



Hygroscopicity, CCN and volatility properties of submicron atmospheric aerosol in a boreal forest environment during the summer of 2010

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Abstract. A Volatility-Hygroscopicity Tandem Differential Mobility Analyzer (VH-TDMA) was applied to study the hygroscopicity and volatility properties of submicron atmospheric aerosol particles in a boreal forest environment in Hyytiälä, Finland during the summer of 2010. Aitken and accumulation mode internally mixed particles (50 nm, 75 nm and 110 nm in diameter) were investigated. Hygroscopicity was found to increase with particle size. The relative mass fraction of organics and SO_4^{2-} is probably the major contributor to the fluctuation of the hygroscopicity for all particle sizes. The Cloud Condensation Nuclei Counter (CCNC)-derived hygroscopicity parameter κ was observed to be slightly higher than κ calculated from VH-TDMA data under sub-saturated conditions, potential reasons for this behavior are discussed shortly. Also, the size-resolved volatility properties of particles were investigated. Upon heating, more small particles evaporated compared to large particles. There was a significant amount of aerosol volume (non-volatile material) left, even at heating temperatures of 280 °C. Using size resolved volatility-hygroscopicity analysis, we concluded that there was always hygroscopic material remaining in the particles at different heating temperatures, even at 280 °C. This indicates that the observed non-volatile aerosol material did not consist solely of black carbon.

1 Introduction

Aerosols, defined as solid or liquid particles or liquid droplets suspended in gas, are ubiquitously present in the atmosphere as a result of biogenic and anthropogenic emissions. Atmospheric aerosol particles contain a myriad of organic and inorganic species, such as sulfates, nitrates, ammonium, carboxylic acids and oxygenated PAHs (Polycyclic Aromatic Hydrocarbons) (Seinfeld and Pandis, 2006; Hallquist et al., 2009). Organic species comprise a significant fraction (20 % to 90 %) of the submicron particle mass depending on the terrestrial conditions and anthropogenic emissions (Zhang et al., 2007; Jimenez et al., 2009).

Aerosol particles can scatter and absorb incoming solar radiation. They can also influence the climate by acting as cloud condensation nuclei (CCN) or ice nuclei (IN), which can enhance the reflection of solar radiation. Both direct and indirect effects of aerosol particles mostly cause negative radiative forcing (IPCC, 2007).

The effect of aerosols on Earth's radiation balance is strongly dependent on aerosol particle size, which, in turn, is a function of relative humidity (RH) and the temperature of ambient air. Depending on the aerosol composition, the size of an aerosol particle may increase 1.1–2.5 times when compared to its original dry size over the RH range of 30–95 %

(Weingartner et al., 2002; Swietlicki et al., 2008). The ability of particles to take up water, called hygroscopicity, is one of the important factors that determine the number concentration of cloud condensation nuclei and further affect the lifetime of the clouds (Reutter et al., 2009; Zhang et al., 2008). Another important property is volatility: aerosols that are exposed to higher temperatures or diluted by mixing with clean air may evaporate, which changes the particle size distribution, both spatially and temporally under atmospheric conditions (Huffman et al., 2009). Volatility is an important parameter when it comes to gas–particle partitioning of semi-volatile and very-low-volatile aerosol compounds, especially aerosol organics. Low-volatile compounds are critical in the new particle formation and growth of nanoparticles (Riipinen et al., 2011). In addition to being crucial for estimating the aerosol radiative forcing, lifetime and mass loadings, hygroscopicity and volatility are also important for obtaining indirect information on the chemical composition of the particles.

Measurements of aerosol hygroscopic properties have been performed extensively around the world both in laboratory and field studies using different techniques, e.g., an Electrodynamic Balance (EB, Tang and Munkelwitz, 1994) and Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA, Liu et al., 1978; Swietlicki et al., 2008). With these techniques hygroscopic properties of many inorganic and some organic compounds have been targeted specifically (Hämeri et al., 2001; Wise et al., 2003; Massoli et al., 2010). Inorganic salts, e.g., ammonium sulfate and sodium chloride, show hysteresis when exposed to an increasing and decreasing relative humidity environment, while organic aerosols can often take up water at lower RH than the Deliquescence Relative Humidity (DRH) of inorganic salts (Sjogren et al., 2008). However, the hygroscopic behavior of multi-component mixtures consisting of both inorganic and organic compounds is poorly understood. Meyer et al. (2009) found that an increase in organic aerosol coating thickness hindered the hygroscopic growth at an RH of 85 %. Their study also showed that the presence of organic aerosol coating seemed to enhance the water uptake of inorganic seeds at RH lower than the DRH of the inorganic component.

The volatility properties of atmospheric aerosols have been investigated using several instruments and techniques. The thermodenuder, one of the primary instruments to study aerosol volatility, has been used extensively (e.g. Wehner et al., 2002; Ehn et al., 2007; Huffman et al., 2008). Bilde et al. (2001) used a laminar flow tube to carry out the evaporation measurements. A Volatility Differential Mobility Particle Sizer (VDMPS), coupling a Thermodenuder and a Differential Mobility Particle Sizer (DMPS), can be used to obtain information on the aerosol particle size distribution after heating (Ehn et al., 2007; Häkkinen et al., 2012). In the atmosphere, compounds partition to various degrees between the gas phase and aerosol particle phase depending on their thermodynamic properties and atmospheric conditions.

For instance temperature, relative humidity, pressure and solar radiation affect aerosol partitioning (Fuzzi et al., 2006). Different compounds evaporate at different temperatures according to their volatility properties (Turpin and Lim, 2001; Raatikainen et al., 2010). Most compounds present in atmospheric aerosol will fully evaporate at temperatures below 300 °C, which is also approximately the maximum temperature used in this study for thermodenuder experiments. However, there are compounds that are non-volatile even at such high temperatures. These include black carbon (BC), sea salt and crustal material. According to previous studies (Backmann et al., 2010; Häkkinen et al., 2012), in addition to BC there may be also other essentially non-volatile compounds, possibly organic polymers or salts, present in submicron atmospheric aerosol.

In this study we investigated the hygroscopicity and volatility properties of ambient aerosols using a Volatility-Hygroscopicity Tandem Differential Mobility Analyzer (VH-TDMA). The measurements were performed in a boreal forest site in southern Finland during a one-month-long campaign from 12 July to 12 August 2010. In addition, a Cloud Condensation Nuclei Counter (CCNC) and a Volatility Differential Mobility Particle Sizer (VDMPS) were used to perform independent aerosol hygroscopicity and volatility measurements. This made it possible to compare different instruments measuring the same aerosol properties as the VH-TDMA. Information about particle chemical composition obtained from an Aerosol Mass Spectrometer (AMS) was also used to support the interpretation of the results. Our main goals were (1) to characterize the size-dependency of aerosol hygroscopicity and volatility in a boreal forest environment and (2) to get new insight into the relationship between aerosol chemical composition and its water uptake properties via the performed measurements. Such information is essential for both light-scattering properties and cloud condensation nuclei activity of atmospheric aerosols.

