Hygroscopic behavior of water-soluble matter extracted from biomass burning aerosols collected at a rural site in Tanzania, East Africa

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Abstract

In this study, we present the hygroscopic behavior of water-soluble matter (WSM) extracted from biomass burning derived particulate matter 2.5 (PM2.5) aerosols collected at a rural background site in Tanzania during June–August 2011. Hygroscopic growth factors, \( g(RH) \), of WSM were measured by hygroscopic tandem differential mobility analyzer (H-TDMA) with an initial dry particle diameter of 100 nm. We observed that the \( g(RH) \) of WSM at 90% relative humidity (RH), \( g(90\%) \), ranged from 1.10 to 1.47 with an average of 1.25 ± 0.12. The H-TDMA retrieved hygroscopicity parameter of WSM, \( \kappa_{WSM} \), ranged from 0.04 to 0.24 with a mean of 0.11 ± 0.07. We found that the observed \( g(90\%) \) is positively correlated with PM2.5 mass fraction of \( K^+ \) (\( R^2 = 0.61 \)), Cl\(^-\) (0.54), and organic carbon (0.58). Moreover, it well correlates with levoglucosan (0.67) and total diacids (0.76), implying that although the inorganic fraction may be the most important factor to control the hygroscopicity; biomass burning organics play a significant role in the hygroscopicity of Tanzanian aerosols. The lower growth factors obtained over the sampling site are probably due to the formation of less water-soluble potassium oxalate (\( K_2C_2O_4 \)) or less hygroscopic \( K_2SO_4 \) particles during atmospheric aging. We observed a moderate correlation (\( R^2 = 0.33 \)) between PM2.5 mass fraction of WSO and \( g(90\%) \). The retrieved \( g(90\%) \) values ranged from 1.0 to 1.25 with a mean of 1.16 ± 0.05. This study demonstrates that the hygroscopicity of Tanzanian aerosols is largely controlled by the emission of biomass burning products and the subsequent chemical aging during atmospheric transport.

1. Introduction

Ambient aerosols are defined as suspended solid and/or liquid particles in the atmosphere. They represent a small fraction of atmospheric mass but have a disproportionately large impact on climate and biogeochemistry [Mahowald et al., 2011; Reddy et al., 2011]. Biomass burning can generate significant amounts of aerosols (2–3 pg yr\(^{-1}\)) [Andreae et al., 2004; Reid et al., 2005], called smoke particles or biomass burning aerosols, which contain a significant amount of water-soluble organic carbon (WSOC) [Simoneit et al., 1999; Graham et al., 2002; Mkoma et al., 2013] and water-soluble organic nitrogen [Mace et al., 2003]. Therefore, biomass burning organic species, formed during pyrolysis of cellulose and emitted to the atmosphere during wood combustion [Simoneit et al., 1999], can potentially alter the hygroscopicity, cloud condensation activity, and the global climate change [Crutzen and Andreae, 1990; Novakov and Corrigan, 1996; Liu and Wang, 2010].

Previous studies have shown that understanding the hygroscopicity of WSOC in atmospheric aerosols is crucial for radiative forcing and other climate model studies [Saxena et al., 1995; Randles et al., 2004; Chan et al., 2005; Jung et al., 2011], and WSOC also have been postulated to play roles similar to that of inorganics in visibility degradation and cloud condensation nuclei (CCN) [Malm and Kreidenweis, 1997; Cruz and Pandis, 1998]. Saxena et al. [1995] reported the importance of organic species that can significantly alter the hygroscopic behavior of particles in the atmosphere. Mochida and Kawamura [2004] studied the hygroscopic properties of levoglucosan and related organics; they considered that oxygenated organics emitted from biomass burning could significantly enhance the hygroscopic growth of atmospheric aerosols. Chan et al. [2005] reported that water-soluble organic compounds such as amino acids (glycine, alanine, serine, glutamine, threonine, arginine, and asparagine) and biomass burning organic species (levoglucosan, mannosen, galactosan, and D-glucose) can potentially affect the hygroscopicity and cloud condensation activities of atmospheric aerosols. However, the knowledge about the hygroscopicity of biomass burning...
aerosol particles is still limited [Mochida and Kawamura, 2004; Chan et al., 2005; Fors et al., 2010; Carrico et al., 2010; Dusek et al., 2011; Martin et al., 2013].

More than 80% of the biomass burning on the globe occurs in tropical regions and further, more than 30% of the tropical biomass burning is estimated to be derived from savanna fires in Africa [Andreae, 1991; Goo et al., 2003]. The major types of biomass burning in Africa include forest and savanna fires [Cachier et al., 1991, 1995; Lacaux et al., 1993; Liu et al., 2000]. Agricultural field burning is recognized as another source of biomass burning aerosols, which may be a regionally very important source of atmospheric aerosols during the dry season [Lacaux et al., 1993].

