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

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Abstract

The Volatility-Hygroscopicity Tandem Differential Mobility Analyzer (VH-TDMA) was applied to study the hygroscopicity and volatility properties of submicron atmospheric aerosol in a boreal forest environment in Hyytiälä, Finland during the summer of 2010. Aitken and accumulation mode particles (50 nm, 75 nm and 110 nm) were investigated. The results suggest that the particles were internally mixed at all sizes. Hygroscopicity was found to increase with 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 slightly higher than κ calculated from VH-TDMA data under sub-saturated conditions, which can be explained by the fact that particulate organics have a different degree of dissolution in sub- and supersaturated conditions. Also, the size-resolved volatility properties of particles were investigated. Upon heating, small particles evaporated more compared to large particles. There was a significant amount of aerosol volume (non-volatile material) left even at heating temperatures above 280 °C. Using size resolved volatility-hygroscopicity analysis, we concluded that there was always hygroscopic material remaining in the particles of different sizes at all different heating temperatures, even above 280 °C. This indicates that the observed non-volatile aerosol material was not consisting 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 parti-

cle 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 the aerosol particle size, which, in turn, is a function of the relative humidity (RH) and temperature of the ambient air. Depending on the aerosol composition, the size of an aerosol particle may increase by 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, also determines the number concentration of cloud condensation nuclei and the lifetime of the clouds. 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 describes the evaporation property of a chemical component. Volatility is an important quantity when we talk about gas-particle partitioning of semi-volatile and very low volatile aerosol compounds. Low volatile compounds are critical in the new particle formation and growth of nanoparticles (Riipinen et al., 2011). Therefore, the hygroscopicity and volatility properties are crucial for estimating the aerosol radiative forcing, lifetime and mass loading, as well as 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 in field conditions using different techniques. These techniques include an electrodynamic balance (EB, Tang and Munkelwitz, 1994), humidity-controlled nephelometer (Dougle et al., 1998) and hygroscopicity tandem differential mobility analyzer (H-TDMA, Liu et al., 1978; Swietlicki et al., 2008). Hygroscopic properties of many inorganic and some organic compounds have been investigated extensively (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 the RH of 85 %. Their study also showed that the presence of organic aerosol coating seemed to enhance the water uptake of inorganic seeds at relative humidities lower than the DRH of that inorganic component.

The volatility property of atmospheric aerosols has been investigated using several instruments and techniques. Thermodenuder, one of the primary instruments to study aerosol volatility, has been used extensively (e.g. Rader and McMurry, 1986; O'Dowd et al., 2000; 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 the temperature, relative humidity, pressure and radiation affect aerosol partitioning (Fuzzi et al., 2006). Many inorganic and organic species have been found to evaporate at temperatures below 300 °C (Turpin et al., 2001; Raatikainen et al., 2010), while some other compounds, such as black carbon (BC) and sea salts, do not. Recent studies suggest that some organics may form very low-volatile compounds, e.g. salts or polymers, under atmospheric conditions (Kalberer et al., 2004; Ehn et al., 2007; Backman et al., 2010; Häkkinen et al., 2012).

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 in 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 from the VH-TDMA. Our main goals were to (1) find out the time and size dependency of aerosol hygroscopicity and volatility in a boreal forest environment, (2) test the performance of the fifth-generation VH-TDMA of the University of Helsinki, and (3) investigate the chemical composition of particles of different sizes and water uptake ability of the non-volatile residual observed in submicron aerosol particles.

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 a more than 40 yr-old pine forest. Aerosol size distribution measurements have been performed continuously since 1996 (Mäkelä et al., 1997). Our study is part of the 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 its meteorological conditions can be found in Williams et al. (2011).

2.2 Instrumentation

2.2.1 VH-TDMA

The VH-TDMA used in this study is a fifth generation University of Helsinki TDMA that measured 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 get charged and are 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. The particles of dry sizes of 50 nm, 75 nm and 110 nm were selected in 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 going into a humidifier while the other one bypassing the humidifier and going 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 Differential Mobility Analyzer (DMA, Hauke type) and a condensation particle counter (CPC, TSI 3010 and 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 humidying particles). The temperature of the thermal denuder was increased continuously from 25 °C to 280 °C, one temperature scan taking place around 45 min. The relative humidity of the aerosol after the humidifier was set to 90 % within 2 % error (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) 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).