2 Materials and methods

2.1 Measurement site

Measurements for this study were conducted at SMEAR II (Station for Measuring Ecosystem–Atmosphere Relations II) located in Hyytiälä, southern Finland (Hari and Kulmala, 2005). The station is surrounded by an over 40-year-old pine forest. Aerosol size distribution measurements have been performed there continuously since 1996 (Mäkelä et al., 1997). Our study is part of HUMPPA-COPEC (Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry) campaign, which started on 12 July 2010 and ended on 12 August 2010. More detailed information about this campaign and meteorological conditions on the site can be found in Williams et al. (2011).

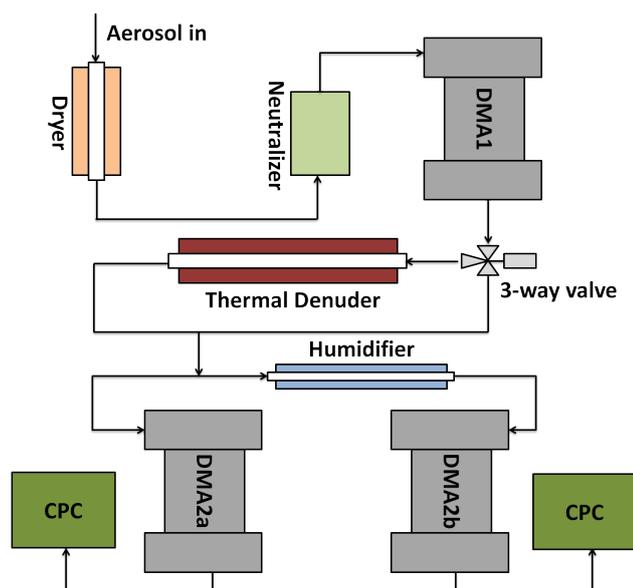


Fig. 1. A schematic of the VH-TDMA instrument system.

2.2 Instrumentation

2.2.1 VH-TDMA

The VH-TDMA used in this study is a fifth-generation University of Helsinki TDMA designed to measure the hygroscopicity and volatility of the ambient aerosols during the HUMPPA-COPEC 2010 campaign. A schematic diagram of VH-TDMA is shown in Fig. 1. The ambient aerosol sample is dried and brought into a neutralizer where the particles are charged and then introduced to a Hauke-type Differential Mobility Analyzer (DMA; Winklmayr et al., 1991). The DMA selects aerosol particles of a certain size based on their electrical mobility, and it can be used to form a monodisperse sample flow. Particles of dry diameters of 50 nm, 75 nm and 110 nm were selected for our study. After the DMA there is a 3-way valve to control the direction of the aerosol flow. The flow may be directed through a thermal denuder or bypass it, after which the flow is split into two ways, one to a humidifier while the other bypasses the humidifier and goes straight to the DMA. Size distribution data and number concentrations from both routines (humidification and non-humidification) were measured using two similar systems, both including a DMA (Hauke type) and a condensation particle counter (CPC, TSI 3010 & TSI 3772). The four different working modes were as follows: dry mode (neither heating nor humidifying particles), V-mode (heating but not humidifying particles), H-mode (not heating but humidifying particles) and VH-mode (heating and humidifying particles). The temperature of the thermal denuder was increased continuously from 25 °C to 280 °C, one temperature scan taking around 45 min. The relative humidity of the aerosol after the humidifier was set to 90 % within 2 % error. More information can

be found from other studies using a similar VH-TDMA setup (Villani et al., 2008; Jonhson et al., 2005).

2.2.2 CCNC

The ability of the ambient aerosol particles to activate into cloud droplets under supersaturated conditions was measured for both size-resolved aerosol and total aerosol population with a Droplet Measurement Technology (DMT) Cloud Condensation Nuclei Counter (CCNC, Roberts and Nenes, 2005) attached to a Hauke-type DMA. After the DMA, a monodisperse aerosol distribution was obtained. The aerosol flow was split into two parallel lines: one directed into a condensation particle counter to determine the total number concentration of particles, and the other one into the CCNC. The CCNC measures the number concentration of particles that activate or become droplets larger than 1 µm at a selected supersaturation. A more detailed description of the instrument can be found in Sihto et al. (2011) and Paramonov et al. (2013). With the described setup, the fraction of activated particles can be obtained as a function of the particle size at each supersaturation, and these activation spectra were used to determine the critical diameter for CCN activation and hygroscopicity parameter κ (Rose et al., 2008; see also Sect. 2.3.2). In this study, five levels of supersaturation were applied: 0.09, 0.22, 0.48, 0.74 and 1.26 %.

2.2.3 VDMPS and DMPS

A twin-Differential Mobility Particle Sizer (DMPS) system measured the number size distribution of ambient aerosol (3–1000 nm in diameter) with a time resolution of 10 min (Aalto et al., 2001). A Volatility-DMPS (VDMPS) consisting of a thermodenuder and a DMPS heated the incoming sample air to 280 °C. The VDMPS determined the number size distribution of 20–1000 nm particles not evaporated in the thermodenuder. Due to noise in the VDMPS data at the larger end of particle sizes, the size range of 20–500 nm was selected for further analysis both from VDMPS and DMPS data (more detailed information in Häkkinen et al., 2012). Due to thermophoresis and Brownian diffusion of small particles, 20 % of the particles larger than 15 nm were lost after passing through the thermodenuder (Ehn et al., 2007).

2.2.4 Aerosol composition

An Aerodyne Compact Time-of-Flight Aerosol Mass Spectrometer (C-ToF AMS, Aerodyne Research Inc., Billerica, USA; Jayne et al., 2000; Drewnick et al., 2005) was used to measure the chemical composition of submicron aerosol particles during this study. Since the C-ToF AMS cannot detect refractory compounds, such as black carbon, crustal materials or metals, the mass concentration of black carbon was measured using an aethalometer (Magee Scientific, Hansen et al., 1984) with a PM_{2.5} inlet. According to Saarikoski et

al. (2005), the contribution of crustal materials and metals to submicron aerosol particle mass in Hyttiälä is minor.

2.2.5 Supporting data

Concentrations of several trace gases were measured at the SMEAR II station at several height levels of the 74-m-high mast (extended to 126 m after the measurement campaign described in this study). In this study gas-phase concentrations of SO₂ (fluorescence analyzer TEI 43 CTL, Thermo Fisher Scientific) and O₃ (UV-light absorption analyzer TEI 49, Thermo Fisher Scientific) were used. A proxy was also determined for the gaseous H₂SO₄ concentration as the ratio of the production from oxidation of SO₂ by OH radicals and sink by condensation onto pre-existing aerosol particle surface. OH radical concentration was approximated by scaling the UV radiation intensity according to the method presented by Petäjä et al. (2009), and the condensation sink by aerosol particles was calculated from measured particle size distributions according to Kulmala et al. (2012).

