Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles

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[1] Biomass burning, which is characterized by pyrolysis as well as vaporization and condensation of biomass constituents, is a significant source of atmospheric organic aerosols. In this study, hygroscopic properties of five organic compounds (levoglucosan, D-glucose, and vanillic, syringic, and 4-hydroxybenzoic acids), which are major pyrolysis products of wood, were measured using a tandem differential mobility analyzer. Levoglucosan, which is typically the most abundant species in wood burning aerosols, showed a significant hygroscopic growth for particles with a diameter of 100 nm. No efflorescence was observed under the measured relative humidity, and a supersaturated condition of levoglucosan-water particles was observed. The growth factors of levoglucosan are 1.08, 1.18, 1.23, and 1.38 at relative humidity (RH) of 60, 80, 85, and 90%, respectively. The measured hygroscopic curves are in general consistent with those estimated from ideal solution theory and Uniquac Functional-Group Activity Coefficient (UNIFAC) and Conductor-Like Screening Model for Real Solvent (COSMO-RS) methods. Significant hygroscopic growth was also observed for D-glucose, whose growth factor is quite similar to that of levoglucosan. However, three model pyrolysis products of lignin (i.e., vanillic-, syringic-, and 4-hydroxybenzoic acids) did not show any hygroscopic growth under the RH conditions up to 95%. On the basis of the organic composition of wood burning aerosols, the water absorption attributed to levoglucosan in wood burning aerosols is calculated to be up to 30% of the organic mass at 90% RH. This study demonstrates that oxygenated organics emitted from biomass burning could significantly enhance the hygroscopic properties of atmospheric aerosols.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; KEYWORDS: hygroscopic properties, biomass burning aerosol, tandem differential mobility analyzer


1. Introduction

[2] Hygroscopic properties of aerosol particles can directly control the size distribution, chemical reactivity, and the lifetime. Furthermore, uptake of water vapor by aerosols modifies the light scattering. These properties are tightly linked to radiative balance on the earth as well as air quality. So far, hygroscopic properties of inorganic salts relevant to atmospheric aerosols are evaluated by a number of laboratory studies [e.g., Tang, 1997], but little is known about such properties of organics and organic/inorganic mixtures. Recently, Dick et al. [2000] discussed the role of organics in controlling the aerosol hygroscopicity based on the ambient measurement, suggesting that the organic-associated water content of atmospheric aerosols is comparable or greater than that of sulfate at low relative humidity (RH). To date, measurements of hygroscopic properties for organic compounds and organic/inorganic mixture are mainly for low molecular-weight dicarboxylic acids [Cruz and Pandis, 2000; Peng et al., 2001a; Prenni et al., 2001], which are known as secondary oxidation products in the atmosphere [e.g., Kawamura and Ikushima, 1993].

[3] Biomass burning is one of the major sources for organic particulate matter in the atmosphere [Liousse et al., 1996]. Particles in biomass burning smoke enriched with hygroscopic organic constituents are suggested to act as efficient cloud condensation nuclei [Novakov and Corrigan, 1996]. The organic compositions of biomass burning aerosols are studied on the fields [e.g., Gao et al., 2003] as well as in controlled environment [Schauer et al., 2001; Fine et al., 2002]. It has been revealed that the organic compositions of biomass burning aerosols are characterized by several particular oxygenated compounds. Among the compounds derived from combustion of cellulose and hemicellulose in biomass, levoglucosan (1, 6-anhydro-β-D-glucose) and other anhydro saccharides are
known as major pyrolysis products [Simoneit et al., 1999] and reported in continental and marine atmosphere [e.g., Simoneit et al., 1999; Mochida et al., 2003]. The fraction of levoglucosan in biomass burning organic aerosol particles reaches up to 30% [Schauer et al., 2001]. Furthermore, a number of compounds have been identified as pyrolysis products of lignin that are also major constituents of woods. Lignin pyrolysis products retain common chemical structures of lignin moiety, such as syringyl (-C₆H₂(OCH₃)₂OH), guaiacyl (-C₆H₃(OCH₃)OH), and hydroxybenzyl (-C₆H₄OH) groups.

