* **2000**, *34*, 4313–4319.
- Peng, C.; Chan, C. K. The water cycles of water-soluble organic salts of atmospheric importance. *Atmos. Environ.* **2001**, *35*, 1183–1192.
- Prenni, A. J.; DeMott, P. J.; Kreidenweis, S. M. Water uptake of internally mixed particles containing ammonium sulfate and dicarboxylic acids. *Atmos. Environ.* **2003**, *27*, 4243–4251.
- Brooks, S. D.; DeMott, P. J.; Kreidenweis, S. M. Water uptake by particles containing humic materials and mixtures of humic materials with ammonium sulfate. *Atmos. Environ.* **2004**, *38*, 1859–1868.

- (6) Badger, C. L.; George, I.; Griffiths, P. T.; Braban, C. F.; Cox, R. A.; Abbatt, J. P. D. Phase transitions and hygroscopic growth of aerosol particles containing humic acid and mixtures of humic acid and ammonium sulphate. *Atmos. Chem. Phys.* **2005**, *6*, 755–768.
- (7) Svenningsson, B.; Rissler, J.; Swietlicki, E.; Mircea, M.; Bilde, M.; Facchini, M. C.; Decesari, S.; Fuzzi, S.; Zhou, J.; Mønster, J.; Rosenørn, T. Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance. *Atmos. Chem. Phys.* **2006**, *6*, 1937–1952.
- (8) Kaku, K. C.; Hegg, D. A.; Covert, D. S.; Santarpia, J. L.; Jonsson, H.; Buzorius, G.; Collins, D. R. Organics in the Northeastern Pacific and their impacts on aerosol hygroscopicity in the subsaturated and supersaturated regimes. *Atmos. Chem. Phys.* **2006**, *6*, 4101–4115.
- (9) Carrico, C. M.; Kreidenweis, S. M.; Malm, W. C.; Day, D. E.; Lee, T.; Carrillo, J.; McMeeking, G. R.; Collett, J. L., Jr. Hygroscopic growth behavior of a carbon-dominated aerosol in Yosemite National Park. *Atmos. Environ.* **2005**, *39*, 1393–1404.
- (10) Lee, Y. S.; Collins, D. R.; Li, R.; Bowman, K. P.; Feingold, G. Expected impact of an aged biomass burning aerosol on cloud condensation nuclei and cloud droplet concentrations. *J. Geophys. Res.* **2006**, *111*, D22204, doi:10.1029/2005JD0064.
- (11) Pitchford, M. L.; McMurry, P. H. Relationship between measured water vapor growth and chemistry of the atmospheric aerosol for Grand Canyon, Arizona, in winter 1990. *Atmos. Environ.* **1994**, *28* (5), 827–839.
- (12) Swietlicki, E.; Zhou, J.; Berg, O. H.; Martinsson, B. G.; Frank, G.; Cederfelt, S.; Dusek, U.; Berner, A.; Birmili, W.; Wiedensohler, A.; Yuskiewicz, B.; Bower, K. N. A closure study of sub-micrometer aerosol particle hygroscopic behavior. *Atmos. Res.* **1999**, *50*, 205–240.
- (13) Hämeri, K.; Väkevä, M.; Aalto, P. P.; Kulmala, M.; Swietlicki, E.; Zhou, J.; Seidl, J. W.; Becker, E.; O'Dowd, D. Hygroscopic and CCN properties of aerosol particles in boreal forests. *Tellus, Ser. B* **2001**, *53B*, 359–379.
- (14) Busch, B.; Kandler, K.; Schütz, L.; Neustüß, C. Hygroscopic properties and water-soluble volume fraction of atmospheric particles in the diameter range from 50 nm to 3.8 µm during LACE 98. *J. Geophys. Res.* **2002**, *107* (D21), 8119, doi:10.1029/2000JD000228.
- (15) Dick, W. D.; Saxena, P.; McMurry, P. H. Estimation of water uptake by organic compounds in submicron aerosols measured during the southeastern Aerosol and Visibility Study. *J. Geophys. Res.* **2000**, *105* (D1), 1471–1479.
- (16) Pósfai, M.; Xu, H.; Anderson, J. R.; Buseck, P. R. Wet and dry sizes of atmospheric aerosol particles: An AFM-TEM study. *Geophys. Res. Lett.* **1998**, *25* (11), 1907–1910.
- (17) Saxena, P.; Hildemann, L. M.; McMurry, P. H.; Seinfeld, J. H. Organics alter hygroscopic behavior of atmospheric particles. *J. Geophys. Res.* **1995**, *100* (D9), 18755–18770.