2.3 Data evaluation

2.3.1 Growth factor

During the VH-TDMA measurements, the distribution of hygroscopic growth factors (GF_H) referred to as the growth factor probability density function (GF-PDF), was obtained. The hygroscopic growth factor using H-mode is defined as

$$\text{GF}(90\% \text{ RH}) = \text{GF}_H = \frac{D_p(T_{\text{room}}, 90\% \text{ RH})}{D_p(T_{\text{room}}, \text{RH}_{\text{dry}})}, \quad (1)$$

where $D_p(T_{\text{room}}, 90\% \text{ RH})$ is the diameter of a particle at the selected RH (in this study 90%), and $D_p(T_{\text{room}}, \text{RH}_{\text{dry}})$ is the size of the particles at dry conditions (below 20% RH) at room temperature.

The volatile growth factor using V-mode is defined in a similar way:

$$\text{GF}(T) = \text{GF}_V = \frac{D_p(T, \text{RH}_{\text{dry}})}{D_p(T_{\text{room}}, \text{RH}_{\text{dry}})}, \quad (2)$$

where $D_p(T, \text{RH}_{\text{dry}})$ is the diameter of a particle after heating to a certain temperature, in this study from 20 °C to 280 °C, without humidification. In this study the temperatures, ranging from 20 °C to 280 °C, were divided into 9 equal intervals. The median value of average volatility growth factors within a certain temperature interval was considered as the median growth factor at the corresponding median temperature. The median temperatures used in this study were 35, 65, 95, 125, 155, 185, 215, 245 and 268 °C.

Using the VH-mode, the VH-mode growth factor of the heated particles can be written following Eqs. (1) and (2):

$$\text{GF}(90\% \text{ RH}, T) = \text{GF}_{\text{VH}} = \frac{D_p(90\% \text{ RH}, T)}{D_p(T_{\text{room}}, \text{RH}_{\text{dry}})}. \quad (3)$$

By dividing the growth factor obtained from the VH-mode with that obtained from the V-mode, coupling Eqs. (2) and (3), we can obtain the actual hygroscopic growth factor of the aerosol residual after heating

$$\text{GF}_{\text{H, residual}} = \frac{\text{GF}_{\text{VH}}}{\text{GF}_V} = \frac{D_p(90\% \text{ RH}, T)}{D_p(T, \text{RH}_{\text{dry}})}. \quad (4)$$

The measured diameter growth factor distributions from the VH-TDMA were inverted using the piecewise linear inversion approach (Gysel et al., 2009). When studying the hygroscopic growth factor distributions, aerosols were characterized by two distinct groups of particles, one taking up little water, termed as less hygroscopic particles and the other one taking up more water but still less than the pure salts, termed as more hygroscopic particles.

2.3.2 Effective hygroscopicity parameters

The particle water uptake can be described by the Köhler equation, which includes the Raoult effect and the Kelvin effect. Petters and Kreidenweis (2007) applied the κ -Köhler model using a single hygroscopic parameter κ to represent hygroscopic growth and cloud condensation nuclei activity of particles. The hygroscopic parameter κ can be defined based on the Köhler theory as follows:

$$S(D) = \frac{D^3 - D_p^3}{D^3 - D_p^3(1 - \kappa)} \exp\left(\frac{4\sigma_{s/a}M_W}{RT\rho_W D}\right). \quad (5)$$

Here, $S(D)$ is the saturation ratio over an aqueous solution droplet, D is the droplet diameter, D_p is the particle dry diameter, $\sigma_{s/a}$ is the droplet surface tension, which was assumed to be the surface tension of water, R is the gas constant, T is the ambient temperature, M_W and ρ_W are the molar mass and density of water, respectively.

For the CCN measurements, using the experimental activation diameter as D_p and varying both κ and the droplet diameter D , the κ parameter can be iterated by finding the minimum difference between the experimental supersaturation S and the theoretical supersaturation $S(D)$ using Eq. (5) (Rose et al., 2010).

For VH-TDMA measurements, κ values can be obtained similarly by

$$S(D_p, \text{GF}_H) = \frac{\text{GF}_H^3 - 1}{\text{GF}_H^3 - (1 - \kappa)} \exp\left(\frac{4\sigma_{s/a}M_W}{RT\rho_W D_p \text{GF}_H}\right) = 0.9, \quad (6)$$

where $S(D_p, \text{GF}_H)$ is the saturation ratio and expressed as the same quantity as the relative humidity of 90% in this study, GF_H is the hygroscopic growth factor obtained from H-mode measurements, D_p is the particle dry diameter, here $D = D_p$. GF_H , $\sigma_{s/a}$ is the droplet surface tension, ρ_W and M_W are the density and molar mass of water, respectively (Petters and Kreidenweis, 2007). Using both CCNC and VH-TDMA data, the obtained κ values at sub- and supersaturated conditions with different particle dry sizes can be compared.

2.3.3 Volume fraction remaining

The volatility of 20–500 nm particles was studied by comparing the ambient and heated particle number and volume size distributions obtained from the DMPS and VDMPS data, respectively. The particle volume size distribution was calculated from the number size distribution data by assuming spherical particles. The volume fraction remaining reveals how much aerosol volume remains in the aerosol after heating and gives indirect information about the aerosol chemical composition as different aerosol species volatilize at different temperatures. Aerosol volatility is obtained as a function of the particle size from the VTDMA, whereas only the volatility of the total aerosol volume/mass can be obtained from the VDMPS measurements.

The volume fraction of aerosol particles remaining after heating was defined by comparing the total volume of heated aerosol ($V_{\text{tot,VDMPS}}$) to the total volume of ambient aerosol ($V_{\text{tot,DMPS}}$) (Häkkinen et al., 2012). The volume fraction remaining (VFR) can be defined as

$$\text{VFR} = \frac{V_{\text{tot,VDMPS}}}{V_{\text{tot,DMPS}}}. \quad (7)$$

We can also define the volume fraction remaining after the heating for certain sized particles as

$$\text{VFR}_{D_p} = \frac{D_p^3(T)}{D_p^3(T_{\text{room}})} = \text{GF}_V^3(T). \quad (8)$$

We compared VFR from VDMPS measurements with VFR_{D_p} obtained from VH-TDMA using V-mode. However, we must note that in the VDMPS analysis the VFR obtained describes the total aerosol volume fraction after heating and, therefore, does not account for particle size effects.

2.3.4 Connections between different parameters

The hygroscopic growth factor GF_H (90 % RH) from the H-mode measurements using the VH-TDMA allowed us to calculate the hygroscopic parameter κ and compare it with the κ obtained from CCNC measurements. The hygroscopic parameter κ is a quantity used commonly to describe the hygroscopicity of atmospheric aerosols. The volatility growth factor (GF_V) obtained from the V-mode measurements, which is related to volume fraction remaining (VFR), was used to determine the volatility of atmospheric aerosols. By coupling GF_V and GF_{VH} obtained from the VH-mode measurements, we can estimate the hygroscopicity of the aerosol material remaining after the heating. This could be an indicator of the presence of oxidized organic components in the particle phase.