Considering the unique chemical constituents of biomass burning aerosols, it is important to know how such unique composition affect the physical, chemical, and optical properties of aerosol particles. In this study, hygroscopic properties of model organic compounds (levoglucosan, D-glucose, and vanillic-, syringic-, and 4-hydroxybenzoic acids) characteristic to biomass burning aerosols were measured using a tandem differential mobility analyzer (TDMA) system. This study mainly focuses on oxygenated organic compounds that are primarily emitted by biomass burning. Here we also discuss an atmospheric chemical implication of the hygroscopic properties of these biomass-burning products.

2. Experimental Method for the Hygroscopicity Measurement of Organics

The schematic of the experimental system is presented in Figure 1. Aerosol particles are produced using an atomizer that is connected to a syringe pump containing aqueous solution of organic compounds (~0.1 wt %). The generated aerosol passes through two diffusion dryers in series, where relative humidity of air is reduced to be <4%. The dried aerosol particles are introduced to a TDMA system at a flow rate of 0.3 l/min, which consists of Am-241 neutralizer, two differential mobility analyzers (TSI model 3081), aerosol humidity conditioner composed of Nafion tube, and a condensation particle counter (CPC, TSI model 3085A). The sample and sheath flow rates of two DMAs are 0.3 and 3 l/min, respectively. Particles of 100 nm diameter at <4% RH are classified by the DMA1, and the RH for the resulting monodisperse aerosol is controlled by an aerosol humidity conditioner. Optionally, the classified particles pass through a humidifier composed of Nafion tube where slightly warmed water is circulated in the outer shell. The sample air is saturated with the water vapor, and then the particles are introduced to the aerosol humidity conditioner. This option is designed to measure the particle diameter under a decreasing RH condition from 100% (dehumidification experiment). In this case, saturated condition of water vapor was confirmed by checking the presence of dews on the window. Conversely, the measurement of the particle diameter without the optional humidifier is conducted under an increasing RH condition from <4% (humidification experiments). The aerosol sample under a controlled RH condition then enters the system of DMA2 + CPC, where size distribution of aerosol particles is measured. The water vapor was supplied through Nafion tube to the DMA2 sheath air, in which RH is controlled to be nearly equal to the RH of the aerosol sample. The RH in DMA2 is monitored at the DMA inlets of sample and sheath airs and also at the outlet of the sheath air, so as to confirm the RH inside the DMA2 tube to be nearly uniform.
When the RH of sample air is over 50% RH, the differences in RH between sample and sheath airs were within 2 and 3% in humidification and dehumidification experiments, respectively. However, the RH differences were within 5% in the case of <50% RH. The water content of RH in sample and sheath airs by their flow rates, is defined as RH in the DMA2 where humidified particle diameters are measured. All the TDMA experiments were conducted at the sample aerosol temperature of 293–295 K.

In this experiments, particles within a narrow electrical mobility band with a modal diameter of 100 nm were flowed out of DMA1. The size distribution measured by DMA2 + CPC also have a narrow single band with a specific width, which is originated from the classification band width of DMA1 described above as well as that of DMA2. In this study, modal diameters of the band obtained by DMA2 + CPC were subjected to the calculation of the particle change. The modal diameters were derived from fittings of the measured size distributions with Gaussian curves. The measurement errors of the modal diameters were estimated by classifying 100 nm dry particles in DMA1 and then measuring the deviations of the modal diameters using DMA2 + CPC under a dry condition. Since both DMA1 and DMA2 were calibrated in the same manner, the deviations may result in errors in diameter measurement originating from DMA. Intraday deviations of the modal diameters were about 1%, and were regarded as errors in diameter in this study.

The ratio of the particle diameter at elevated RH relative to that at <4% is presented as hygroscopic growth factor (HGF) in this study. Supersaturated conditions of the relative humidity are presented as hygroscopic growth factor (HGF) in this study. Supersaturated conditions of the relative humidity are presented as hygroscopic growth factor (HGF) in this study.