2.2.3 VDMPS and DMPS

A twin-Differential Mobility Particle Sizer (DMPS) system was used to measure the ambient aerosol number size distribution (3–1000 nm in diameter) with a time resolution of 10 min (Aalto et al., 2001). A Volatility-DMPS (VDMPS) system consisting of a thermodenuder and a DMPS heated the incoming sample air to 280 °C. The VDMPS determined the number size distribution of particles of 20–500 nm in diameter, which did not evaporate in the thermodenuder (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 or sea salt, the mass concentration of black carbon was measured using an aethalometer (Magee Scientific, Hansen et al., 1982) with a $PM_{2.5}$ inlet. According to Saarikoski et al. (2005), the contribution of sea salt to submicron aerosol particle mass in Hyytiälä is minor.

2.2.5 Supporting data

Concentrations of several trace gases are 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). Here we utilized measured gas-phase concentrations of SO_2 (fluorescence analyzer TEI 43 CTL, Thermo Fisher Scientific) and O_3 (UV-light absorption analyzer TEI 49, Thermo Fisher Scientific). We also calculated a proxy for the gaseous H_2SO_4 concentration as the ratio of the production from oxidation of SO_2 by OH radicals and sink by condensation onto pre-existing aerosol particle surface. In this calculation, the 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 as the growth factor probability density function (GF-PDF), was obtained. The hygroscopic growth factor using H-mode is defined as

$$GF(90\,\%\,RH) = GF_H = \frac{D_p(T_{room}, 90\,\%\,RH)}{D_p(T_{room}, RH_{dry})},$$ (1)

where $D_p(T_{room}, 90\%\,RH)$ is the diameter of a particle at the selected RH, in this study 90 %, and $D_p(T_{room}, RH_{dry})$ 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 similar way:

$$GF(T) = GF_V = \frac{D_p(T, RH_{dry})}{D_p(T_{room}, RH_{dry})}, \tag{2}$$

where $D_p(T, RH_{dry})$ is the diameter of a particle after heating to a certain temperature, in this study from 20 °C to 280 °C, without humidification. Eq. (2) was used to describe the behavior of aerosol particles when exposed to a heating condition without passing through a humidifier unit. 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.

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

$$GF(90\%\,RH, T) = GF_{VH} = \frac{D_p(90\%\,RH, T)}{D_p(T_{room}, RH_{dry})}. \tag{3}$$

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:

$$GF(90\%\,RH, T, \text{aersol residual}) = \frac{GF_{VH}}{GF_V}. \tag{4}$$

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. 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).

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:

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

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

where $S(D)$ is the saturation ratio and express the same quantity as 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, $\sigma_{s/a}$ 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 of aerosol particles remaining after heating was defined by comparing the total volume of heated aerosol ($V_{tot,VDMPS}$) to the total volume of ambient aerosol ($V_{tot,DMPS}$) (Häkkinen et al., 2012). The volume fraction remaining (VFR) can be defined as follows:

$$VFR = \frac{V_{tot,VDMPS}}{V_{tot,DMPS}}. \tag{7}$$

We can also define the volume fraction remaining after heating for certain size particles as follows:

$$VFR\_D_p = \frac{D_p^3(T)}{D_p^3(T_{room})} = GF_V^3(T). \tag{8}$$

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 obtained VFR 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 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. During the whole period, the hygroscopicity distributions mainly showed one mode with the median GF_H varying between 1.1 and 1.5. This suggests that the studied particles were relatively well internally 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 were 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 more hydrophobic 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 also 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 modest influence on the aerosol hygroscopicity based on roughly the constant mass fraction of around 6 % during the whole period. It should be noted that in this study the measured $PM_{2.5}$ BC mass was assumed to be solely in submicron particles. The data in Fig. 2 suggests 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 (Org/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 Org/SO_4^{2-} ratios indicating smaller contribution from the hygroscopic sulphate. The bulk composition data 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 (positive correlation). 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 turns increases aerosol hygroscopicity (Cappa et al., 2013).

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, the particles during the background period were more hygroscopic than the ones during the biomass burning period, which is due to the fact that there were larger amounts of organics in the particles during the
5   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 particles to say anything conclusive about how the hygroscopicity dependent on the particle size (the availability of data can be noticed from Fig. 2). During the background period the smaller particles were observed to have lower hygroscopicity as
10   compared with the larger particles (Fig. 4 upper panel). This can be due to e.g. higher degree of oxidation of 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 at the GF_H of around 1.05, indicating that marginally hygroscopic particles were also present occasionally.

