Hygroscopic properties of atmospheric particles emitted during wintertime biomass burning episodes in Athens

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\textbf{ABSTRACT}

This study explores the Cloud Condensation Nuclei (CCN) activity of atmospheric particles during intense biomass burning periods in an urban environment. During a one-month campaign in the center of Athens, Greece, a CCN counter coupled with a Scanning Mobility Particle Sizer (SMPS) and a high resolution Aerosol Mass Spectrometer (HR-AMS) were used to measure the size-resolved CCN activity and composition of the atmospheric aerosols.

During the day, the organic fraction of the particles was more than 50%, reaching almost 80% at night, when the fireplaces were used. Positive Matrix Factorization (PMF) analysis revealed 4 factors with biomass burning being the dominant source after 18:00 until the early morning. The CCN-based overall hygroscopicity parameter $\kappa$ ranged from 0.15 to 0.25. During the night, when the biomass burning organic aerosol (bbOA) dominated, the hygroscopicity parameter for the mixed organic/inorganic particles was on average 0.16. The hygroscopicity of the biomass-burning organic particles was 0.09, while the corresponding average value for all organic particulate matter during the campaign was 0.12.

1. Introduction

Atmospheric aerosols play an important role in the Earth’s atmosphere, affecting the local and global climate (Vestin et al., 2007). Aerosol particles can affect the global radiation budget by scattering and absorbing solar radiation and thus have a direct effect on climate. In addition, depending on their physical and chemical properties, aerosols can serve as Cloud Condensation Nuclei (CCN) thereby indirectly affecting climate by modifying the cloud reflectivity and lifetime (Kauffman et al., 2002; Cerully et al., 2011 and references therein). The indirect effect of atmospheric particles on climate depends among others on their size and hygroscopic properties (Fors et al., 2010). Increased concentrations of CCN result in the formation of more but smaller cloud droplets (Vestin et al., 2007), which can lead to suppression of precipitation and increase of cloud lifetimes and cloud cover (Vestin et al., 2007; Rosenfeld et al., 2008; Fors et al., 2010).

Biomass burning is a major source of fine atmospheric particles on a global scale (Andreae and Rosenfeld, 2006). Forest fires and domestic wood burning for heating and cooking are two of the most important sources (Martin et al., 2013). Areas influenced by biomass burning usually exhibit high concentrations of CCN, with potential effects on regional climate (Hennigan et al., 2012). The chemical composition of aerosol particles produced by biomass burning is in general related to the combustion conditions (Vestin et al., 2007). Biomass burning particles consist mainly of organic species and black carbon, but also contain low concentrations of inorganic species, representing usually less than 15% of the particulate mass. The extent of the contribution of inorganic components depends on fuel composition and the efficiency of the burning process (Reid et al., 2005).

Biomass burning organic aerosol (bbOA) can be emitted as primary particles, but can also be formed by the oxidation of coemitted gaseous organic vapors and subsequent condensation of their less volatile compounds, leading to the formation of secondary organic aerosol. The chemical aging of bbOA involves both homogeneous and heterogeneous oxidation but also cloud-processing. While primary particles emitted by fossil fuel combustion are in general hydrophobic, fresh bbOA is relatively hygroscopic and can serve as CCN (Semeniuk et al., 2007). Atmospheric aging of bbOA further increases its hygroscopicity. In
general, the hygroscopicity of organic aerosol tends to increase as it is oxidized in the atmosphere. The organic aerosol O:C (atomic oxygen to carbon) ratio is often used as an indicator of its oxidation state.

Biomass burning emissions have also important impacts on regional air quality. The contribution of biomass burning to the mass concentration of the organic aerosols during air pollution episodes was found to be around 40% in Beijing and 70% in a rural site in Austria (Duan et al., 2004; Caseiro et al., 2009). Biomass burning OA has also been found to be a significant contributor to wintertime organic aerosol concentrations in Paris (Crippa et al., 2013), while its contribution in the southeastern US is close to 30% during winter (Zhang et al., 2010).

In order to understand the impact of biomass burning emissions on climate, the hygroscopic properties of the corresponding particles must be known. The CCN activity and the water uptake of aerosols can be parameterized using the parameter $κ$ as a measure of the hygroscopicity of atmospheric particles (Petters and Kreidenweis, 2007). Typical values for this parameter at supersaturated conditions derived from CCN measurements range from zero for non-hygroscopic, insoluble particles to 1.3 for particles consisting of NaCl (Petters and Kreidenweis, 2007).