Table 1. Mass Fraction (Percent) of Organic Compounds in Wood Burning Aerosols

<table>
<thead>
<tr>
<th>Organic Compound</th>
<th>Pine</th>
<th>Oak</th>
<th>Eucalyptus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levoglucosan(^b)</td>
<td>18.1</td>
<td>16.6</td>
<td>30.9</td>
</tr>
<tr>
<td>Other sugars(^b)</td>
<td>5.3</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Syringol and substituted syringols(^b)</td>
<td>0.0</td>
<td>8.3</td>
<td>7.1</td>
</tr>
<tr>
<td>Guaiacol and substituted guaiacols(^b)</td>
<td>6.8</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Phenol and substituted phenols(^b)</td>
<td>1.7</td>
<td>6.1</td>
<td>1.0</td>
</tr>
<tr>
<td>n-Alkanoic, n-alkenoic, and resin acids</td>
<td>6.0</td>
<td>2.0</td>
<td>1.4</td>
</tr>
<tr>
<td>UCM and PAHs</td>
<td>10.5</td>
<td>14.4</td>
<td>7.2</td>
</tr>
<tr>
<td>Other identified organics</td>
<td>1.0</td>
<td>1.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Unextractable and nonelutable organics</td>
<td>50.5</td>
<td>47.7</td>
<td>49.8</td>
</tr>
</tbody>
</table>

*Data assimilated from Schauer et al. [2001].
\(^b\)The compounds subjected to the hygroscopicity measurements.


Table 1 compiles organic composition of wood burning aerosols (PM2.5) from Schauer et al. [2001]. As shown in the table, levoglucosan, a major pyrolysis product of cellulose and hemicellulose, contributes substantially (16.6–30.9%) to the total organics in PM2.5. Substituted guaiacols, syringols, and phenols, all of which are pyrolysis products of lignin, compose about 8.5–15.7% of organics in PM2.5. The rest of identified compounds are relatively minor and many of them, such as polycyclic aromatic hydrocarbons (PAHs) and unresolved complex mixture (UCM; highly branched and cyclic alkanes) are insoluble in water and are not likely to contribute to the particle growth. n-Alkanoic, n-alkenoic, and resin acids are not likely to contribute to the hygroscopic growth, because of the presence of long chain hydrophobic alky groups. Andrews and Larson [1993] reported that a compound having the similar structure, sodium dodecyl sulfate, did not show any significant hygroscopic growth at RH up to 90%. However, it should be noted that coatings of particles by such surfactants are suggested to slightly enhance the water uptake by the particles [Andrews and Larson, 1993].

As model compounds for biomass burning aerosols, the following water-soluble organic compounds were subjected to the hygroscopicity experiments in this study: levoglucosan, syringic acid (as substituted syringols), vanillic acid (as substituted guaiacols), and 4-hydroxybenzoic acid (as substituted phenols). Further, D-glucose, a hydrolysis product of cellulose and levoglucosan, was also
examined for hygroscopic properties. Although hydrated sugars are not reported by Schauer et al. [2001] (Table 1), various hydrated monosaccharides and disaccharides such as D-glucose were also detected in biomass burning aerosols [Nolte et al., 2001]. The chemical structures of organic compounds studied are presented in Figure 2. In the case of HGF and DRH experiments using levoglucosan, hydrolysis of levoglucosan in water solution was confirmed not to occur during the experiments by analyzing the levoglucosan and a potential hydrolysis product (glucose) using a GC-MS method [Mochida et al., 2003].

4. Results and Discussion

4.1. Growth Factors of Levoglucosan

[12] In Figure 3, the measured hygroscopic growth factors of levoglucosan for 100 nm dry particles are plotted against RH. As seen in the figure, the growth factors of levoglucosan particles increase as the RH increases. The growth factor changes do not depend on the history of RH, i.e., whether the RH setting was achieved by increasing from <4% (open circles) or by decreasing from 100% (solid triangles). The agreement of HGFs between two experiments also warrants that under the controlled moisture conditions the growing/shrinking particles are in equilibrium with the surrounding water vapor. The HGFs of levoglucosan at 60, 80, 85, and 90% RH are 1.08, 1.18, 1.23, and 1.38, respectively. A stepwise increase in the growth factor, which can typically be seen for inorganic compounds accompanying deliquescence phase transitions at the DRH, was not observed for levoglucosan.