15   ## 3.1.2   Comparison with CCN

Figure 5 shows that the aerosol hygroscopicity parameter κ obtained from the HT-DMA was lower than that obtained from the CCNc. This difference indicates that the κ-Köhler theory cannot well describe the water activity throughout the relative humidity range from sub- to supersaturated conditions. Cerully et al. (2011) investigated parti-
20   cle 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 the measurements by Cerully et al. (2011) 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).
25   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 hygroscopicity for

spring and lower hygroscopicity of aerosols during summer. This can also explain the fact that κ values from Cerully et al. (2011) were higher than ours for all sizes.

Laboratory studies have reported inconsistencies in aerosol hygroscopicity between the subsaturated and supersaturated conditions (Petters et al., 2009b; Prenni et al., 2007; Wex et al., 2010). 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). However, the study by Good et al. (2010) showed that κ_{CCN} was in close agreement with κ_{HTDMA} when the air masses were more varied but generally showed trajectories originating from the European continent. In other words, the differences in aerosol hygroscopicity under subsaturated and supersaturated conditions are also affected by the air mass origins.

General patterns of κ as a function of particle diameter were quite similar from both HTDMA and CCNc measurements – large particles tended to have higher hygroscopicity than small particles (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 tells us how much aerosol volume remains in the aerosol after heating and gives us indirect information about the aerosol chemical composition as different aerosol species volatilize at different temperatures. From the VTDMA aerosol volatility is obtained as a function of the particle size, whereas from the VDMPS measurements only the volatility of the total aerosol volume/mass can be obtained.

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. Small particles were observed to evaporate more at lower temperatures than bigger particles, probably due to Kelvin effect and differences in the particle chemical composition. Larger particles were probably also more aged 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 summer time 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 obtained VFR (Riipinen 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 are hygroscopic. The best candidates for such 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 sul-

fate (AS) particles start to evaporate at temperature above 100 °C, and volatilize completely at temperature above 150 °C. Huffman et al. (2008) reported that AS starts to volatilize around 110 °C, but does not evaporate completely even at temperatures above 230 °C. Philippin et al. (2003), Burtscher et al. (2001) and Villani et al. (2008) have found that AS volatilizes completely at temperature around 180 °C. Ammonium nitrate has been found to evaporate at temperature around 60 °C, while NaCl and $NaNO_3$ particles evaporate at temperatures higher than 500 °C. Most organic compounds evaporate at relative low temperatures, for example, citric acid evaporates completely at temperatures above 110 °C (Tritscher et al., 2011). 98 % of SOA evaporated at temperatures around 75 °C in the study by An et al. (2007).

In our study, the hygroscopic growth factors increased with increasing temperatures up to about 150 °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. After heating to above 150 °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 similar behavior was seen for 75 nm particles between the temperatures of about 150 °C and 220 °C. It is more likely that there were more oxidized organic compounds remaining in the particles after heating up to 220 °C, and, thus, an increased hygroscopic growth factor was observed. However, for 50 nm particles, this decreasing and increasing behavior of hygroscopic growth factor was not observed. This suggests that the chemical composition of smallest particles was more homogenous than that of the larger ones, and that most of the mass of the smallest particles were made up of organic compounds.

At the highest heating temperature of 280 °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):

$$\kappa_{\text{mix}} = \sum_i \varepsilon_i \kappa_i. \tag{9}$$

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 aethelometer 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 aethelometer data are from 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 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

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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 ($GF_{H,BC} = 1$). The volume fraction of black carbon (ε_{BC}) has already been obtained from the AMS and aethelometer data by assuming that the density of black carbon is $1.9\,\mathrm{g\,cm^{-3}}$ and that of organics is $1.2\,\mathrm{g\,cm^{-3}}$ (Turpin et al., 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:

$$GF_{H,nv}^3 = \sum_i \varepsilon_i GF_{H,i}^3 = \varepsilon_{BC,nv} GF_{H,BC,nv}^3 + \varepsilon_{OOA,nv} GF_{H,OOA,nv}^3. \qquad (10)$$

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), $\varepsilon_{BC,nv}$ is the volume fraction of BC in the non-volatile aerosol residual ($= \varepsilon_{BC}/\varepsilon_{nv}$), and $\varepsilon_{OOA,nv}$ is the volume fraction of low-volatile organics in the residual ($= 1 - \varepsilon_{BC,nv}$). 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).