In this study, we examined the hygroscopic properties of water-soluble matter (WSM) in particulate matter 2.5 (PM$_{2.5}$) aerosol particles collected at Morogoro, Tanzania in eastern Africa in order to characterize the physical and chemical properties of African biomass burning aerosols. Previous studies on PM$_{10}$ and PM$_{2.5}$ aerosol particles from Tanzania reported carbonaceous components, levoglucosan, mannosan and water-soluble inorganic ions [Mkoma et al., 2013], molecular composition of dicarbonyl acids, ketocarboxylic acids, α-dicarbonyls, and fatty acids [Mkoma and Kawamura, 2013]. In this study, we measured, using a hygroscopic tandem differential mobility analyzer (H-TDMA), hygroscopic properties of the WSM, which were extracted from biomass burning PM$_{2.5}$ aerosol samples. Here we discuss the link between hygroscopicity and the chemical composition of aerosols. We also present the calculated g(RH) of water-soluble organic matter (WSOM) to compare with chemical compositions of the WSM.

2. Experimental

2.1. Aerosol Sampling

Aerosol samples (PM$_{2.5}$) were collected on precombusted (450°C for 4 h) quartz filters (Pallflex 2500QATUP, 47 mm) at 2.7 m above ground level using low volume sampler (Gent type, flow rate 17 L min$^{-1}$) during June–August 2011 at a rural background site, Morogoro (06°47′40.8″S, 37°37′44.5″E; altitude 504 m above sea level), Tanzania, in East Africa. The interval of sample collection was 24 h, and the filters were exchanged at 7:30 A.M. LT. After sampling, the filter samples were kept in a clean glass vial with a Teflon-lined screw cap and stored in a freezer at −20°C. In total nine quartz filters, collected during June–August 2011, were used in this study. The aerosol samples were influenced by the biomass burning, determined based on backward trajectory analysis and fire information (see Figures S1 and S2 in the supporting information). We chose the nine aerosol samples that originated from almost same source regions but experienced a different amount of biomass burning plumes. We considered that there is a strong link between the hygroscopicity and the intensity of biomass burning plumes over the sampling site. The sampling site and method are described elsewhere [Mkoma and Kawamura, 2013; Mkoma et al., 2013].

Agriculture is the main industry in Morogoro, where important sources of local aerosols are field burning of crop residue and agriculture waste. Emissions from livestock (dairy cattle or farm) and domestic as well as forest fires are also considerable sources over Tanzania [Mkoma and Kawamura, 2013; Mkoma et al., 2013].

2.2. Analysis of Chemical Species

To determine water-soluble organic carbon (WSOC), a punch of 2.59 cm$^2$ from each quartz fiber filter was extracted with 15 mL organic-free ultrapure water (resistivity of >18.2 MΩ cm, Sartorius arium 611 UV). For inorganic ions (NH$_4^+$, SO$_4^{2−}$, NO$_3^−$, Na$^+$, Cl$^−$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$), a punch of 2.59 cm$^2$ of each quartz fiber filter was extracted twice with 5 mL ultrapure water. These extracts were filtrated through a syringe filter (Millex-GV, 0.22 μm pore size, Millipore) after ultrasonication (15 min) and analyzed using a total organic carbon (TOC) analyzer (Model TOC-Vcsh, Shimadzu, Kyoto, Japan) [Miyazaki et al., 2011] and an ion chromatograph (761 Compact IC, Metrohm, Switzerland) [Mkoma et al., 2013], respectively.

Major anions and cations were measured using a SI-90 4E Shodex column with 4 mmol an eluent of 1.8 mmol Na$_2$CO$_3$ plus 1.7 mmol NaHCO$_3$ (Showa Denko, Tokyo, Japan) and Metrosep C2-150 (Metrohm) column with 4 mmol tartaric acid plus 1 mmol dipicolinic acid as the eluent, respectively. The volume of injection loop was 200 μL for inorganic ions [Mkoma et al., 2013]. For WSOC measurements, the water extracts were acidified with 1.2 M HCl and purged with pure air to remove dissolved inorganic carbon and volatile organics [Miyazaki et al., 2011].

A filter punch of 1.54 cm$^2$ from each filter was used to determine the concentrations of organic carbon (OC) and elemental carbon using a field-type carbon analyzer (Sunset Laboratory Inc., USA) with thermal/optical transmission method [Birch and Cary, 1996] following the Interagency Monitoring of Protected Visual
Environments thermal evolution protocol. Detailed analytical procedures can be found elsewhere [Wang et al., 2005; Mkoma et al., 2013].