[13] The bulk DRH of levoglucosan at 20°C was obtained to be 80% by the method described in the experimental section. For 100 nm particles, the corresponding RH, at which the concentration of solution in the droplets is equal to bulk saturated solution, is higher than the bulk DRH by about 1–2% because of the surface tension effect (see explanations below for details). Hence the growth of levoglucosan particles below 81–82% RH as shown in Figure 3 indicates the presence of metastable supersaturated condition of the levoglucosan-water mixture. Since the supersaturated condition can be seen by increasing RH from RH < 4%, the particle at RH < 4% may also be supersaturated and not be in the form of dried solid. Such large discrepancies between efflorescence relative humidity and DRH are often reported for both organic and inorganic species [Peng et al., 2001a, 2001b; Lightstone et al., 2000]. Although the actual dry diameter of levoglucosan is smaller than that at 4% RH, the very low relative humidity (4% RH) suggests that the fraction of water in the mixture is minor. Hence we consider that the growth factor measured in this study is nearly identical to that from completely dried particle.

[14] In order to evaluate the obtained HGF from the thermodynamic point of view, HGF of levoglucosan was estimated theoretically by several models. First, the growth curve of levoglucosan was estimated applying a theory for ideal solution. Assuming the ideal solution condition, the water activity $a_w$ of the mixed solution is equal to the molar ratio of water in the mixed solution. Since the growth factor measurement using the TDMA is on volume basis, the hygroscopic growth factor $G$ was calculated from the molar ratios by the equation:

$$G = \left\{ \frac{(x_W m_W / p_W) + (x_L m_L / p_L)}{(x_W m_W / p_W) + (x_L m_L / p_L)} \right\}^{1/3}, \ x_W + x_L = 1, \ (1)$$

where $x$, $m$, and $p$ mean molar ratio, molecular weight, and density, respectively. Meanwhile, the subscripts W and L represent water and levoglucosan, respectively. This equation is reliable if the partial molar volumes of organics and water are not largely different from those of pure compounds.
While RH(%)/100 is simply equal to \( a_w \) over the flat interface of air-liquid, the relation between water activity \( a_w \) and RH for small droplets can be expressed by Köhler equation:

\[
RH(\%)/100 = a_w \exp \left( \frac{4\sigma m_w}{p_w RTD_p} \right),
\]

where \( D_p \) and \( \sigma \) are particle diameter and surface tension of the solution, respectively. The surface tension of the solution \( \sigma \) is approximated by that of pure water, and then the exponential term in equation (2) ranges 1.01–1.02 for 100 nm particles. It is reported that some monosaccharides dissolved in water enhance the surface tension [Docoslis et al., 2000], whereas some polysaccharides depress it. Hence the exponential term above may be slightly underestimated or overestimated in the case of levoglucosan-water system. However, considering that the amplitude of \( \Delta \sigma \) due to the presence of sugar in solution is mostly lower than the absolute value of \( \sigma \) for pure water [Docoslis et al., 2000], additional shift in RH by taking into account the \( \Delta \sigma \) due to sugar should not be larger than the uncertainty of RH measurement in this study (2% RH). The growth curve estimated based on the assumptions above is presented as solid line in Figure 3.

Furthermore, two vapor-liquid equilibrium (VLE) calculations based on the UNIFAC group contribution method [Hansen et al., 1991] and the quantum-physical calculation method, COSMO-RS [Eckert and Klamt, 2002, 2003], were also applied for the estimate of the growth curve. The results are superimposed on Figure 3. UNIFAC group contribution method is widely used to predict the activities in mixed organic solution, and it is used for the estimate of the water activities of aqueous organic solution [Saxena and Hildemann, 1997]. COSMO-RS method is a relatively new approach for the estimate of VLE, and has advantage to be able to treat isomers. The relation between molar ratio and water activity was estimated using the VLE calculations, and the HGF was calculated based on the assumptions in equations (1) and (2).