3 Results and discussion

3.1 Hygroscopicity and CCN properties

3.1.1 General behavior of hygroscopic growth

In this section we present the measured hygroscopic growth of aerosol particles using the H-mode in the VH-TDMA. The time series of the retrieved GF-PDFs of particles with diameters of 50 nm, 75 nm and 110 nm for the period from 24 July 2010 to 7 August 2010 are illustrated in Fig. 2. In many previous studies, the hygroscopic growth factor distributions of ambient aerosol have shown two or more modes rather than a broad distribution, indicating that aerosol particles have been externally mixed (Weingartner et al., 2002; Swietlicki et al., 2008). In this study, the hygroscopicity distributions mainly showed one mode during the whole period, with the median GF_H varying between 1.1 and 1.5. This suggests that, internally, the studied particles were relatively well-mixed. The variation in the median GF_H can be explained by the influence of different air masses.

GF_H fluctuated the most during 29–30 July 2010. Williams et al. (2011) reported that biomass-burning signals (air masses from Russia) were detected at the SMEAR II station in Hyytiälä during those days (26–30 July). The GF_H of ~ 1.3 – 1.4 was more stable after the wild fire episode from 31 July to 2 August 2010. This period can be considered as the background period. From 5 August 2010 onwards, aerosols were less hygroscopic with a lower median GF_H of ~ 1.1 – 1.2 . During these days strong peaks in the concentrations of O_3 , SO_2 and pentane were observed (Williams et al., 2011). This time period can also be linked to the Russian wild fires, and can be considered as the biomass-burning period. The background and biomass-burning periods are marked in Fig. 2.

The time series of the aerosol chemical composition from the AMS and aethalometer measurements are also illustrated in Fig. 2. Black carbon had a modest influence on the aerosol hygroscopicity based on roughly constant mass fraction of around 6 % (mean BC mass fraction of 5.88 %, with standard deviation of 2 %) during the whole period. It should be noted that in this study the measured $\text{PM}_{2.5}$ BC mass was assumed to be solely in submicron particles (Jaffrezo et al., 2005; Saarikoski et al., 2008), as reported size-resolved BC data show usually < 20 % of the BC mass is tied with coarse mode particles in urban areas (Hitzenberger and Tohno, 2001). The data in Fig. 2 suggest that the relative mass fraction of organics and SO_4^{2-} in the particulate phase was probably the major contributor to the fluctuation of the GF_H . The correlation between GF_H and the ratio between the organic and sulphate mass concentrations ($\text{Org}/\text{SO}_4^{2-}$) obtained from the AMS data was stronger for the largest particles (110 nm, see Fig. 3). Lower values of GF_H were associated with higher $\text{Org}/\text{SO}_4^{2-}$ ratios, indicating a smaller contribution from the hygroscopic sulphate. To note the bulk composition data

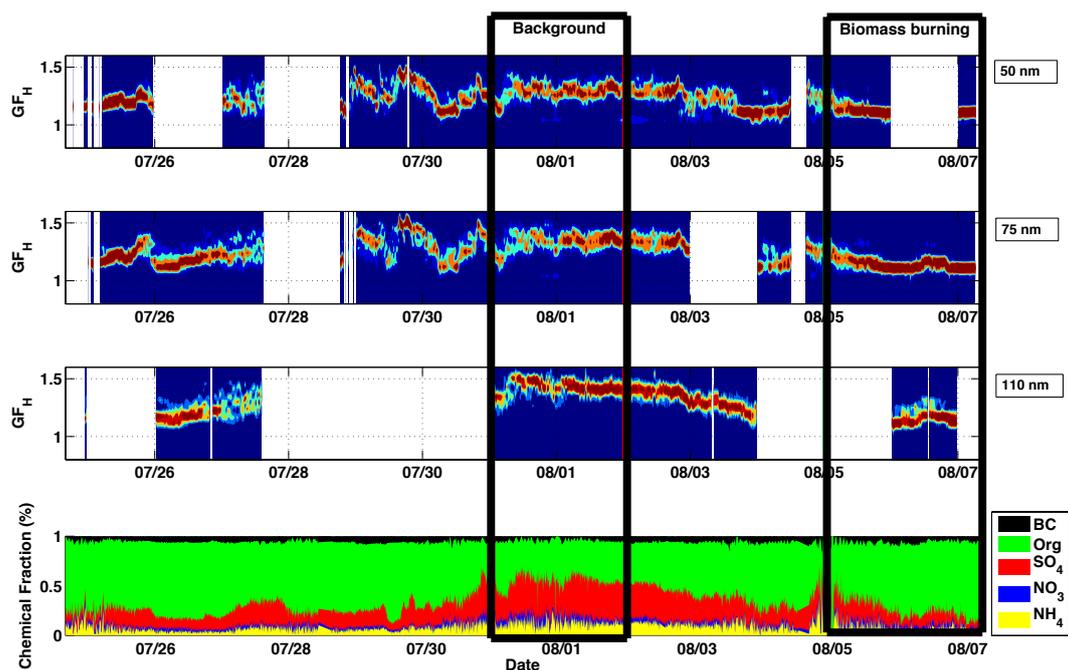


Fig. 2. Time series of hygroscopic growth factor distribution (GF-PDF) for 50 nm, 75 nm and 110 nm-sized particles (three upper panels), and mass fraction of chemical components in particles (lower panel) from period between 24 July 2010 and 7 August 2010.

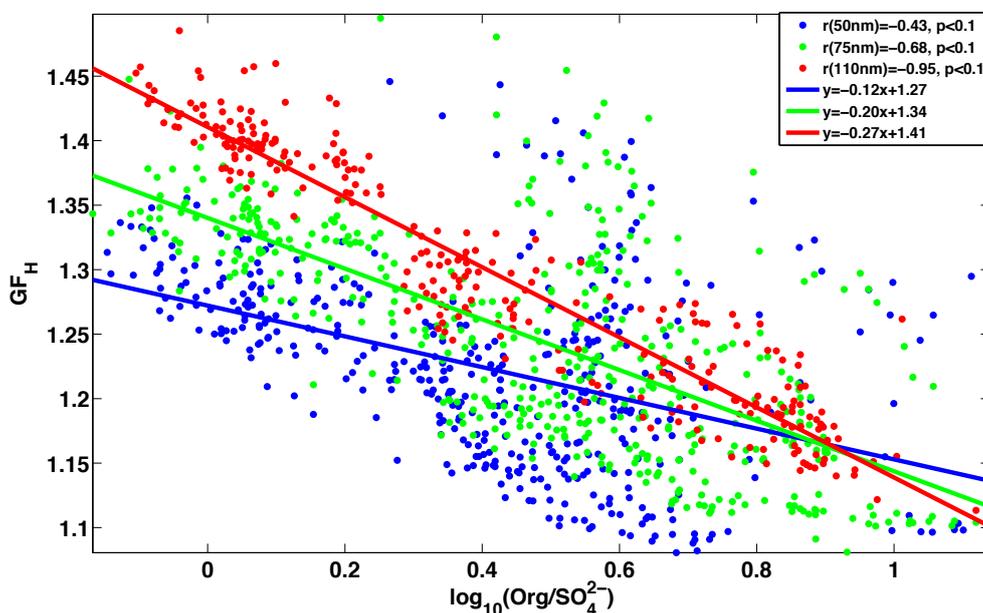


Fig. 3. Correlations between the average hygroscopic growth factor and the ratio between the concentrations of particulate organics and sulfates from AMS data for three different particle sizes.

from the AMS and aethalometer reflect the composition of > 100 nm particles better than that of the smaller particles.