Water-soluble dicarboxylic acids were determined by the method described elsewhere [Kawamura and Ikushima, 1993]. Briefly, a 1.54 cm² punch of each filter was extracted with organic-free ultrapure water (10 mL) under ultrasonication (10 min × 3 times). These extracts were adjusted to pH = 8.5–9.0 with 0.1 M KOH and concentrated using rotary evaporator under vacuum and then derivatized with BF₃/n-butanol at 100°C for 1 h. After the concentration using a nitrogen blow down to near dryness, n-hexane (100 μL) was added to the ester fraction and the derivatives were determined using a gas chromatographic (GC) flame ionization detector. Peaks were identified by comparing GC retention time with an authentic standard and confirmed by mass spectral examination using a gas chromatograph mass spectrometer (GC-MS). The results are presented elsewhere [Mkoma and Kawamura, 2013].

For the determination of levoglucosan (LG), the filter samples were analyzed by the method described in Fu and Kawamura [2011]. Briefly, a piece (1.54 cm²) of each filter sample was extracted 3 times with dichloromethane/methanol (2:1; vol/vol) under ultrasonication for 10 min. Sugar compounds in the extracts were derived to trimethylsilyl ethers with 50 μL of N,O-bis-(trimethylsilyl) trifluoroacetamide containing 1% trimethylsilyl chloride and 10 μL of pyridine at 70°C for 3 h. The derivatives were diluted with addition of 140 μL of n-hexane containing 1.43 ng μL⁻¹ (internal standard: C₁₃ n-alkane) and then determined with a GC-MS. Fragment ions of m/z 217 and 204 were used for the quantification of LG [Fu et al., 2012]. The results are presented elsewhere [Mkoma et al., 2013].

### 2.3. Measurement of Particle Hygroscopicity

Hygroscopicity of WSM particles that were generated from water extracts of aerosol-filtered samples were measured using a H-TDMA with an initial dry particle diameter of 100 nm. All H-TDMA experiments were performed at 287–294 K with a mean of 291 K and atmospheric pressure of 1 atm. The instrumentation and methodology used in this study were described in detail by Mochida and Kawamura [2004] and Boreddy et al. [2014]. Briefly, a piece of the quartz filter with 7 mm in diameter was extracted with organic-free ultrapure water (7 mL) under ultrasonic bath (5 min × 3 times). The water extracts were then filtrated (Milllex-GV, 0.22 μm, Millipore disk filter) and used for H-TDMA measurements. The aerosol particles were generated by nebulizer from WSM and were dried (5% RH) by two silica gel diffusion dryers connected in series and were introduced into the H-TDMA.

The H-TDMA consists of two differential mobility analyzers (DMAs, TSI model 3081), an aerosol bipolar charger (Am-241), humidifiers (optional prehumidifier and aerosol humidity conditioner composed of a Nafion tube) for the aerosols and sheath flow, and a condensation particle counter (CPC, TSI model 3010). The monodispersed particles with an initial diameter of 100 nm at RH <5% were classified by the first DMA (DMA1), which was operated with a constant flow of 0.3 and 3 L/min for the polydisperse aerosol and sheath air, respectively. Monodispersed dry particles were introduced to the RH-controlled (5%–95%) humidity conditioner in hydration experiments or to the prehumidifier (where the RH is about 95%) in dehydration experiments. The resulting particle size was measured using the second DMA (DMA2), and the particle numbers were counted by a CPC. More details on RH control and size distribution are described in Mochida and Kawamura [2004].

The hygroscopic growth factor, g(RH), of an aerosol particle can be defined as the ratio of the particle diameter at elevated RH relative to that of the initial dry particles and is given by the following equation:

\[
g(RH) = \frac{D(RH)}{D_0}
\]

where \(D_0\) is the initial dry particle diameter at RH <5% and \(D(RH)\) is the diameter at an elevated RH.

A shape correction factor (\(\chi\)) was introduced to interpret the measured \(g(RH)\) [Kreidenweis et al., 2005] due to the nonspherical shape of the particles or for restructuring. The restructuring can be defined as the reduction of particle diameter at low RH during hydration experiment caused by the internal mixing of water-soluble organic components with inorganic species such as (NH₄)₂SO₄ [Sjogren et al., 2007] or NaCl [Krämer et al., 2000]. The \(\chi\) can be defined as follows:
particles. Although the theoretical growth factors are calculated with a volume equivalent diameter ($D_v$) during hydration experiment due to the restructuring of aerosol particles. It is also noteworthy that the H-TDMA measures a mobility diameter ($D_{mob}$), which indicates a slight restructuring of WSM particles. Similar results were observed by Gysel et al. [2004].

To validate proper H-TDMA sizing and operation, pure (NH$_4$)$_2$SO$_4$ particles were generated and introduced to H-TDMA system to measure the growth factor at 85% RH. The $g$(85%) of (NH$_4$)$_2$SO$_4$ was 1.57 ± 0.01 ($n = 3$), which agrees well with the theoretical growth factor ($g$(85%) = 1.56) using the thermodynamic aerosol inorganic model [Clegg et al., 1998]. Moreover, we performed reproducibility test, which showed that the analytical errors of $g$(RH) were ~3% at 90% RH.