- (18) Gysel, M.; Weingartner, E.; Nyeki, S.; Paulsen, D.; Baltensperger, U.; Galambos, I.; Kiss, G. Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol. *Atmos. Chem. Phys.* **2004**, *4*, 35–50.
- (19) Aklilu, Y.; Mozurkewich, M.; Prenni, A. J.; Kreidenweis, S. M.; Alfara, M. R.; Allan, J. D.; Anlauf, K.; Brook, J.; Leaitch, W. R.; Sharma, S.; Boudries, H.; Worsnop, D. R. Hygroscopicity of particles at two rural, urban influenced sites during Pacific 2001: Comparison with estimates of water uptake from particle composition. *Atmos. Environ.* **2006**, *40*, 2650–2661.
- (20) Mochida, M.; Kawamura, K. Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles. *J. Geophys. Res.* **2004**, *109*, D21202, doi:10.1029/2004JD004962.
- (21) Clegg, S. L.; Brimblecombe, P.; Wexler, A. S. Thermodynamic model of the system  $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{H}_2\text{O}$  at 298.15 K. *J. Phys. Chem. A* **1998**, *102*, 2155–2171.
- (22) Wang, H.; Kawamura, K.; Shooter, D. Carbonaceous and ionic components in wintertime atmospheric aerosols from two New Zealand cities: Implications for solid fuel combustion. *Atmos. Environ.* **2005**, *39*, 5865–5875.
- (23) Kawamura, K. Identification of C2–C10  $\omega$ -oxocarboxylic acids, pyruvic acid C2–C3  $\alpha$ -dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC-MS. *Anal. Chem.* **1993**, *65*, 3505–3511.
- (24) Kawamura, K.; Ikushima, K. Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere. *Environ. Sci. Technol.* **1993**, *27*, 2227–2235.
- (25) Mochida, M.; Kawamura, K.; Umamoto, N.; Kobayashi, M.; Matsunaga, S.; Lim, H.-J.; Turpin, B. J.; Bates, T. S.; Simoneit, B. R. T. Spatial distribution of oxygenated organic compounds (dicarboxylic acids, fatty acids and levoglucosan) in marine aerosols over the western Pacific and off coasts of East Asia: Asian outflow of organic aerosols during the ACE-Asia campaign. *J. Geophys. Res.* **2003**, *108* (D23), 8638, doi:10.1029/2002JD003249.
- (26) Zelenyuk, A.; Cai, Y.; Chieffo, L.; Imre, D. High precision density measurements of single particles: The density of metastable phases. *Aerosol Sci. Technol.* **2006**, *40*, 197–217.
- (27) Stokes, R. H.; Robinson, R. A. Interactions in aqueous non-electrolyte solutions. I. Solute-solvent equilibria. *J. Phys. Chem.* **1966**, *70*, 2126–2130.
- (28) Kiss, G.; Varga, B.; Galambos, I.; Ganszky, I. Characterization of water-soluble organic matter isolated from atmospheric fine aerosol. *J. Geophys. Res.* **2002**, *107* (D21), 8339, doi:10.1029/2001JD000603.
- (29) Rose, D.; Wehner, B.; Ketzel, M.; Engler, C.; Voigtländer, J.; Tuch, T.; Wiedensohler, A. Atmospheric number size distributions of soot particles and estimation of emission factors. *Atmos. Chem. Phys.* **2006**, *6*, 1021–1031.
- (30) Nyeki, S.; Baltensperger, U.; Coulson, G.; Galambos, I.; Gysel, M.; Kiss, G.; Krivácsy, Z.; Colbeck, I. Properties of humic-like organics isolated from atmospheric fine aerosol: Aerosol volatility. *J. Aerosol Sci.* **2003**, S225–S226.
- (31) Peng, C.; Chan, M. N.; Chan, C. K. The hygroscopic properties of dicarboxylic acids and multifunctional acids: Measurements and UNIFAC predictions. *Environ. Sci. Technol.* **2001**, *35*, 4495–4501.

Received for review December 28, 2006. Revised manuscript received August 2, 2007. Accepted August 6, 2007.

ES063092M