We notice that our approach of assuming only three-component aerosol system 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 have to be obtained in order to get more accurate results of the GF_{VH} estimation.

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4 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 the HUMPPA-COPEC 2010 campaign. Several particle sizes (50, 75 and 110 nm) were investigated in detail and two different types of air massed 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 also used in the analysis. Aerosol hygroscopicity was compared using the two independent data sets from VH-TDMA and CCNc. 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 previously observed and it can be usually explained by the fact that particulate organics have different degrees of dissolution 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 κ (0.20) based on ZSR mixing rule.

The volatility property obtained from the VH-TDMA during the studied period was compared with the aerosol volatility behavior investigated using an independent data set from VDMPS. Summer time data from the same site measured earlier, during 2008–2009, using the same VDMPS system were also included in the analysis for comparison. The two independent instruments showed a 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) was 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 but non-BC aerosol material in submicron ambient particles. This material can be, e.g., organic salts or organic polymers from aerosol aging. The volatility behavior of the different-size particles was different, which indicates that the chemical composition varied with the particle size. For the smallest particles, the actual hygroscopic growth factor for aerosol residual after heating was relatively stable. This could be explained by their chemical composition being more homogenous than that for large particles, and that the organic compounds were the major species in 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 connects to the amount of extremely oxidized organic vapors in the atmosphere (Ehn et al., 2012)

The hygroscopicity of this non-volatile non-BC aerosol material was estimated, and a reasonable hygroscopic growth factor of 1.21 for 110 nm particles was obtained. In the future it would be important to obtain information about the hygroscopic properties of different low-volatile organics e.g. organic salts. Prisle et al. (2010) measured the critical supersaturation of 100 nm particles consisting of 95 % of sodium decanoate 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. This would help us 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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Table 1. Calculated hygroscopicity κ value (κ_{mix}) based on the 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 aethelometer 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
(NH$_4$)$_2$SO$_4$	0.6[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	

κ_{mix} = 0.20			
κ_{HTDMA}	0.12 (50 nm)	0.12 (75 nm)	0.15 (110 nm)	
κ_{CCN}	0.12 (41 nm)	0.14 (55 nm)	0.17 (70 nm)	0.28 (102 nm)
	0.22 (203 nm)			

[a] Petters and Kreidenweis (2007); [b] Sihto et al. (2011); [c] Dinar et al. (2006); [d] Turpin et al. (2001); [e] Roberts and Jones (2004)