2.4. Hygroscopicity Parameter ($\kappa$)

The hygroscopicity parameter, $\kappa$, introduced by Petters and Kreidenweiss [2007], was used to describe the hygroscopicity of the aerosol particles; $\kappa$ is defined according to

$$Kappa, \kappa = \frac{\left( g(RH) - 1 \right) \left( 1 - a_w \right)}{a_w}$$

$$a_w = RH \left( \exp \left( \frac{4 \sigma_{s,water} M_w}{RT \rho_w g(RH) D_0^3} \right) \right)^{-1}$$

where $a_w$ is the water activity, $\rho_w$ is the density of water, $M_w$ is the molar mass of water, $\sigma_{s,water}$ is the surface tension of the solution-air interface, $R$ is the universal gas constant, $T$ is the Kelvin temperature, and $D_0$ is the droplet diameter. In this model, the number of soluble entities is assumed to be independent of water activity.

3. Result and Discussion

3.1. Hygroscopic Growth Curves of WSM

Figure 1 shows changes in the $g$(RH) of the water-soluble matter (WSM) of aerosol particles nebulized from water extracts of the ambient aerosol samples collected at Morogoro, Tanzania, as a function of RH under hydration and dehydration experiments. The $g$(RH) of WSMs below 30% RH was removed for all samples during hydration experiment due to the restructuring of aerosol particles. It is also noteworthy that the $g$(RH) are corrected using the dynamic shape correction factor ($\chi$), which indicates a slight restructuring of particles. Although the theoretical growth factors are calculated with a volume equivalent diameter ($D_v$), the H-TDMA measures a mobility diameter ($D_{mob}$), which is only equal to the $D_v$ for a spherical particle. The $D_{mob}$ of a nonspherical particle must be shape corrected to obtain the $D_v$. The calculated dynamic shape correction factors ($\chi$) of all laboratory-generated WSM particles in this study ranged from 1.04 to 1.09 with a mean of 1.06 ± 0.02 as shown in Table 1. We also found a moderate correlation between $\chi$ and WSOM ($R^2 = 0.46$), indicating that the presence of water-soluble organic components with low deliquescence RH might induce this microstructural rearrangement of WSM particles. Jung et al. [2011] reported that high abundance of WSOM partially contributes to microstructural rearrangement of Ulaanbaatar PM$_{2.5}$ aerosols. Similar results were observed by Gysel et al. [2004].

The measured growth factors at 90% RH of all WSM particles, $g$(90%)$_{WSM}$, during hydration experiment ranged from 1.1 to 1.47 with a mean of 1.25 ± 0.12 (see Table 1 and Figure 2). The measured $g$(90%) of Tanzanian aerosols are comparable to that of biomass burning organic species (1.26) such as levoglucosan and mannosan [Chan et al., 2005; Mochida and Kawamura, 2004] and Amazonian biomass burning aerosols (1.05–1.24) [Zhou et al., 2002; Swietlicki et al., 2008] as well as continental aerosols (1.27 ± 0.03) collected at Storm Peak Laboratory (SPL) in the Park Range of northwestern Colorado [Hallar et al., 2013]. The H-TDMA derived kappa of WSM ($\kappa_{WSM}$) ranged from 0.04 to 0.24 with a mean of 0.11 ± 0.07 during the study period. Several studies have
focused on the biomass burning particles emitted from open vegetation fires [Kaufman et al., 1998; Lee et al., 2006; Vestin et al., 2007; Petters et al., 2009]. Andreae and Rosenfeld [2008] reported that biomass burning particles have wide $\kappa$ values ranging from 0.01 to 0.55 for grass burning. Dusek et al. [2011] reported an average $\kappa$ of 0.08 for 100 nm particles for freshly emitted particles from the burning of different hard and soft woods under controlled laboratory conditions. Demott et al. [2009] derived $\kappa$ values (0.02–0.56) from H-TDMA data from biomass combustion particles. Interestingly, the mean of $\kappa_{WSM}$ (0.11) in this study is comparable to that of smoke aerosols dominated by carbonaceous species, which typically had a unimodal growth factor with mean $\kappa$ of 0.1 (range: 0–0.4) [Carrico et al., 2010].

Table 1. Dynamic Shape Correction Factor ($\chi$), Water-Soluble and -Insoluble Fractions of PM$_{2.5}$ Hygroscopic Growth Factor ($g(90\%)$), and Hygroscopicity Parameter ($\kappa$) of Particles Nebulized From Water-Soluble Matter (WSM) Extracted From PM$_{2.5}$ Aerosol Samples Collected at Tanzania