Oxidized organic aerosols have values around 0.1, while for individual organic acids values up to 0.25 have been measured (Petters and Kreidenweis, 2007; Engelhart et al., 2012; Asa-Awuku et al., 2009). Please note that the values of $κ$ for organic aerosol derived at sub-saturated conditions from Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) (Brechtel and Kreidenweis, 2000) or other measurements can be quite different from those above 100% RH that are the focus of the present study. On the other hand, inorganic compounds typically present in aerosols have much higher hygroscopicity $κ$ values: 0.61 for (NH$_4$)$_2$SO$_4$, 0.67 for NH$_4$NO$_3$, and 0.90 for H$_2$SO$_4$.

The hygroscopicity of particles produced by biomass burning has been measured under various ambient atmospheric conditions or in smog chambers. Latham et al. (2013) reported a value of 0.18 ± 0.13 for both fresh and long-range transported (aged) biomass burning particles. Other works report $κ$ hygroscopicity values around 0.2-0.3 during biomass burning events (Rose et al., 2010; Bougiatioti et al., 2016).

Lab experiments showed that hygroscopicity $κ$ of the water soluble fraction of particles produced by the combustion of sagebrush and duff core was 0.25 and 0.15 respectively (Carrico et al., 2008). Engelhart et al. (2012) measured a $κ$ parameter ranging from 0.16 to 0.6 for fresh biomass burning emissions of various fuels while for their aged emissions $κ$ was 0.2 ± 0.1. From similar experiments Martin et al. (2013) calculated $κ$ values ranging from 0.03 to 0.39 for beech wood combustion. This work also reported that hygroscopicity increases with aging, due to the formation of more oxidized organics and also because of the formation of inorganic salts. However, residential wood burning of Organic Aerosol (OA) has not been characterized extensively under ambient conditions. Florou et al. (2017) reported that bbOA dominate the organic fraction of PM$_1$ measured in two Greek cities during the winter, while it has been found to be a significant contributor to OA in recent ambient measurements (Poulain et al., 2011; Ge et al., 2012; Aurela et al., 2015).

In this work, we investigate the composition and properties of biomass burning particles in an urban environment, the center of Athens, during winter of 2013, when wood burning in fireplaces for domestic heating was a dominant source. One of the advantages of the study is that it includes a mixture of fuels, burn conditions, and realistic bbOA that has remained in the atmosphere a few hours.

2. Experimental

2.1. Sampling site

Athens is a city of around 4 million residents surrounded by the Parnitha mountain (1 413 m asl) in the North, Penteli mountain (1 109 m asl) in the North-East, Hymettus mountain (1 026 m asl) in the East, and by the Saronic Gulf in the South-West. It has significant air quality problems due to its population density, the meteorology and the morphology of the area. Sampling was conducted at the National Observatory of Athens (NOA site, 37°58′23.99″N 23°43′12.06″E) located on a hill, at the center of Athens, from 12 January to 7 February of 2013. The low concentration data from an almost continuously rainy week were excluded from the analysis because of the low bbOA levels during that period. The following results are based on the data collected during 10–15 January and 23 January to 7 February of 2013.

2.2. Instrumentation

The hygroscopic properties of the aerosols were measured using a Cloud Condensation Nuclei Counter (CCNC, DMT Technologies; Roberts and Nenes, 2005) operated in Scanning Mobility CCN Analysis (Moore et al., 2010) mode. A Differential Mobility Analyzer (DMA; TSI model 3080) scanning the size range from 10 to 490 nm was employed to provide the CCN counter with monodisperse aerosol, the total number concentration of which was monitored by a water-based Condensation Particle Counter (TSI model 3787). Simultaneously, a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) was continuously monitoring the chemical composition and size distribution of PM$_1$ particles, while a Multi Angle Absorption Photometer (MAAP 5012, Thermo Scientific) was measuring the black carbon (BC) concentration. Additional details can be found in Florou et al. (2017).

2.3. Data analysis

2.3.1. Scanning Mobility CCN Analysis (SMCA)

SMCA involves the sampling of classified aerosol from a scanning DMA by a CPC and CCN concurrently (Moore et al., 2010). Before introduced in the DMA, the ambient air is first dried (RH < 5%) by passing through a diffusion drier. During a voltage scan cycle of the DMA, the counts of CN and CCN as a function of scan time are obtained with the supersaturation in the CCN instrument maintained constant. After about 4 DMA scan cycles (12 min total), the supersaturation is stepped by 0.2% supersaturation units, ranging from 0.19 to 0.91%. The deviation of the flow chamber temperature of the instrument from the nominal was checked for each scan and scans with temperature deviation more than 15% were discarded.