We also studied the correlation between GF_H and concentrations of chemical species both in particle phase and in gaseous phase: SO_2 , O_3 , H_2SO_4 -proxy and SO_4^{2-} , BC and organics. Among these six variables, the hygroscopic growth

factor correlated best with gas phase O_3 and aerosol sulfate concentration. The correlation between GF_H and O_3 might be linked to the fact that high ozone concentrations indicate more effective atmospheric oxidation, which in turn, increases aerosol hygroscopicity (Cappa et al., 2013). The positive correlation between GF_H and sulphate is due to the fact

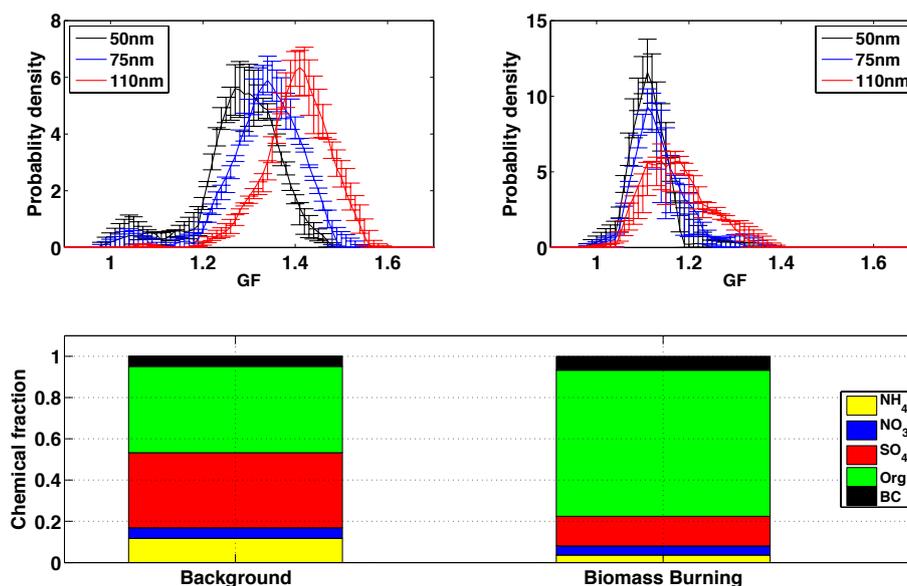


Fig. 4. The upper panel presents the growth factor probability density functions for the two distinct periods selected for the case studies (left panel: background; right panel: biomass-burning) for 50 nm, 75 nm and 110 nm-sized particles. The lower panel illustrates the mass fractions of different aerosol components during these periods obtained from AMS and aethalometer measurements. Note that during the biomass-burning period there were unfortunately too few data points for 50 nm and 110 nm-sized particles to conclude anything about the size-dependency of aerosol hygroscopicity.

that aerosol particles containing more sulphate are more hygroscopic.

Case studies of the median GF-PDF with different particle dry sizes and chemical composition of submicron particles during the two distinct periods (background period from July 2010 to 2 August 2010 and biomass-burning period from 5 August 2010 to 7 August 2010) are shown in Fig. 4. In general, during the background period the particles were more hygroscopic than the ones during the biomass-burning period, due to the fact that there were larger amounts of organics in the particles during the biomass-burning period (Fig. 4 bottom panel). However, it is important to note that during the biomass-burning period there were, unfortunately, too few data points for 50 nm and 110 nm-sized particles to conclude anything about the size-dependency of hygroscopicity (see, e.g., Fig. 2). During the background period the smaller particles were observed to have lower hygroscopicity as compared with the larger particles (Fig. 4 upper panel). This can be due to, e.g., higher degree of oxidation in the larger particles or uncertainties in the Kelvin term of Eq. (6). During the background period, in addition to the dominant peaks in the GF-PDF (1.25–1.4, depending on particle size), there were also small modes in the GF_H of around 1.05, indicating that marginally hygroscopic particles were also occasionally present.

3.1.2 Comparison with CCN

Figure 5 shows that the aerosol hygroscopicity parameter κ obtained from the HTDMA was lower than that obtained from the CCNC. This difference indicates that the κ -Köhler theory cannot accurately describe the water activity throughout the relative humidity range from sub- to supersaturated conditions. Cerully et al. (2011) investigated particle hygroscopicity and CCN activity at the same measurement site in Hyytiälä. Their κ values were higher than ours for all sizes, which could result from the fact that their measurements were performed during the spring (from March through May 2007), whereas our data were from the summer when larger amounts of biogenic secondary organic aerosol is expected to be present (Paramonov et al., 2013). Sihto et al. (2011) analyzed CCNC measurements at the same station from July 2008 to June 2009 and reported the critical diameter with the smallest values occurring in spring and largest values for summer, which corresponds to higher aerosols hygroscopicity for spring and lower hygroscopicity during summer.

Laboratory studies have reported inconsistencies in aerosol hygroscopicity between subsaturated and supersaturated conditions (Petters et al., 2009; Prenni et al., 2007; Wex et al., 2010). Several factors may contribute to these observations. First, it is known that organic compounds have different degrees of dissolution at sub- and supersaturated conditions, and different components with varying solubilities in the same particle may exhibit discontinuous hygroscopicity (Prenni et al., 2007). Second, the particle mixing state

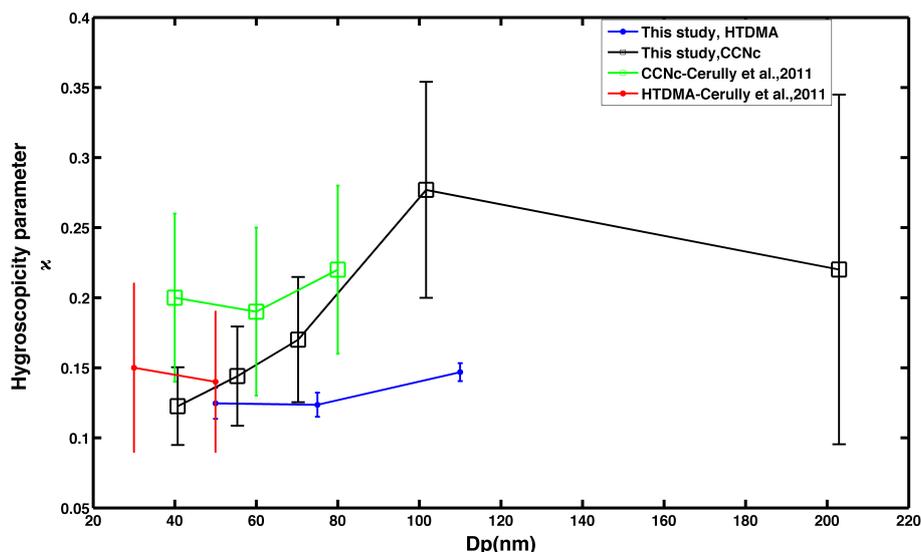


Fig. 5. Calculated κ values (κ_{HTDMA} and κ_{CCNC}) as a function of particle dry diameter using HTDMA and CCNC measurements from this study and from the study by Cerully et al. (2011).

and potential phase separation (liquid or solid phases) could make aerosol hygroscopicity depend on RH (Zardini et al., 2008; Henning et al., 2012). The observed differences in hygroscopicity between the sub- and supersaturated conditions could partially be due to the different characteristic designs of the instruments. For example, the HTDMA and CCNC have different residence times for the aerosol to reach equilibrium at the desired RH or supersaturation (Juranyi et al., 2009). The study by Good et al. (2010) found a close agreement between κ_{CCNC} and κ_{HTDMA} when sulfate and ammonium comprised the majority of the aerosol mass. This suggests that aerosol composition, and especially the presence of organic compounds, play a key role in the differences in the aerosol hygroscopicity between sub- and supersaturated conditions.