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Dynamic Shape Correction Factor ($\chi$)</th>
<th>Fraction of PM$_{2.5}$ Water-Soluble</th>
<th>Water-Insoluble</th>
<th>$g(90%)_{WSM}$</th>
<th>$\kappa_{WSM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TN06 JUN11</td>
<td>1.07</td>
<td>0.33</td>
<td>0.67</td>
<td>1.30</td>
<td>0.13</td>
</tr>
<tr>
<td>TN07 JUN11</td>
<td>1.04</td>
<td>0.28</td>
<td>0.72</td>
<td>1.14</td>
<td>0.05</td>
</tr>
<tr>
<td>TN09 JUN11</td>
<td>1.05</td>
<td>0.29</td>
<td>0.71</td>
<td>1.20</td>
<td>0.08</td>
</tr>
<tr>
<td>TN28 JUL11</td>
<td>1.04</td>
<td>0.35</td>
<td>0.64</td>
<td>1.10</td>
<td>0.04</td>
</tr>
<tr>
<td>TN29 JUL11</td>
<td>1.07</td>
<td>0.53</td>
<td>0.47</td>
<td>1.41</td>
<td>0.20</td>
</tr>
<tr>
<td>TN02 AUG11</td>
<td>1.07</td>
<td>0.42</td>
<td>0.58</td>
<td>1.47</td>
<td>0.24</td>
</tr>
<tr>
<td>TN05 AUG11</td>
<td>1.05</td>
<td>0.24</td>
<td>0.76</td>
<td>1.28</td>
<td>0.12</td>
</tr>
<tr>
<td>TN06 AUG11</td>
<td>1.05</td>
<td>0.24</td>
<td>0.76</td>
<td>1.16</td>
<td>0.06</td>
</tr>
<tr>
<td>TN07 AUG11</td>
<td>1.05</td>
<td>0.25</td>
<td>0.75</td>
<td>1.22</td>
<td>0.09</td>
</tr>
<tr>
<td>Average</td>
<td>1.05</td>
<td>0.32</td>
<td>0.68</td>
<td>1.25</td>
<td>0.11</td>
</tr>
</tbody>
</table>
This is further supported by the study of ammonium being involved with the formation of organic acid salts by heterogeneous reactions. Above, we performed regression analysis between g(90%)(WSM) and PM2.5 mass fractions of chemical species as shown in Figure 3. Figure 3a clearly demonstrates that the growth factors are largely affected by biomass burning products due to a good correlation between g(90%)(WSM) and levoglucosan (LG), a tracer of biomass burning. Although it is also clear that the two data points on the top right of the Figures 3g and 3h are isolated from others (e.g., NH₄⁺ and K⁺), they are characterized by high growth factors and high abundances of levoglucosan as seen by the superimposed concentrations, indicating that those two data points are strongly influenced by biomass burning. Therefore, Figure 3 clearly demonstrates an importance of biomass burning on the hygroscopicity of aerosols, although there is a difference in g(90%)(WSM) between the cluster on the bottom left and other two points on the top right as stated above. Further, we performed t test between g(90%)(WSM) and PM2.5 mass fractions of chemical species. The results (two-tailed p value) are reported for each fraction in Figure 3, confirming that the overall difference is considered to be statistically significant (p < 0.05) for all the mass fractions except for NH₄⁺, which is related to biomass mass burning products.

We found relatively strong correlations between g(90%)(WSM) and biomass burning tracers such as K⁺ (R² = 0.61) and Cl⁻ (R² = 0.54), implying that water-soluble inorganics from biomass burning are important for the growth factor of total water-soluble matter over Tanzania during the study period. Moreover, the g(90%)(WSM) strongly correlates with PM2.5 mass fractions of total diacids (R² = 0.76, see Figure 3b) and LG (R² = 0.67, see Figure 3a); the latter compound is produced by the pyrolysis of cellulose and hemicellulose and has been used as a unique molecular tracer of biomass burning aerosols [Simonett et al., 1999; Fraser and Lakshmanan, 2000]. These results suggest that although inorganic fractions may be the most important factor to control the hygroscopicity, it is noteworthy that biomass burning organic species can significantly contribute to the hygroscopicity over Tanzania aerosols based on the strong linkage between g(90%)(WSM) and mass fractions of total diacids and LG in PM2.5.

SO₄²⁻ showed no correlation with g(90%)(WSM), but NH₄⁺ showed the positive correlation. We found that NH₄⁺ is significantly correlated with organic acids (R² = 0.80, not shown as a figure) but not with SO₄²⁻ (R² = 0.02), suggesting that ammonium is involved with the formation of organic acid salts by heterogeneous reactions. This is further supported by the study of Reid et al. [1998], who found that NH₄⁺ was highly correlated with oxalate and other organic species rather than SO₄²⁻ in the regional hazes dominated by biomass burning smoke in Brazil. Similar results were reported by Reid et al. [2005]. We also calculated ionic mass balance; the results showed that aerosols over Tanzania are alkaline. The ratio of cation to anion equivalents ranged 9–24 with a mean of 10.9 ± 4.9. The t test results showed that the overall difference is considered to be statistically significant. The two-tailed p value is < 0.0001. Therefore, it is very likely that the relation between SO₄²⁻ and g (90%)(WSM) obtained in this study may be due to the formation of less hygroscopic K₂SO₄ particles during atmospheric aging [Magi and Hobbs, 2003], which decreases the hygroscopic growth of aged aerosols. It is
further supported by a moderate correlation ($R^2 = 0.33$) between mass fractions of WSOC and $g(90\%)_{WSM}$. These points will be discussed thoroughly as below.