As shown in Figure 3, the measured growth curve is within the deviation of the estimated curves from the different three approaches. The overall agreements between measured and predicted HGFs suggest that the high hygroscopicity of levoglucosan observed in this study is reasonable. However, the ideal solution theory reproduces the measured HGF curves even better than the other two approaches although it is the simplest. One possible explanation for this unexpected result is that the VLE calculations using UNIFAC and COSMO-RS are rather flawed for the levoglucosan-water system. UNIFAC is optimized for organic compounds with lesser fraction of polar functional groups and its VLE estimate is less reliable for organic compounds whose polar functional groups are separated by less than three or four carbon atoms [Fredenslund and Sørensen, 1994]. Since levoglucosan contains three OH groups in series, thermodynamic parameters estimated by UNIFAC for this compound could potentially be invalid. Meanwhile, COSMO-RS cannot take into account local structures such as hydration, which is known to exist in many sugar-water systems. Hence although the reasonable agreement between UNIFAC and COSMO-RS has been reported for many systems, their validity to the levoglucosan-water system, including supersaturated condition, still needs to be investigated.

However, there is another possible explanation why simple ideal solution theory gives better prediction than other VLE methods. Since the growth factor is on volume basis, an assumption on the partial molar volume in the mixed system is necessary so as to convert the molar ratio estimated by VLE methods to the growth factor, as equation (1). Hence changes in partial molar volume possibly cancel out, at least in part the deviation of the growth factor from the ideal solution curve. Comparison of particle growth measurements both by volume basis (TDMA) and by mass basis, e.g., elctrodynomic balance (EDB) method [Peng et al., 2001a, 2001b], will potentially be a useful approach to evaluate this issue in the future.

4.2. Growth Factors of D-Glucose

The measured growth factors of D-glucose are plotted in Figure 4 as a function of RH. D-glucose particles also showed water uptake in all measured RH range. No significant difference was found in the curves of HGFs between two different RH systems; humidification (open circles) and dehumidification (solid triangles) experiments. The bulk DRH of D-glucose at 20°C was obtained to be 90% by the bulk solution method, which is in agreement with the previous literature value of 89.1% [Rüegg and Blanc, 1981] within the RH error (2% RH). Owing to the surface tension effect presented in equation (2), corresponding RH for 100 nm D-glucose particles is slightly higher, about 91–92% RH. Hence the growth of D-glucose particles below 91–92% RH indicates that they are present as metastable supersaturated droplets. The growth factor at 60, 80, 85, and 90% RH are 1.08, 1.18, 1.24, and 1.37, respectively, being quite similar to those of levoglucosan.

In the case of D-glucose, hygroscopic growth has been measured previously by Peng et al. [2001a] using an electrodynamic balance (EDB) experiment as a function of RH. The EDB experiment measures change in particle masses, whereas TDMA measures that in particle sizes. By assuming the size change from mass change based on the theory in equation (1), the growth factor of D-glucose was calculated from the EDB data. The obtained HGFs from EDB data are 1.11, 1.17, 1.23, 1.39 at 60, 80, 85, and 90% RH, which are very close to the values we obtained in this study. The EDB experiments [Peng et al., 2001b] also suggest that by drying a D-glucose particle, water evaporates until the droplet becomes completely water-free. Hence under dry conditions (<4% RH) in this TDMA experiment, residual water in D-glucose particles may also be negligible although D-glucose can be present as hydrate crystal even under dry conditions. Thus the HGF of D-glucose presented here may be nearly identical to the growth factor from anhydrous dried particles.

The growth curves of D-glucose estimated by ideal solution theory, UNIFAC, and COSMO-RS were also shown in Figure 4. In the case of COSMO-RS calculation, The D-glucose water solution was simply assumed to be composed of the mixture of \( \alpha \)- and \( \beta \)-D-glucose. As in the case of levoglucosan, ideal solution theory gives a reasonable prediction for the HGFs of D-glucose although the deviations from the measured values are larger in the case of...
levoglucosan. This means that the activity coefficient of water in the particle is not largely different from unity, as far as the assumption presented in equation (1) is true.

4.3. Growth Factors of Lignin Pyrolysis Products

In contrast to levoglucosan and D-glucose, three model compounds of lignin products, 4-hydroxybenzoic (Figure 5), vanillic and syringic acids (growth curves not shown), did not show any significant particle growth at 100-nm particle diameter under the RH conditions up to 95%. Apparently, the characteristic of particle change is different from those estimated by three model approaches, as shown in Figure 5. Instead of the particle growth, a slight decrease in particle diameter was observed at elevated RH condition for these three lignin pyrolysis products. The reason for this is not clear, but a similar behavior was reported by Gysel et al. [2002] for NaCl-water system. They attributed a decrease in particle diameter at elevated RH to the restructuring of particle shapes that affect the mobility diameter, and the same explanation may apply for this case. In addition, evaporation of organics from particles in the TDMA system may be another plausible explanation for the decrease in particle diameter, as suggested for NH₄NO₃ experiment [Lightstone et al., 2000].