General patterns of κ as a function of particle diameter were quite similar from both HTDMA and CCNC measurements: the aerosol hygroscopicity increased with increasing particle diameter up to 100–200 nm (see Fig. 5). This observation is in good agreement with CCNC-derived κ values reported by Gunthe et al. (2009) and Rose et al. (2008) and with HTDMA-derived κ values reported by Vestin et al. (2007) who reported average values of κ of 0.12 for Aitken mode particles and κ of 0.20 for accumulation mode particles. Our VH-TDMA results showed an average value of $\kappa = 0.12$ for Aitken mode particles and $\kappa = 0.15$ for accumulation mode particles (see Table 1).

3.2 Volatility and its connection to hygroscopicity

3.2.1 Comparison with VDMPS results

The VFR as a function of the heating temperature obtained from both VTDMA and VDMPS measurements using data from this study and from Häkkinen et al. (2012) is compared in Fig. 6. More small particles were observed to evaporate at lower temperatures than bigger particles, probably due to differences in the particle chemical composition. Larger particles were probably also aged more than smaller particles, and, therefore, likely to have lower volatilities.

Our results obtained using the VTDMA are comparable with the volatility behavior of aerosols obtained using the VDMPS (this study and the summertime data from Häkkinen et al., 2012). At high temperatures, above 200 °C, aerosol particles were slightly more volatile when using the VTDMA as compared to VDMPS. It should be noted that the residence time in the VTDMA (approximately 10 s) is higher than the one in VDMPS (around one second), which gives more time for the aerosols to evaporate. The design of the heating unit will also affect the VFR obtained (Riipinen et al., 2010). In more detail, the VFR from VDMPS data was obtained for polydisperse aerosol volume distribution (20–500 nm); the VFR obtained describes the volatility of relatively large particles rather than small ones. VFR from VTDMA data was, instead, obtained for monodisperse aerosol and, thus, the largest difference in the VFRs (VDMPS vs. VTDMA) is observed between VDMPS and VTDMA-50 nm. It should be noted that the difference between VFRs of VDMPS and VTDMA-150 nm is not very large, indicating that the difference in the residence times (1 s vs. 10 s) is not that important when studying the aerosol in Hyytiälä. For comparison, the

Table 1. Calculated hygroscopicity parameter κ_{mix} based on the Zdanovskii–Stokes–Robinson (ZSR) mixing rule compared with measured κ values using HTDMA (κ_{HTDMA}) and CCNC (κ_{CCN}). Chemical information used in the calculation was obtained from AMS and aethalometer data. Values (κ , density) without reference are assumptions. We also assume the unknown species are not hygroscopic and are not taken into calculations for mixtures.

Compounds	κ	mass fraction	density (kg m^{-3})	volume fraction ε
$(\text{NH}_4)_2\text{SO}_4$	0.615 ^a	0.26	1770 ^c	0.21
Organics	0.1 ^b	0.61	1200 ^d	0.71
Black carbon	0	0.06	1900 ^e	0.04
Unknown	0	0.07		0.04
Particle			1400	
$\kappa_{\text{mix}} = 0.20$				
κ_{HTDMA}	0.12 (50 nm)	0.12 (75 nm)	0.15 (110 nm)	
κ_{CCN}	0.12 (41 nm) 0.28 (102 nm)	0.14 (55 nm) 0.22 (203 nm)	0.17 (70 nm)	

^a Petters and Kreidenweis (2007).

^b Sihito et al. (2011).

^c Dinar et al. (2006).

^d Turpin and Lim (2001).

^e Roberts and Jones (2004).

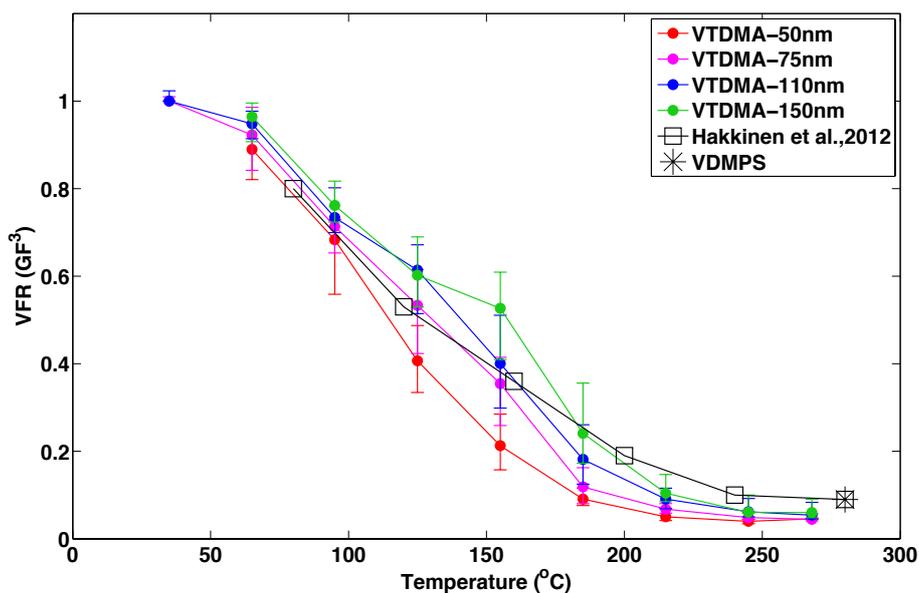


Fig. 6. Volume fraction remaining (VFR) calculated from volatile growth factor (GF_V) obtained from the VTDMA measurements as a function of heating temperature for four different particle sizes. In addition, VFR values from VDMPS analysis using data of HUMPPA-COPEC campaign (black star) and summertime data set used in Häkkinen et al. (2012) using VDMPS (black squares) are also presented.

mass fraction remaining of a laboratory-generated aerosol, α -pinene, at 200 °C was around 50 % lower when a 10 s residence time was used compared to the 1 s residence time (Ripinen et al., 2010).