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 (no unit)
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	$\varepsilon_{BC,nv}$	0.80
Volume fraction of OOA in non-volatile residual	$\varepsilon_{OOA,nv}$	0.20
Hygroscopic growth factor of OOA	$GF_{H,OOA,nv}$	1.21
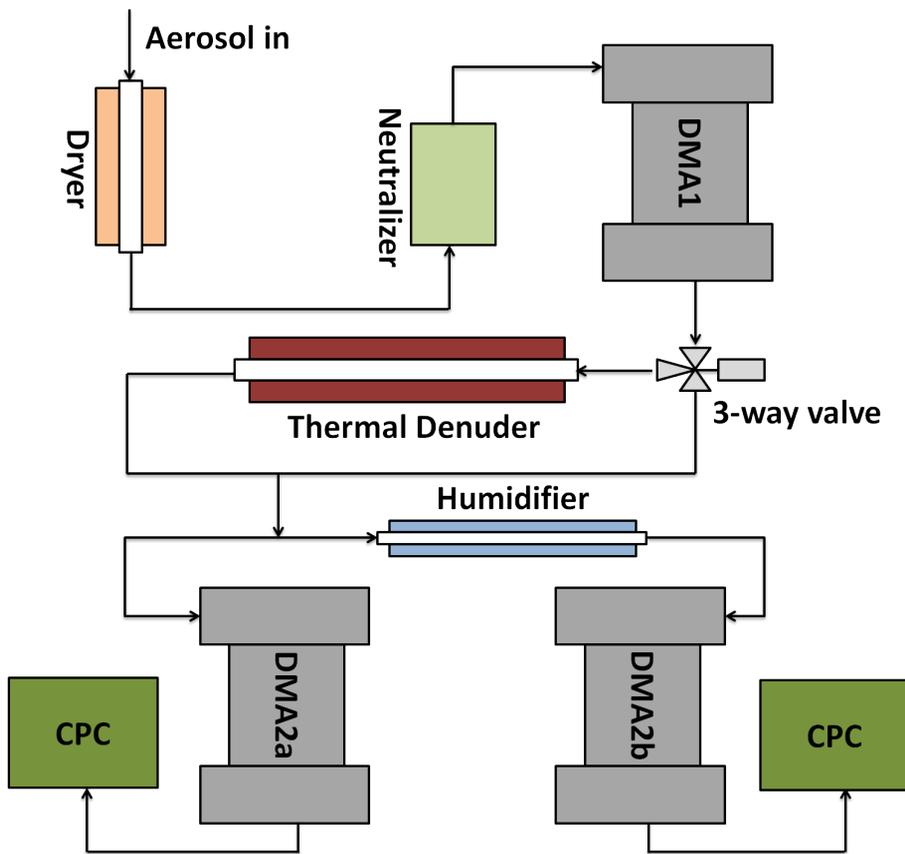
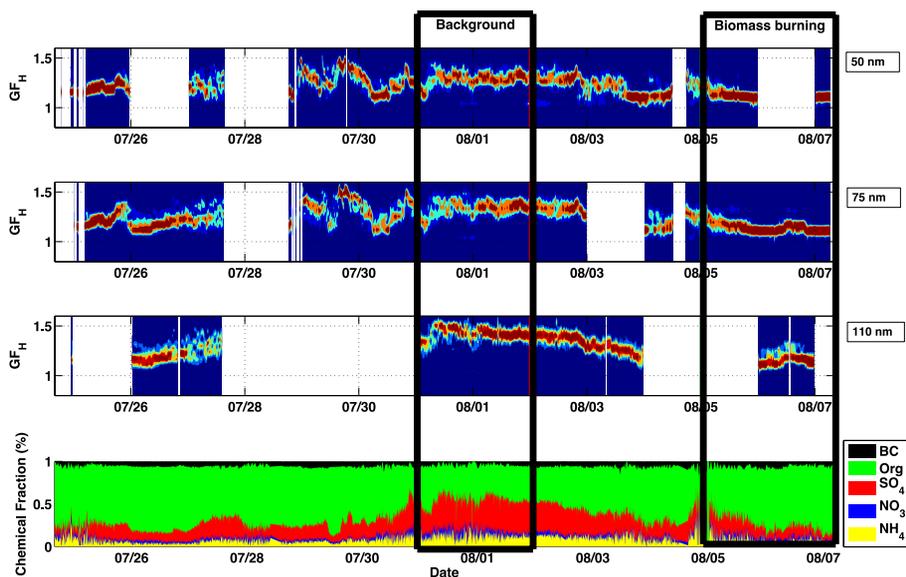**Fig. 1.** A schematic of the VH-TDMA instrument system.

Fig. 2. Time series of hygroscopic growth factor distribution (GF-PDF) for 50 nm, 75 nm and 110 nm-sized particles (upper three panels), and mass fraction of chemical components in particles (lower panel) from period between 24 July 2010 and 7 August 2010.
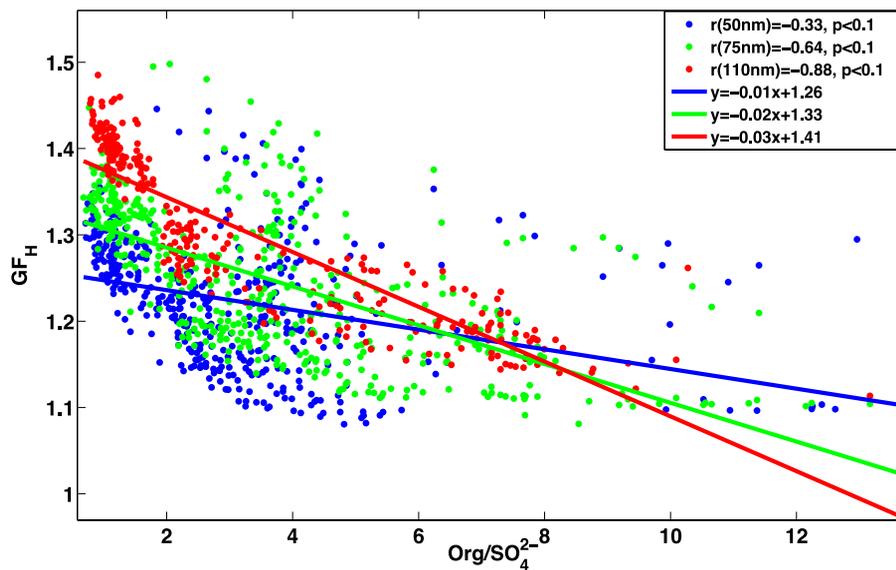
Fig. 3. Correlations between the average hygroscopic growth factor and the ratio between the concentrations of particulate organics and sulfates from AMS data for three different particle sizes.