During a DMA voltage scan cycle (135 s), the mobility diameter varied between 10 and 490 nm; the ratio of CCN to CN counts (1 s accumulation time) normalized by their respective flow rates, and accounting for multiple-charge effects (Moore et al., 2010) provides the timeseries of CCN efficiency of the classified aerosol. An aerosol inversion procedure (e.g. from the TSI, Inc. Aerosol Instrument Manager) can then be applied to obtain the aerosol and CCN size distributions. From the size-resolved data obtained during a full supersaturation cycle, we then express the activation ratio ($R_a$ = CCN/CN) of particles with size $d_{pp}^*$ as a function of supersaturation, $R_a(S)$, and fit to the following function:

$$ R_a(S) = \frac{CCN(S, d_{pp}^*)}{CN(d_{pp}^*)} = \frac{E^*}{1 + \left(\frac{S}{S^*}\right)^C} $$

(1)

where $E^*$ refers to the asymptote of the corresponding sigmoid and expresses the maximum fraction of particles that activate at high supersaturation, and $S^*$ is the critical supersaturation, at which half of the particles of size $d_{pp}^*$ activate. $C$ is a fitting constant which is proportional to the slope of the sigmoid function and expresses the chemical heterogeneity of the activated particles (Cerully et al., 2011).

$R_a(S)$ can be related to the hygroscopicity distribution (i.e., mixing state) of particles with dry diameter $d_{pp}^*$ as follows. Expressing $S$ and $S^*$ of Equation (1) in terms of the hygroscopicity parameter, $κ = 4A^2/27d_{pp}^*S^3$ (where $A = 4M_w\sigma_w/(RT\rho_w)$), $M_w$, $\sigma_w$, $\rho_w$ is the molecular...
weight, surface tension and density of water, \( R \) the universal gas constant, and \( T \) the average temperature in the CCNC column; Petters and Kreidenweis, 2007) gives:

\[
R_{fi}(x) = \frac{CCN(x, d_p)}{CN(x, d_p)} = \frac{E^*}{1 + (\kappa/\kappa^*)^{c/2}}
\]  

where \( \kappa^* \) is the characteristic hygroscopicity factor, for which \( S/\kappa \) can be expressed as \( (\kappa/\kappa^*)^{-1/2} \). From Equation (2), the probability distribution function of \( \kappa \), \( p(\kappa) \), can be obtained after differentiation and normalization as (Cerully et al., 2011; Bougiatioti et al., 2011):

\[
p(\kappa) = \frac{1}{E^*} \frac{dR_{fi}(x)}{d\kappa} = -\frac{C^*(\kappa/\kappa^*)^{c-1}}{2\kappa^*(1 + (\kappa/\kappa^*)^{c/2})^2}.
\]  

The standard variation of \( \kappa \), \( \sigma(\kappa) \), around \( \kappa^* \) is a measure of the degree of heterogeneity (chemical dispersion) of particles with a diameter \( d_p^* \) and is calculated from Equation (3) as (Lance et al., 2013):

\[
\sigma^2(\kappa) = \frac{\int_{0}^{\infty} (\kappa - \kappa^*)^2 p(\kappa) d\kappa}{\int_{0}^{\infty} p(\kappa) d\kappa}
\]  

One value of \( \kappa^* \pm \sigma(\kappa) \) every 1 h was obtained for diameters ranging between 40 and 120 nm. The observed hygroscopicity parameter \( \kappa \) of particles is then related to the hygroscopicity of its chemical constituents following the rule given by Petters and Kreidenweis (2007):

\[
\sum \kappa_i \kappa_i = \kappa
\]  

where \( \kappa_i \) are the volume fractions of all particle components, \( \kappa_i \) their hygroscopicity and \( \kappa \) the total hygroscopicity.