3.2.2 Hygroscopicity of non-volatile fraction

Figure 7 shows the values of GF_{VH} and GF_V as well as their ratio for 50 nm, 75 nm and 110 nm particles. It should be noted that the particle size mentioned here is the original dry

size of particles selected by the first DMA. The ratio between GF_{VH} and GF_V demonstrates the actual hygroscopic growth factor of the residual material after heating. Since this ratio was always larger than 1, we can conclude that there was always hygroscopic material remaining in the particle phase during the whole temperature range for all particles sizes. This indicates that at high heating temperatures, in addition to black carbon, there were also other very low volatile compounds that were hygroscopic. In Hyytiälä, concentrations of

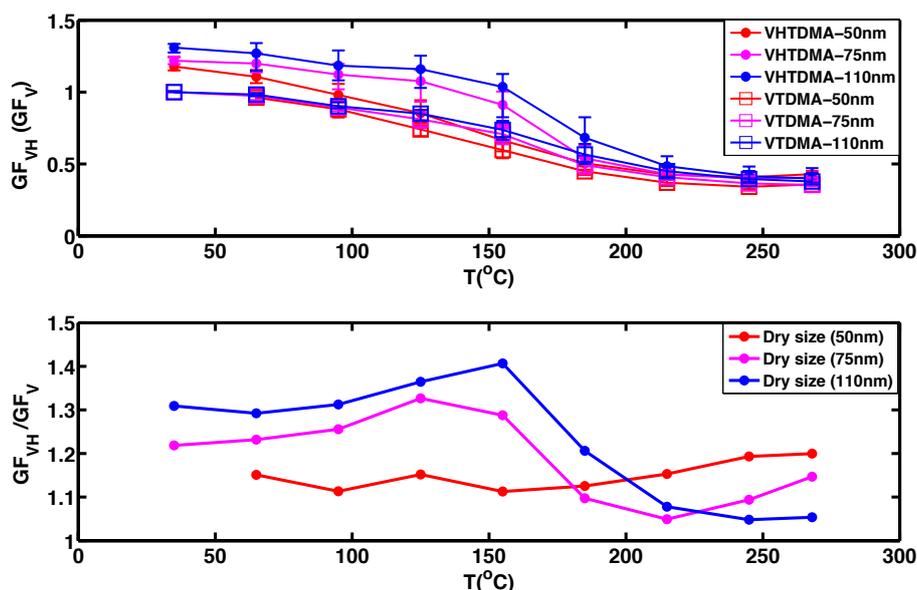


Fig. 7. GF_{VH} with respect to the median thermodenuder temperature obtained from VH-TDMA at $RH=90\%$, compared with the growth factor (GF_V) from VTDMA of this study for 50 nm, 75 nm and 110 nm particles (upper panel) and the ratio between GF_{VH} and GF_V as a function of the heating temperature (lower panel).

sodium chloride and potassium salts are typically quite low (Saarikoski et al., 2005), so their contribution to the chemical composition of the aerosol tends to be minor, especially in the submicron size range. Hence, the best candidates for such low-volatile compounds could be, e.g., highly-oxidized organic compounds, since high O:C values in the particulate phase have been associated with both high hygroscopicity and low volatility (Donahue et al., 2011; Mei et al., 2013; Cappa et al., 2013; Kuwata et al., 2013).

Atmospheric aerosols consist of a large number of different organic and inorganic compounds of different volatilities. Tritscher et al. (2011) reported that ammonium sulfate (AS) particles start to evaporate at temperatures above $100\text{ }^\circ\text{C}$, and volatilize completely at temperatures above $150\text{ }^\circ\text{C}$. Huffman et al. (2008) reported that AS starts to volatilize around $110\text{ }^\circ\text{C}$, but does not evaporate completely even at temperatures above $230\text{ }^\circ\text{C}$. Philippin et al. (2003), Burtscher et al. (2001) and Villani et al. (2008) have found that AS volatilizes completely at temperatures around $180\text{ }^\circ\text{C}$. Ammonium nitrate has been found to evaporate at temperatures around $60\text{ }^\circ\text{C}$, while NaCl and NaNO_3 particles evaporate at temperatures higher than $500\text{ }^\circ\text{C}$. Most organic compounds evaporate at relative low temperatures, for example, relatively low-volatile organic acid, citric acid, evaporates completely at temperatures above $110\text{ }^\circ\text{C}$ (Tritscher et al., 2011). In the study by An et al. (2007), 98% of secondary organic aerosol (SOA) evaporated at temperatures around $75\text{ }^\circ\text{C}$.

In our study, the hygroscopic growth factors increased with increasing temperatures up to about $150\text{ }^\circ\text{C}$ for 75 nm and 110 nm particles. This means that the volatilized compounds were less hygroscopic than those remaining in the

particles after heating up to this temperature. After heating to above $150\text{ }^\circ\text{C}$, the hygroscopic growth factor of the remaining aerosol material for 110 nm particles decreased rapidly, which could be explained by the evaporation of the hygroscopic inorganic compounds, especially ammonium sulfate. A roughly similar behavior was seen for 75 nm particles. However, for 50 nm particles, this initially decreasing and then increasing pattern of the hygroscopic growth factor was not observed. One potential reason for the observed differences is that the smallest particles (50 nm here) had such a small sulfate fraction that its evaporation did not influence the temperature dependence of this curve in the lower part of Fig. 7. The gradual decrease in GF of 50 nm particles with an increasing temperature in the upper part of Fig. 7 is most likely due to the presence of organic compounds of different saturation vapor pressures (i.e., volatility) in these particles.

At the highest heating temperature of $280\text{ }^\circ\text{C}$ we observed a size dependence of the ratio of GF_{VH} and GF_V . This might indicate that there were different amounts of organic compounds in the particles of different dry sizes.

3.3 Theoretical analysis of the hygroscopic parameter

Based on the Zdanovskii–Stokes–Robinson (ZSR) relation (Stokes and Robinson, 1966), the hygroscopic growth factor (or hygroscopic parameter κ) of a mixed particle can be estimated from the hygroscopic growth factor (or hygroscopic parameter κ) of each component of the particles with respect to their volume fractions (see, e.g., Gysel et al., 2007; Swietlicki et al., 2008):

Table 2. Parameters used in the estimation of hygroscopicity (hygroscopic growth factor) of very-low-volatile organics denoted here as OOA (oxidized organic aerosol) based on VH-TDMA data (particle diameter 110 nm, relative humidity 90 % and temperature 268 °C) (see Eq. 10).

Parameter name	parameter	value
V-mode growth factor	GF _V (RH _{dry} , 268 °C)	0.38
VH-mode growth factor	GF _{VH} (90 % RH, 268 °C)	0.40
Hygroscopic growth factor of non-volatile residual	GF _{H,nv}	1.05
Hygroscopic growth factor of BC in non-volatile residual	GF _{H,BC,nv}	1
Volume fraction of non-volatile residual in aerosol	ε _{nv}	0.05
Volume fraction of BC in aerosol	ε _{BC}	0.04
Black carbon volume fraction in non-volatile material	ε _{BC,nv}	0.80
Volume fraction of OOA in non-volatile residual	ε _{OOA,nv}	0.20
Hygroscopic growth factor of OOA	GF _{H,OOA,nv}	1.21

$$\kappa_{\text{mix}} = \sum_i \varepsilon_i \kappa_i. \quad (9)$$

Here ε_i is the volume fraction of component i in the dry particle, and κ_i is the hygroscopic parameter of the corresponding chemical compound i .