Rural sites are generally characterized by aged air masses that show an internally mixed aerosol, because atmospheric processes tend to gradually transform the aerosols toward a state of internal mixing. This mixing state can vary because rural areas may experience both aged and freshly formed aerosols. It is traditionally documented that atmospheric processes (aging) tend to make atmospheric aerosols more hygroscopic. However, it is not clear in the case of biomass burning aerosols. Field studies have shown that aged biomass burning particles are less hygroscopic than fresh biomass burning particles [Chan et al., 2005] due to the conversion of more hygroscopic KCl in a fresh biomass burning particle to less hygroscopic K$_2$SO$_4$ or KNO$_3$ in aged biomass burning particles [Posfai et al., 2003; Li et al., 2003]. Recently, Engelhart et al. [2012] quantified the hygroscopic properties of particles freshly emitted from biomass burning and after several hours of photochemical aging in smog chamber for 12 biomass fuels commonly burned in North American wildfires. They found that photochemical aging reduces the variability of biomass burning hygroscopicity parameter ($\kappa$).

Figure 3. Scatter plots between $g(90\%)_{WSM}$ versus PM$_{2.5}$ mass fractions of different chemical species in the PM$_{2.5}$ aerosols collected at Morogoro, Tanzania. The color scale indicates intensity of biomass burning, represented by the concentrations of levoglucosan (LG) (a tracer of biomass burning).
The conversion of freshly emitted organic species such as LG ($g(90\%) = 1.38$, Mochida and Kawamura [2004]) into simple organic acids (C$_2$-C$_5$) is also possible during photochemical aging [Gao et al., 2003]. It is known that oxalic acid, whose growth factor $g(85\%)$ is 1.03 [Peng et al., 2001], is an oxidation product of many organic compounds with a relatively low vapor pressure and therefore quite common in the organic fraction of aerosols [Buchholz and Mentel, 2008]. Oxalic acid is the most abundant dicarboxylic acid detected in biomass burning particles [Graham et al., 2002]. Therefore, it is reasonable to assume that the formation of potassium oxalate (K$_2$C$_2$O$_4$) through heterogeneous reactions may depress the hygroscopicity in Tanzania because K$_2$C$_2$O$_4$ is a less water-soluble salt [Buchholz and Mentel, 2008].

In order to better interpret the importance of the above mentioned evidences (formation of K$_2$SO$_4$ and K$_2$C$_2$O$_4$) in our samples, we performed a regression analysis between the concentration of potassium and oxalic acid (C$_2$di), and potassium and sulfate. The results are plotted in Figure 4. We found an excellent correlation between potassium versus C$_2$di ($R^2 = 0.96$) and potassium versus sulfate ($R^2 = 0.90$). These results support that potassium oxalate and potassium sulfate are formed by chemical aging during atmospheric transport of aerosols [Posfai et al., 2003; Chan et al., 2005].

Further, Martin et al. [2013] have recently studied the hygroscopic properties of fresh and aged biomass burning particles from beach wood under controlled laboratory conditions in several smog chamber experiments. They found that $\kappa$ of fresh wood combustion generally increases with aging, whereas in smoldering phase experiment, $\kappa$ decreased with increasing time. Therefore, it is important to note that biomass burning fuel characteristics, as well as the combustion conditions such as flaming or smoldering, are of great importance to the hygroscopicity of biomass burning particles [Carrico et al., 2010].

Figure 5 shows the temporal variation of $g(90\%)_{WSM}$ along with LG/PM$_{2.5}$ mass ratio and organic carbon mass ratios in Tanzania during the sampling period. Highest $g(90\%)_{WSM}$ were observed on TN02AUG11 followed by TN29JUL11 and lowest on TN28JUL11. Moderate Resolution Imaging Spectroradiometer (MODIS) satellite image shows that severe fire plumes were observed during 29 July to 7 August 2011 [Mkoma and Kawamura, 2013; Mkoma et al., 2013] and is shown in Figure 6a as a typical result. We performed the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model and the FIRMS (fire information for resource management...
system) for each sample during the study period in order to check how far or close biomass burning fire plumes were to the sampling site and how much each sample was affected. To make the point clearer, we also embedded the $g(90\%)$, WSOC, and LG concentrations for each sample on the fire map. Please see Figures S1 and S2 in the supporting information. As clearly seen in Figure S1, biomass burning fire plumes are very intensive during 6 June and 29 July to 5 August 2011 and are very close to the sampling site. The mass ratios of LG/PM$_{2.5}$ and LG/OC showed similar variation with $g(90\%)$ WSM, but not with WSOC/OC, indicating that a strong link should exist between the $g(90\%)$ WSM and the amount of biomass burning organics in Tanzanian aerosols. Figure 5 also reveals that, based upon mass ratios, $g(90\%)$ WSM over Tanzania significantly depend on the amounts of biomass burning organic species and partially on the amounts of WSOC (Figure 3c). This is further supported by the backward air mass trajectory analysis.