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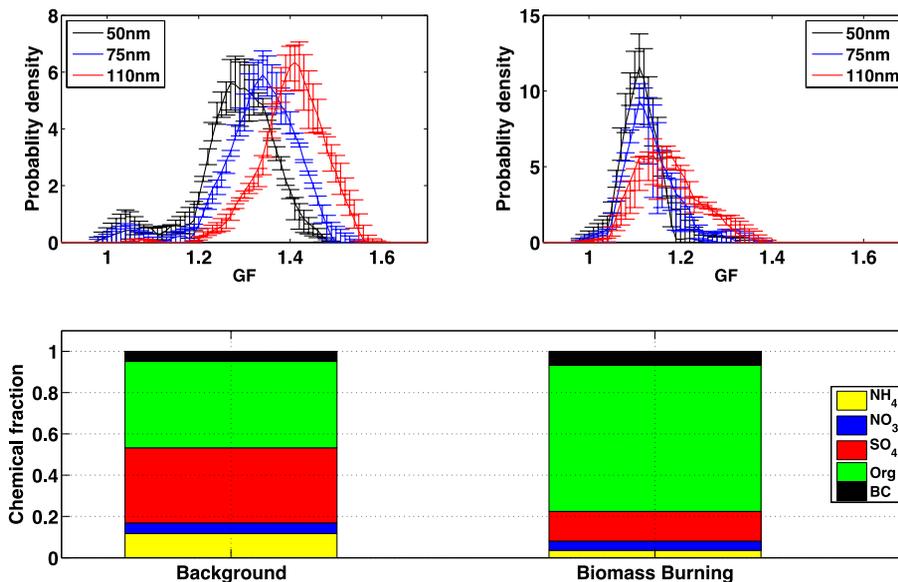
Fig. 4. The upper panel presents growth factor probability density function for the two distinct periods selected for case studies (left panel: background; right panel: biomass burning) for 50 nm, 75 nm and 110 nm sized particles. The lower panel illustrates the mass fractions of different aerosol components 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 particles to say anything conclusive about hygroscopicity dependence on particle size.
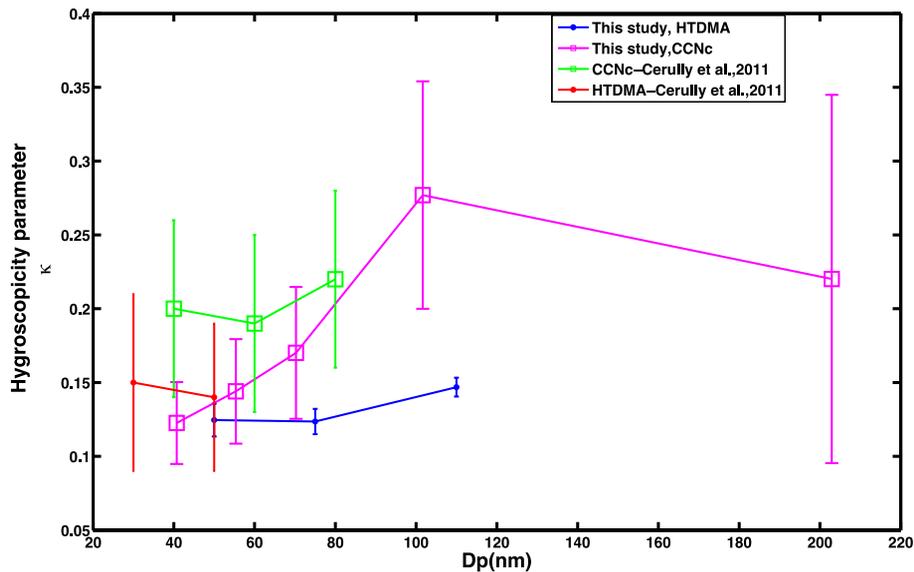
Fig. 5. Calculated κ values (κ_{HTDMA} and κ_{CCN}) as a function of particle diameter using HTDMA and CCNc measurements from this study and from the study by Cerully et al. (2011).
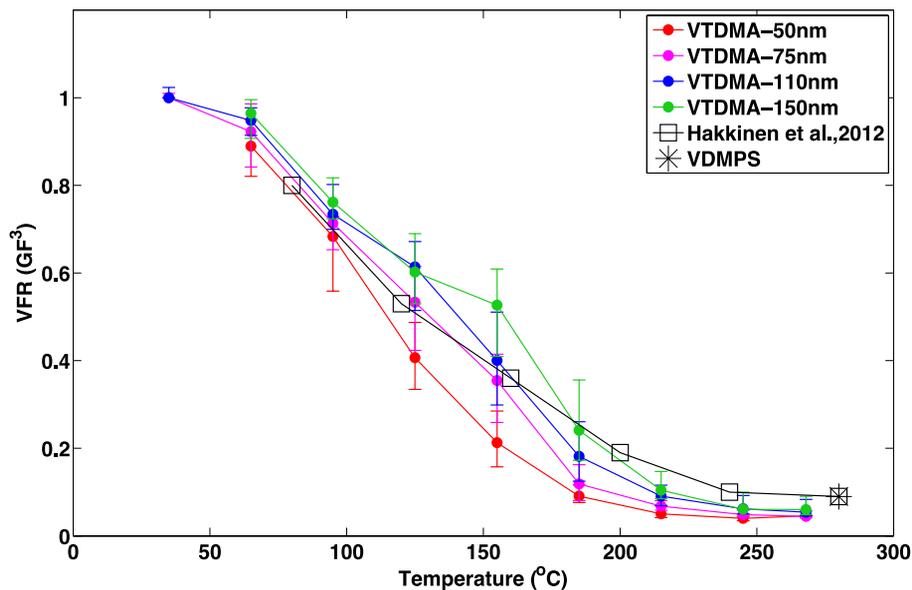
Fig. 6. Volume fraction remaining (VFR) calculated from volatile growth factor (GF$_V$) obtained from the VTDMA measurements as a function of heating temperature for four different particle sizes. In addition VFR values from VDMPS analysis using data of HUMPPA-COPEC campaign (black star) and summertime data set used in Häkkinen et al. (2012) are also presented (black squares).