Let us first assume a three-component system consisting of ammonium sulphate, organics and black carbon. Based on the AMS and aethalometer data, the volume fraction of these three components can be obtained, and they are listed in Table 1. Earlier studies have frequently used the value of $\kappa_{\text{org}} = 0.1$ for pure organic aerosol and $\kappa = 0.6$ for ammonium sulfate (Sihto et al., 2011; Gunthe et al., 2009; Dusek et al., 2010; Petters and Kreidenweis, 2007). By selecting the same values and assuming further that black carbon does not uptake water at all, we get an average κ for the mixture of 0.20. This κ value is close to our experimental results obtained from HTDMA and CCNC (see Table 1). To obtain a better agreement between the theoretical calculation and HTDMA results, measurements of larger sized particles should be performed, since AMS and aethalometer data are from a bulk sample and thus, the chemical information is more reliable for larger particles. Some error is introduced into our analysis when masses are converted to volumes since the densities of many organic species are unknown, and the density of aerosol particles is often size dependent (Zelenyuk et al., 2005).

The non-volatile aerosol volume fraction (ε_{nv}) can be determined from the VTDMA data using V-mode at the highest temperature of 268 °C (which is the median temperature of highest-heating temperature interval). The hygroscopicity of this residual was also determined using VH-mode and V-mode (GF_{H,nv}). Let us assume that this non-volatile material consists of black carbon and some other very low-volatile component, such as highly oxidized organics, organic salts or polymers (denoted here OOA, oxidized organic aerosol). Also, let us assume that black carbon does not evaporate at all (GF_{V,BC} = 1). The volume fraction of black carbon (ε_{BC}) has already been obtained from the AMS and aethalometer data by assuming that the density of black carbon is

1.9 g cm⁻³ and that of organics is 1.2 g cm⁻³ (Turpin and Lim, 2001). The hygroscopic growth factor (hygroscopicity) of the highly oxidized organic aerosol in the non-volatile residual (GF_{H,OOA,nv}) can be estimated using the ZSR mixing rule again:

$$\text{Gf}_{\text{H,nv}}^3 = \sum_i \varepsilon_i \text{Gf}_{\text{H},i}^3 = \varepsilon_{\text{BC,nv}} \text{GF}_{\text{H,BC,nv}}^3 + \varepsilon_{\text{OOA,nv}} \text{GF}_{\text{H,OOA,nv}}^3, \quad (10)$$

where GF_{H,nv} is obtained from the ratio of GF_{VH} and GF_V (268 °C), GF_{H,BC,nv} is the hygroscopic growth factor of BC in the non-volatile residual (assumed to be 1), ε_{BC,nv} is the volume fraction of BC in the non-volatile aerosol residual (= ε_{BC} / ε_{nv}) and ε_{OOA,nv} is the volume fraction of low-volatile organics in the residual (= 1 - ε_{BC,nv}). The values of the parameters needed for the estimation of GF_{H,OOA,nv} are presented in Table 2. This analysis was performed for the largest particles (110 nm in diameter) only. For 110 nm particles GF_{H,OOA,nv} of 1.21 was obtained. This corresponds to a κ value of 0.09 (see Eq. 6). Prisle et al. (2010) measured the critical supersaturation of 100 nm particles consisting of 95 % of sodium decanoate (which is a low-volatile organic compound) by mass, and reported a value of 0.27 %, which corresponds to a κ value of 0.19. Their study also obtained a critical supersaturation of 0.32 % for 100 nm particles consisting of 95 % of sodium dodecanoate by mass, which corresponds to a κ value of 0.14.

We notice that our approach of assuming an aerosol system of only three-component causes uncertainties. Careful examination of the dependence of particle composition on particle size, hygroscopicity of black carbon as well as the volatility of different species must be obtained in order to get more accurate results of the GF_{VH} estimation.

4 Summary and conclusions

A Volatility Hygroscopicity Tandem Differential Mobility Analyzer (VH-TDMA) was used to measure the hygroscopicity and volatility of the ambient aerosols from 24 July to

7 August 2010 in Hyytiälä, Finland as a part of HUMPPA-COPEC 2010 campaign. Several particle sizes (50, 75 and 110 nm) were investigated in detail and two different types of air masses were observed – air masses from biomass-burning in Russia and background air. In general, larger particles were more hygroscopic than smaller ones. Black carbon was observed to have little influence on hygroscopicity of aerosol in this study, whereas the competition between the aerosol mass fractions of organics and SO_4^{2-} was most likely the main contributor in determining the variation in aerosol hygroscopicity.

In addition to VH-TDMA, other data sets, such as data collected with the CCNC, were used in the analysis. The aerosol hygroscopicity was determined using the two independent data sets, from both VH-TDMA and CCNC, and these data were compared with each other. The CCNC-derived values of the hygroscopicity parameter κ were slightly higher than the ones derived from the HTDMA measurements. The same feature has been observed previously and usually it has been explained by the fact that many organic compounds have different solubilities in sub- and supersaturated conditions. The HTDMA-derived values of κ , especially for the largest particle size of 110 nm (0.15), were in closest agreement with the predicted value of κ (0.20) based on ZSR mixing rule.

The volatility properties obtained from the VH-TDMA during the studied period were compared with the aerosol volatility behavior investigated using an independent data set from VDMPS. Summertime data (during 2008–2009) from the same site measured earlier, using the same VDMPS system, were also included in the analysis for comparison. The two independent instruments showed good agreement with each other. Small particles evaporated more compared with larger particles when heated. At temperatures above 200 °C, 80 % of the aerosol material (by volume) evaporated from the particles. However, there was still a significant amount of aerosol volume left at these high temperatures (non-volatile aerosol residual).

The hygroscopicity of the particles after heating up to different temperatures was investigated. There was always hygroscopic material remaining in particles of different sizes at all heating temperatures, even at the highest heating temperature of 280 °C. Since black carbon is hydrophobic, this result supports recent studies that have found very-low-volatile, yet hygroscopic material that is not BC, in submicron ambient particles. This material can be, e.g., organic salts or organic polymers from aerosol aging. Different sized particles had different volatility behavior, which indicates that the chemical composition varied with particle size. For the smallest particles, the hygroscopic growth factor for aerosol residual after heating was relatively stable. This could be explained by organic compounds being the majority species of the smallest particles. A similar analysis with the VH-TDMA would be beneficial to address the spatial variability of the hygroscopicity of the non-volatile cores and whether it is related

to the amount of extremely oxidized organic vapors in the atmosphere (Ehn et al., 2012)

The hygroscopicity of the non-volatile, non-BC aerosol material was estimated with a hygroscopic growth factor of 1.21 for 110 nm particles. In the future it would be important to obtain information about the hygroscopic properties of different low-volatile organics, e.g., organic salts. This would help to further interpret the VH-TDMA results in order to better understand the chemical properties of submicron aerosol particles, most importantly, particulate organics.

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