In the case of humidification experiments, the absence of particle growth is consistent with the fact that the DRHs of syringic, vanillic, and 4-hydroxybenzoic acids measured in this study by the bulk method exceed 97% (upper limit to measure reliably for the RH sensor). However, in the case of dehumidification experiments from saturated condition of water vapor, the absence of particle growth may be due to either one of the following two possibilities. The first case is that the particles deliquesced at the humidifier under the saturated water vapor condition and then effloresced again at RH > 95%. The second case is that the particle did not deliquesce in the humidifier within the limited residence time (about 1 min).

In order to further seek the possible presence of supersaturated condition of lignin pyrolysis products, a different type of experiment was conducted for 4-hydroxybenzoic acid. First, a pressurized carrier gas entering the atomizer to nebulize the organic-water solution was humidified so that the water content in the carrier gas corresponds to about 80% RH at 1 atm. The RH of aerosol samples increases to about 90% after the water evaporates from mist, and the aerosol was directly introduced to DMA1 without passing through the aerosol dryer. After the system was operated for hours so that the RH of sheath air circulating DMA1 becomes equal to that in the sample air, particles with 100 nm diameter were selected, followed by drying process down to 10% RH in the aerosol humidity conditioner. Then the resulting size distributions were measured by DMA2 + CPC. In this experiment, particles passing through DMA1 never experienced RH lower than 80% after they are emitted as aqueous droplets from the atomizer. No apparent change in particle diameter was observed between DMA1 and DMA2, while significant “decrease” in diameter was expected in DMA2 in the case that particles were aqueous in DMA1 (see Figure 5 for the expected differences in diameters at 10 and 90% RH). Hence it is concluded that supersaturated condition of 4-hydroxybenzoic acid is not likely present under RH < 80% in our experimental system.

The growth factors of measured organic compounds at 60, 80, 85, and 90%, as well as the measured DRH are summarized in Table 2. The estimated uncertainties of HGFs are also presented in the table. They originate from the uncertainty of RH as well as that of particle diameter measurement.
4.4. Atmospheric Implications

[26] It is often suggested that aerosol particles enriched with organic compounds become more hygroscopic as a result of atmospheric oxidation [Saxena et al., 1995]. However, this study suggests that particles emitted by the burning of woods and plants already contain large amount of hygroscopic organics, i.e., levoglucosan and other relevant anhydrosugars and hydrosugars. Although the HGFs of levoglucosan and D-glucose obtained in this study are lower than that for (NH₄)₂SO₄, a major inorganic constituent of fine aerosol particles (e.g., HGF is 1.45 at 80% RH in our TDMA study), HGFs of levoglucosan and D-glucose are comparative and even larger than some other hygroscopic organics. For instance, the HGFs of levoglucosan and D-glucose are larger than that of water-soluble humic like organics present in atmospheric aerosols, whose HGFs are 1.08–1.17 at 90% RH [Gysel et al., 2004].

[27] The ability of levoglucosan and D-glucose to retain water can also be compared with that of total organic matter in aerosol particles. The mass ratio [particle mass at 80% RH]/[dry particle mass] of organic fraction in 0.2 μm aerosol particles in Tennessee was assumed to be 1.5 [Dick et al., 2000], whereas the corresponding ratio for levoglucosan is \((G^3 - 1)/\rho_v + \rho_L/\rho_L = 1.40\) at 80% RH. Hence levoglucosan (and also D-glucose) has ability to retain water that is nearly comparable to that of the estimated typical water-soluble organic fraction observed in Tennessee. Assuming that levoglucosan comprises 30% of organic mass (from Table 1), the water content of the particle attributed to levoglucosan is calculated to be 12, 15, and 30% of the organic mass at 80, 85, and 90% RH, respectively. Since the amounts of black carbon and inorganic species are far less than those of organics in the case of wood burning aerosols [Schauer et al., 2001], the amount of water retained by levoglucosan is significant even on the total aerosol mass basis.