In order to check the influence of biomass burning fire plumes on the hygroscopicity, we computed 5 day backward air mass trajectories at an altitude of 200 m for every 24 h for the samples TN09JUN11 (background sample) and TN29JUL11 (intensive biomass burning sample) [Draxler and Rolph, 2012], whose results are shown in Figures 6b and 6c, respectively. The air mass trajectory sectors for both the samples showed similar transport pathways and source regions, i.e., originated from the Indian Ocean via the passage over the lands of Madagascar, Tanzania, and finally arrived over the sampling site (see Figure S2 in the supporting information for all samples during sampling study period). Therefore, it should be noted from Figures 6b and 6c that the observed hygroscopicity over

Figure 6. (a) Ten day MODIS fire map detected by MODIS satellite from NASA website over southern and eastern Africa and Madagascar during 30 July to 7 August 2011. A typical 5 day backward air mass trajectories at an altitude of 200 m for every 24 h for the samples (b) TN09JUN11 (background sample) and (c) TN29JUL11 (intensive biomass burning sample) using the HYSPLIT model from NOAA/Air Resources Laboratory.
the sampling site is mainly controlled by the enhanced biomass burning or local field burning, but not on the source regions. We also conclude that local biomass burning plays an important role in controlling the hygroscopicity of atmospheric particles and the air quality over Tanzania, East Africa.

3.3. Hygroscopic Growth of WSOM

Generally, hygroscopic measurements of aerosol particles are conducted for the mixture of water-soluble inorganic ions and organic components. Therefore, it is very difficult to directly determine the hygroscopicity of WSOM in atmospheric aerosols. The additional water, which cannot be explained by the water-soluble inorganic matter (WSIM), can be then attributed to the WSOM. The $g(RH)_{WSOM}$ can be estimated as follows [Seinfeld and Pandis, 1998; Cruz and Pandis, 2000; Jung et al., 2011]:

$$g(RH)_{WSOM} = \left( \frac{(g(RH)_{WSM})^{3} - (\varepsilon_{WSIM}g(RH)_{WSIM})^{3}}{\varepsilon_{WSOM}} \right)^{\frac{1}{3}}$$

(5)

where $\varepsilon_{WSIM}$ and $\varepsilon_{WSOM}$ represent the volume fractions of WSIM and WSOM in the WSM, respectively (Table 2). The $g(RH)_{WSM}$ and $g(RH)_{WSIM}$ represent the growth factors of water-soluble matter (measured by H-TDMA) and water-soluble inorganic matter (calculated using the ISORROPIA II model), respectively.

Table 2. Calculated Volume Fractions of Water-Soluble Inorganic Matter (WSIM), Water-Soluble Organic Matter (WSOM), Growth Factor of Water-Soluble Organic Matter ($g(90\%)_{WSOM}$), and Hygroscopicity Parameter ($\kappa_{WSOM}$) for the Tanzanian Aerosols

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Volume Fractions</th>
<th>Water-Soluble Organic Matter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WSIM</td>
<td>WSOM</td>
</tr>
<tr>
<td>TN06 JUN11</td>
<td>0.17</td>
<td>0.83</td>
</tr>
<tr>
<td>TN07 JUN11</td>
<td>0.27</td>
<td>0.73</td>
</tr>
<tr>
<td>TN09 JUN11</td>
<td>0.41</td>
<td>0.59</td>
</tr>
<tr>
<td>TN28 JUL11</td>
<td>0.30</td>
<td>0.70</td>
</tr>
<tr>
<td>TN29 JUL11</td>
<td>0.35</td>
<td>0.65</td>
</tr>
<tr>
<td>TN02 AUG11</td>
<td>0.39</td>
<td>0.61</td>
</tr>
<tr>
<td>TN05 AUG11</td>
<td>0.39</td>
<td>0.61</td>
</tr>
<tr>
<td>TN06 AUG11</td>
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<td>0.74</td>
</tr>
<tr>
<td>TN07 AUG11</td>
<td>0.33</td>
<td>0.67</td>
</tr>
<tr>
<td>Average</td>
<td>0.32</td>
<td>0.68</td>
</tr>
</tbody>
</table>

$^{a}$Not included in average.