### 2.3.2. Calibration of the CCN instrument

The calibration of the instrument supersaturation was performed by determining the critical diameter \( D_{pc} \) of (NH₄)₂SO₄ particles that activate at the instrument supersaturation. For this, a dilute ammonium sulfate solution was prepared and used in a syringe pump. The syringe pump provided an atomizer continuously with the solution, producing wet ammonium sulfate particles. The air stream containing the particles passed through a diffusion drier and the dried particles were introduced to the classifier. As in SMCA operation, the total (CN) and activated (CCN) particles were simultaneously measured for classified particles of mobility size between 10 and 460 nm. The process was repeated for a range of streamwise temperature gradient. For each supersaturation, the characteristic “critical diameter” \( D_{pc} \) of particles that have a critical supersaturation equal to the instrument supersaturation is determined – and Köhler theory (with appropriate considerations for solution non-idealities and dry particle non-sphericity; Moore et al., 2010) is used to express \( D_{pc} \) in terms of supersaturation. For the calculations, an ammonium sulfate dry density of 1770 kg m⁻³ and surface tension of the solution equal to 0.0706 N m⁻¹ was used.

### 2.3.3. AMS

The chemical composition of the non-refractory submicron particulate mass (NR-PM₁) was measured in real-time by an Aerodyne high resolution time-of-flight-aerosol mass spectrometer (HR-ToF-AMS). The concentrations of the major PM₁ components were measured every 6 min using both mass spectrum (MS) and particle time of flight data (pToF). In this study only the V-mode data are presented. The heater was operating at 600° C for the aerosol thermal desorption and the tungsten filament for electron ionization (EI) was at 70eV. The Peak Integration by Key Analysis (PIKA) software for the high resolution data was used for the analysis of the HR-ToF-AMS dataset. The Collection Efficiency (CE) during the campaign was calculated using the algorithm of Kosteniou et al., (2007) and was on average 0.85. A time-dependent CE has been applied to our data.

Five types of calibration for the AMS were performed during the Athens campaign. Flow calibration, aerosol particle beam alignment, chopper servo position, particle velocity and ionization efficiency (IE) calibrations using an SMPS and size-selected monodisperse ammonium nitrate particles. The IE calibration was also performed once a week. More details about the AMS calibration can be found in Florou et al. (2017).

### 3. Results and discussion

#### 3.1. Particle chemical composition

Organic compounds dominated the PM₁ composition during the campaign, representing on average 58% of its mass, followed by BC with 20.4%. Sulfate contributed 10%, nitrates 5.1%, ammonium 4.2% and potassium and chloride ions each 1.1%. The corresponding average concentrations were 6.5 μg m⁻³ for organic species, 2.3 μg m⁻³ BC, 1.1 μg m⁻³ sulfates, 0.6 μg m⁻³ nitrates, 0.5 μg m⁻³ ammonium, and potassium and chloride 0.1 μg m⁻³ each.

The average diurnal variations of organics and sulfates measured by the AMS are shown in Fig. 1. Organic aerosol concentrations increased after 16:00–17:00 continuously until 23:00 peaking a little before midnight. Sulfate on the other hand exhibited an almost constant average profile with a concentration around 1 μg m⁻³. This constant profile is characteristic of species that are not produced locally but are transported to the site.

Fig. 2 shows the diurnal variation of the organic aerosol fraction, which dominated the PM₁ mass composition throughout the day. A
3.2. Particle CCN activity and hygroscopicity

The average diurnal variability of the critical supersaturation $\kappa_S$ for different particle sizes is shown in Fig. 4. The variability of this parameter for the same particle sizes expresses changes in their composition. Particles with diameters of 40 nm have not been used in the following analysis since their $\kappa_S$ was higher than the instrument's maximum supersaturation (0.91%). Smaller particles activated at higher supersaturation values, as expected from Köhler theory.

The main characteristic of the average $\kappa_S$ diurnal profiles is a sharp increase in the morning, between 7:00 and 10:00. During this period there is a significant contribution of HOA traffic emissions to the organic aerosol mass (Fig. 3). These results suggest significant HOA contributions to particles in the 50–100 nm range, something expected for traffic in a major urban area.

Smaller particles had larger absolute variations of their $\kappa_S$ during the day compared to the larger ones (70–100 nm). Such discrepancies could be due to differences in the sources and chemical composition of particles of different sizes. This suggests that the CCN properties of the small particles may not represent the bulk composition of PM$_1$ and vice versa. The size segregated chemical composition provided by the AMS showed chemical composition differences in the 50–100 nm diameter range targeted by the CCN counter. However, the size distribution of the AMS was rather noisy for the smaller particle diameters. Particles having dry mobility diameters of 85 and 100 nm consisted mostly of organic compounds (57 and 55% respectively) and their composition followed the diurnal pattern of the total organic fraction in PM$_1$. Fig. 5 shows the average diurnal variations of the non-refractory inorganic and organic fractions as measured by the AMS for the 80 and 100 nm particles. An average particle density value of 1.41 was used to convert the AMS vacuum diameter to mobility, in order to match the SMPS diameter.