[28] Levoglucosan and other hygroscopic compounds in biomass burning aerosols may not be deliquesced initially because of its high temperature. However, the relatively low DRH of levoglucosan measured in this study suggests that levoglucosan in biomass burning aerosols can deliquesce at least when the ambient relative humidity is comparable to its bulk DRH. Furthermore, once they deliquesced, they possibly show the supersaturated hygroscopic growth in the real biomass burning aerosols, as is observed in this study.

[29] However, we did not obtained a clue that lignin pyrolysis products contribute to the growth of aerosol particles. Other identified pyrolysis products of lignin have chemical structures such as –CHO, –R, –R-OH, –R-CHO, –R-COOH instead of –COOH [Nolte et al., 2001]. Hence considering the less polarity of these functional groups than –COOH, majority of other lignin products may have lower water solubility than –COOH and they do not likely show particle growth at the RH range used in this study. This in turn suggests that formation of more polar organic compounds by the atmospheric oxidation of lignin products have room to increase hygroscopic properties of aerosol particles.

[30] The growth characteristics of real biomass burning aerosols may depend on geometric distribution of compounds in the particle, mixing state in solution with other organic/inorganic constituents, and chemical transformation by oxidation in the air. While Prenti et al. [2003] reported that the growth factor of the mixtures of dicarboxylic acids and ammonium sulfate can be expressed by the sum of water absorption predicted from two pure compounds such like Zdanovskii, Stokes, and Robinson (ZSR) approach [Stokes and Robinson, 1966], Chan and Chan [2003] suggested some deviation from the ZSR explanation for some organic/inorganic mixtures. Furthermore, change in DRH in mixed system as reported by Andrews and Larson [1993] is an important factor for hygroscopic properties of atmospheric aerosol particles. If supersaturated condition of organics-water mixture can exist in the real atmosphere, compounds that do not show hygroscopic growth in the single component system (such as lignin products in this study) possibly contribute to the particle growth below its DRH. In this sense, further study on the properties of the mixed aerosol system is necessary for more quantitative and reliable prediction of the hygroscopic properties of biomass burning aerosols.

5. Conclusions

[31] Five organic compounds (levoglucosan, D-glucose, 4-hydroxybenzoic, vanillic, and syringic acids), which are uniquely found in biomass burning aerosol particles, have been subjected to the measurements of hygroscopic properties using a tandem differential mobility analyzer system. Levoglucosan, as a typical anhydrosugar, is shown to be substantially hygroscopic under the all RH range measured (<5–95% RH). Furthermore, D-glucose as a typical hydrosugar, which may be primarily emitted and/or formed secondary by the hydrolysis of unhydrosugar, showed a hygroscopic growth as well.
The growth curves of levoglucosan and D-glucose were well represented by those estimated from the ideal solution theory of the organic-water mixture. However, other three water-soluble organic compounds (4-hydroxybenzoic, vanillic, and syringic acids) that are formed by pyrolysis of lignins did not show any hygroscopic growth up to 95% RH. The capacity of levoglucosan to retain water was evaluated by taking into account its relative abundance in real biomass burning aerosol particles, and found to be substantial even on the total organic mass basis. [32] For levoglucosan and D-glucose, the deliquescence relative humidity was found to be substantially lower than that of other three organics, and these particles have revealed to grow below their deliquescence relative humidity. The behavior of particle growth down to RH < 4% is similar to those observed for ambient aerosols [Dick et al., 2000]. Hence they possibly contribute to the particle growth in ambient biomass burning aerosols under their deliquescence relative humidity. [33] This study focused on hygroscopic properties of pure organic compounds characteristic to biomass burning aerosol particles. In real biomass burning aerosols, they are more complex in composition, hence the deviation in water-uptake capacity from pure organics cannot be ruled out. In addition, possibly different efflorescence behavior of the organics in the mixed system may alter the contribution of less hygroscopic compounds. Such changes in hygroscopic properties in the mixed system will be needed in the future studies.

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