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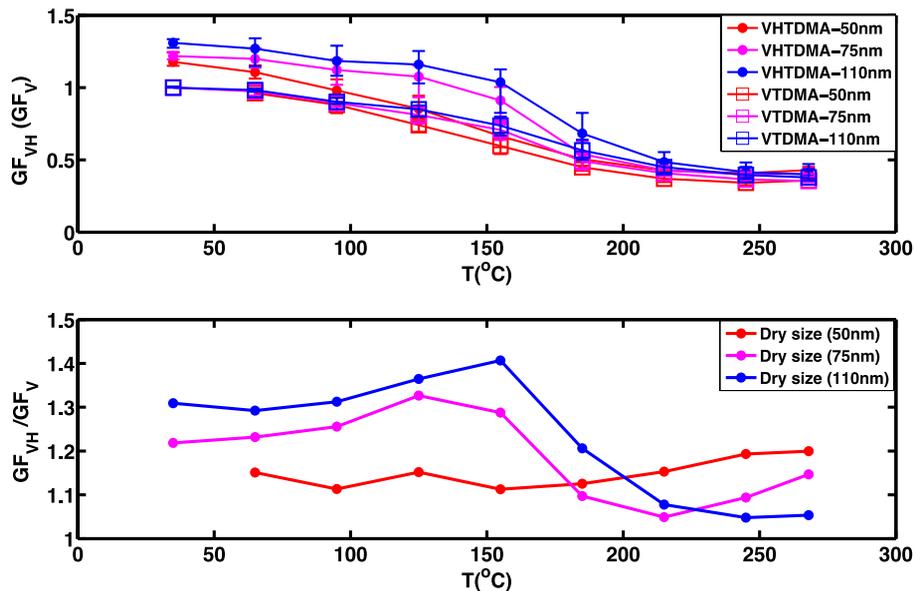Printer-friendly Version

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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).

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