The hygroscopic properties of the particles are strongly affected by the presence of inorganic compounds which are generally more hygroscopic compared to the organics. As shown in Fig. 5, the composition of 80 and 100 nm particles followed the average diurnal trend of PM$_1$ OA and also had quite similar composition as the bulk PM$_1$. For this reason, the averaged hygroscopic properties of 80–100 nm particles will be used here to approximate the average properties of PM$_1$ organics.

The average diurnal profile of the estimated total (organics and inorganics) hygroscopicity factor $\kappa$ for different particle diameters and the average $\kappa$ ($\kappa_{av}$) of 80–100 nm particles are shown in Fig. 6. The total particle hygroscopicity depends on both the hygroscopicity of the corresponding organic components and on the contribution of the inorganic species to the particle mass. Biomass burning emissions started to increase around 18:00 (Fig. 3) and dominated the number and mass concentration of the aerosols until midnight. During that period, the average hygroscopicity was constant with a $\kappa_{av}$ value equal to 0.16 ± 0.006. After midnight $\kappa$ increased to 0.19 and started to decrease sharply at around 6:00, when the contribution of traffic emissions became significant as indicated by the HOA diurnal profile (Fig. 3). Due to the hydrophobic nature of the HOA particles emitted from traffic, hygroscopicity dropped between 06:00 and 8:00, increasing again to values up to 0.25 after 12:00 due to dilution of the emitted particles and photochemistry. The decrease of $\kappa_{av}$ from around
0.25 to 0.2 between 13:00–14:00 can be attributed to the presence of HOA, together with the relatively hydrophobic cooking emissions that peaked at the same time. The $\kappa_{av}$ values remained high (between 0.2 and 0.25) from noon until the beginning of biomass burning early in the evening (around 17:00) when residents went back to their homes and started using their fireplaces.

The average hygroscopicity factor $\kappa$ of particles having diameter from 80 to 100 nm had similar average diurnal profile as the O:C ratio (Fig. 7). However, the correlation between $\kappa$ and average O:C during the entire campaign was rather poor ($R^2 = 0.17$). This can be explained by the fact that other factors (e.g. inorganic PM$_1$ contribution) are more important than the organic O:C in determining the average hygroscopicity of particles. Previous work (Massoli et al., 2010; Martin et al., 2013; Lathem et al., 2013) has also suggested that organic hygroscopicity may not be especially sensitive to O:C for values less than 0.5 like those encountered in this study. Moore et al. (2011) and Lathem et al. (2013) have also reported low correlations between O:C and overall hygroscopicity in studies of areas with high bbOA levels.

The ratio of the standard deviation of the hygroscopicity, $\sigma(\kappa)$ divided by $\kappa$ expresses the degree of heterogeneity (chemical dispersion) of the particles. The average diurnal profile of the chemical dispersion $\sigma(\kappa)/\kappa$ is shown in Fig. 8. The heterogeneity peaked between 7:00 and 11:00, around the same time when average hygroscopicity dropped (Fig. 6). This can be attributed to the increase of HOA-like traffic contribution to the total aerosol concentration that becomes significant during this period. The fresh traffic emissions coexist with significant numbers of particles containing inorganics and more hygroscopic organics (Fig. 3). This behavior was more pronounced for particles larger than 60 nm while the diurnal profile of the smaller particles showed less variability.

The diurnal variation of the activated fraction $E^*$ (see Equation (2)) of particles of different diameters at the maximum supersaturation (0.91%) is shown in Fig. 9. In general, the smaller the particles, the lower the corresponding maximum activated fraction measured. This is 0.09 after 3:00 OOA becomes an important OA when hydrophobic traffic related emissions started becoming significant. Around the same time, the corresponding critical supersaturation decreased, according to Fig. 4. Smaller particles also presented a similar behavior during the HOA peak but had a larger variability during the day. The particle size is more critical for the activation of the particles but the variations of the chemical composition are probably responsible for the activation fraction variations at a given diameter. Typical size distributions during periods of high bbOA and high HOA in this study can be found in Gkatzelis et al. (2016) (please see Figs. 6 and 7 of that study).