*ISORROPIA II [Nenes et al., 1998, 1999; Fountoukis and Nenes, 2007] is a computationally efficient and rigorous thermodynamic equilibrium model, which exhibits robust and rapid convergence under all aerosol types with high computational speed. This model treats the thermodynamics of $K^{+}$–$Ca^{2+}$–$Mg^{2+}$–$NH_{4}^{+}$–$Na^{+}$–$SO_{4}^{2–}$–$NO_{3}^{–}$–$Cl^{–}$–$H_{2}O$ aerosol system, but organic species are not taken into account. It applies the Zdanovskii-Stokes-Robinson (ZSR) equation to estimate the aerosol liquid water content with the input of aerosol chemical composition measured by IC [Mkoma et al., 2013]. The temperature was set to 294 K. The growth factors are derived from the cubic root of the wet particle volume ($V_{dry} + V_{w}$) over the cubic root of the dry particle volume ($V_{dry}$).

The ISORROPIA II model assumes that the

Figure 7. Temporal variations of $g(90\%)_{WSOM}$ during the study period at Morogoro, Tanzania. We also showed $g(90\%)_{WSM}$ for comparison.
aerosol curvature effect can be ignored and water uptake of aerosols has no effect on the ambient vapor pressure.”

The retrieved $g(90\%)_{WSOM}$ for all the samples during the study period is shown in Figure 7. We clearly found that the obtained $g(90\%)_{WSOM} > 1$ for the biomass burning influenced samples. The rest of the samples showed $g(90\%)_{WSOM} \leq 1$, indicating that biomass burning is an important factor to control the hygroscopic growth over the sampling site. The H-TDMA derived hygroscopicity parameters of WSOM, that is, $\kappa_{WSOM}$, ranged from 0.01 to 0.11 with a mean of 0.06 ± 0.04 (Table 2). The $g(90\%)_{WSOM}$ varied between 1.03 and 1.25 with a mean value of 1.16 ± 0.05 (Table 2). The mean value (1.16) is slightly higher than of the HULIS (Humic-Like Substances) of K-Pushza, Hungary, (1.08–1.17) reported by Gysel et al. (2004) and lower than biomass burning organics such as levoglucosan (1.29), mannosan (1.28), and galactosan (1.27) [Mochida and Kawamura, 2004; Chan et al., 2005]. Jung et al. [2011] reported high growth factors of WSOM ($g(85\%) = 1.11–1.35$; mean = 1.22 ± 0.08) for Ulaanbaatar aerosols from Mongolia during cold winter in 2007. However, the present results are comparable with those of background continental PM$_{2.5}$ aerosol particles generated from isolated WSOC (1.10 ± 0.03) collected at Storm Peak Laboratory (SPL) in the Park Range of northwestern Colorado [Hallar et al., 2013].

Based on the observed $g(90\%)_{WSM}$ and significant link between the PM$_{2.5}$ fraction of chemical species and the growth factor of WSM as well as WSOM, we emphasize that Tanzania PM$_{2.5}$ aerosols contained high abundance of biomass burning products that significantly contribute to the increased hygroscopicity during the intensive biomass burning season. Moreover, these results are supported by the studies of Mkoma et al. [2013a, 2013b], which demonstrated that emissions from mixed biomass and biofuel burning activities largely influence the air quality in Tanzania, East Africa.

4. Conclusions

In this study, we investigated the hygroscopic properties of water-soluble fraction from biomass burning derived PM$_{2.5}$ aerosols collected at a rural background site in Tanzania, East Africa, using H-TDMA.

The measured $g(90\%)_{WSM}$ and $\kappa_{WSM}$ at Tanzania ranged from 1.10 to 1.47 and 0.04 to 0.24 with mean of 1.25 ± 0.12 and 1.01 ± 0.06, respectively. These results are comparable to those of previously reported biomass burning aerosols. The link between $g(90\%)_{WSM}$ and PM$_{2.5}$ mass fractions of chemical compositions reveals that although the inorganic fractions appear to be important factor in the hygroscopicity, biomass burning organic species play an important role in the hygroscopicity of Tanzanian PM$_{2.5}$ aerosols. WSOC may be partially responsible for the growth factors. We suggest that the formation of potassium oxalate (K$_2$C$_2$O$_4$) through heterogeneous reaction between organic and inorganic species could reduce the hygroscopic growth of aged aerosol particles. The present study also suggests the formation of less hygroscopic K$_2$SO$_4$ particles during atmospheric aging of biomass burning aerosols.

The mean value of $g(90\%)_{WSOM}$ was 1.16 ± 0.12 ranging between 1.03 and 1.25. These values are well correlated with total diacids/PM$_{2.5}$ mass ratios with a correlation coefficient of $R^2 = 0.65$ (not shown in the figure). The present study demonstrates that based on the strong link between $g(90\%)_{WSM}$ and PM$_{2.5}$ mass fractions of chemical species, freshly emitted biomass burning species can significantly contribute to the hygroscopicity of Tanzanian aerosols during the sampling period. The obtained $g(90\%)_{WSOM}$ in this study would be very important for radiative forcing and climate model studies because there are no studies on growth factors of organic aerosols in East Africa where biomass burning is very common but air pollution information is very limited.

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