3.3. Organic aerosol hygroscopicity

The particle hygroscopicity parameter is equal to the sum of the hygroscopicity parameters of all components multiplied by their volume fraction (see Equation (5)). Despite the low fraction of the inorganic species compared to the dominating organic compounds, the former affect the hygroscopicity of the particles significantly. In order to explore the hygroscopic properties of the organic components of the aerosols, the hygroscopicity of organics, $\kappa_{org}$ needs to be estimated.

ISORROPIA II (Fountoukis and Nenes, 2007) was used to estimate the concentrations of the chemical components of the inorganic fraction of the particles. This model requires as input the concentrations of the inorganic ions NH$_4^+$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, and K$^+$, relative humidity and temperature conditions and can provide the concentration of the inorganic salts in the aerosol phase (Fountoukis and Nenes, 2007). ISORROPIA-II solves a system of equations describing the various equilibrium reactions in the system taking into account the non-ideality of the corresponding aqueous solutions. The model can also estimate in its reverse mode of operation the concentrations of the various inorganic aerosol components as well as the concentrations of vapors in equilibrium with the particulate phase using as inputs the measured concentrations of the various ions together with the temperature and relative humidity. By dividing the corresponding salt mass concentration by its density, the volume fractions of the inorganic components can be calculated and applied to Equation (5). The hygroscopic parameter corresponding to the organic compounds, $\kappa_{org}$, was then estimated using the measured $\kappa_{av}$ for $\kappa$ in Equation (5) and assuming that black carbon (BC) has a $\kappa = 0$.

The estimated $\kappa_{org}$ varies from 0.06 to 0.21 as shown in Fig. 10. During the night biomass burning emissions dominate and the corresponding $\kappa_{org}$ is 0.09. After 3:00 OOA becomes an important OA.
component so $\kappa_{org}$ increases. OOA, which is quite hygroscopic ($\kappa$ values reported in literature are around 0.25–0.3; Kreidenweis et al., 2008; Chang et al., 2010), dominated the organic aerosol composition between 10:00–17:00 thus explaining the increase of the organic aerosol hygroscopicity at that time. Estimations of $\kappa_{org}$ from open fires and lab measurements (Moore et al., 2011; Lathem et al., 2013) also suggest values around 0.1 for biomass burning organics.

4. Conclusions

The chemical composition and hygroscopic properties of atmospheric aerosol in Athens during the winter of 2013 were studied. The PM$_1$ was dominated by organic species during the campaign, with an average organic mass fraction of 0.58, followed by black carbon (20% of PM$_1$). PMF analysis showed that the most important contributor to the organic aerosol concentrations was biomass burning which started in the evening and peaked during the night. HOA from traffic peaked during the morning rush hour, affecting the hygroscopic behavior of the aerosols in the morning. During the HOA peak, the critical supersaturation of the particles studied here (50 nm $\leq d_p \leq$ 100 nm) was higher due to the hydrophobic nature of HOA. The maximum chemical variability of the particles is also observed during this period.

Size-resolved chemical composition data provided by the HR-AMS revealed differences in the composition of smaller (50–70 nm) and bigger particles (80–100 nm) and showed that the properties of the PM$_1$ bulk composition can be represented reasonably well by the properties of bigger particles. These particles were found to be relatively hygroscopic, with the maximum activated fraction (at 0.9% supersaturation) reaching almost unity during most of the day, except for the morning traffic period. The average hygroscopicity of these particles ranged roughly from 0.15 to 0.25. The lowest values are observed during the HOA peak, as expected, while the highest were observed between 04:00–16:00 when oxygenated organics dominated the organic mass. The average hygroscopicity of the mixed (organic/inorganic) particles during the night when biomass burning particles prevailed was around 0.16. The diurnal profile of $\kappa_{org}$ was very similar with the profile of the O:C ratio but no correlation was observed.

Using a thermodynamic model to predict the inorganic composition of the inorganic fraction, the hygroscopicity of the 80–100 nm organic particles was estimated. The organic hygroscopicity $\kappa_{org}$ was on average 0.12 during the campaign, while during the biomass burning period it was on average 0.09. We find that a strong increase in externally mixed particles (expressed as a broadening of the hygroscopicity distribution) was observed for all particle sizes except for the smallest.

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