



**Hygroscopicity of
submicron aerosol in
the boreal forest**

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**Relating the hygroscopic properties of
submicron aerosol to both gas- and
particle-phase chemical composition in
a boreal forest environment**

**J. Hong¹, J. Kim², T. Nieminen^{1,3}, J. Duplissy¹, M. Ehn¹, M. Äijälä¹, L. Hao²,
W. Nie^{1,4}, N. Sarnela¹, N. L. Prisle¹, M. Kulmala¹, A. Virtanen², T. Petäjä¹, and
V.-M. Kerminen¹**

¹Department of Physics, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland

²Department of Applied Physics, University of Eastern Finland, Kuopio 70211, Finland

³Helsinki Institute of Physics, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland

⁴Institute for Climate and Global Change Research & School of Atmospheric Sciences,
Nanjing University, Nanjing, 210093, China

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Correspondence to: J. Hong (juan.hong@helsinki.fi)

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Abstract

Measurements of the hygroscopicity of 15–145 nm particles in a boreal forest environment were conducted using two Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) systems during the Pan-European Gas-AeroSOIs-climate interaction Study (PEGASOS) campaign in spring 2013. Measurements of the chemical composition of non-size segregated particles were also performed using a High-Resolution Aerosol Mass Spectrometer (HR-AMS) in parallel with hygroscopicity measurements. On average, the hygroscopic growth factor (HGF) of particles was observed to increase from the morning until afternoon. In case of accumulation mode particles, the main reasons for this behavior were increases in the ratio of sulfate to organic matter and oxidation level (O:C ratio) of the organic matter in the particle phase. Using an O:C dependent hygroscopic growth factor of organic matter (HGF_{org}), fitted using the inverse Zdanovskii–Stokes–Robinson (ZSR) mixing rule, clearly improved the agreement between measured HGF and that predicted based on HR-AMS composition data. Besides organic oxidation level, the influence of inorganic species was tested when using the ZSR mixing rule to estimate the hygroscopic growth factor of organics in the aerosols. While accumulation and Aitken mode particles were predicted fairly well by the bulk aerosol composition data, the hygroscopicity of nucleation mode particles showed little correlation. However, we observed them to be more sensitive to the gas phase concentration of condensable vapors: the more there was sulfuric acid in the gas phase, the more hygroscopic the nucleation mode particles were. No clear dependence was found between the extremely low-volatility organics (ELVOCs) concentration and the HGF of particles of any size.

1 Introduction

Atmospheric aerosols can influence Earth's climate both directly and indirectly through affecting the radiation balance, or altering the albedo, lifetime and precipitation patterns

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environment due to the diverse properties of these compounds and their temporal variability (Hämeri et al., 2001; Ehn et al., 2007; Raatikainen et al., 2010; Hong et al., 2014).

Measurements of the hygroscopicity of newly-formed particles are critical to obtain information on the chemical species involved in the particle formation. This is because the direct determination of the chemical composition of those newly formed particles or nucleation mode particles under field conditions is still challenging, as only a small amount of mass is attributed to the newly formed particles (Ristovski et al., 2010; Wu et al., 2013). Recent studies have been looking at the connection between new particle formation and low volatility organic species in the atmosphere (Paasonen et al., 2010; Kulmala et al., 2013; Nieminen et al., 2014). Ehn et al. (2014) reported that a significant contribution to the growth of newly-formed 3–25 nm particles could be attributed to these ELVOCs. Hence, by examining the hygroscopic growth factor of nucleation and Aitken mode particles, we can also potentially get a better insight into the water affinity of these extremely low volatile organics, assumed to be non-hygroscopic or less hygroscopic than many inorganics.

In this study, we carried out measurements of the hygroscopicity of nucleation, Aitken and accumulation mode particles at a boreal forest site in Hyytiälä, located in Southern Finland. The main goal of this work is to find out how the hygroscopic properties of ambient submicron aerosols are connected to the aerosol chemical composition and concentration of condensable vapors in the gas phase in this environment. In order to address this issue, we will (1) investigate the diurnal pattern of the hygroscopicity of different-sized sub-micron particles, (2) carry out a closure study between the HTDMA-measured hygroscopic growth factor and the HR-AMS derived hygroscopic growth factor and (3) study the influence of condensable vapors, including H_2SO_4 and ELVOCs, on particles hygroscopicity.

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2 Materials and methodology

2.1 Measurements

The measurements were carried out between 6 April and 3 June 2013 as part of the PEGASOS campaign at SMEAR II (Station for Measuring Ecosystem–Atmosphere Relations II) located in Hyytiälä, Southern Finland (Hari and Kulmala, 2005). The site is surrounded by a 53-year-old pine forest.

Hygroscopic properties of aerosol particles were measured using a nano-Hygroscopicity Tandem Differential Mobility Analyzer (nHTDMA) and a HTDMA that is part of a Volatility-Hygroscopicity Tandem Differential Mobility Analyzer (VH-TDMA) system. A detailed description of the nHTDMA and VH-TDMA systems and their background principle can be found in Keskinen et al. (2013) and Hong et al. (2014). Briefly, particles of six dry mobility diameters (15, 20, 30, 60, 100 and 145 nm; RH < 10 %) were selected by a nano DMA (TSI 3085) for 15 and 20 nm particles and a Hauke-type Differential Mobility Analyzer (DMA; Winklmayr et al., 1991) for 30–145 nm particles, then the aerosol flow was going through a humidifier with a controlled RH, where they were taking up water and growing in size. Then the aerosols were introduced into a second DMA and a condensation particle counter (CPC, TSI 3010 & TSI 3772), where the growth factor distribution was measured. The relative humidity in the sheath flow of the second DMA was kept at 90 % within an accuracy of ± 2 %.

The hygroscopicity of particles is often described using a hygroscopic growth factor (HGF) as:

$$\text{HGF} = \frac{D_p}{D_0}, \quad (1)$$

where D_p is the particle mobility diameter after humidification to 90 % RH, and D_0 is the mobility diameter measured under dry conditions (RH < 10 %).

The number size distribution of 3–1000 nm particles has been measured continuously at the SMEAR II station in Hyytiälä using a twin Differential Mobility Particle Sizer

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(DMPS) since January 1996 (Aalto et al., 2001). The non-refractory chemical composition and O : C of submicron aerosols were measured using a High Resolution Aerosol Mass Spectrometer (HR-AMS, Aerodyne Research Inc., Billerica, USA). Detailed descriptions of the instrument, measurement and data processing can be found in other publications (DeCarlo et al., 2006; Canagaratna et al., 2007). The O : C ratio was calculated from the relative mass concentrations of C and O in the whole ion fragments across the organic mass spectrum in the HR-AMS data (Aiken et al., 2007). Sulfuric acid and ELVOCs concentrations were measured with a Chemical Ionization Atmospheric Pressure interface Time-Of-Flight mass spectrometer (CI-API-TOF, Jokinen et al., 2012) that used nitrate as reagent ion. The sulfuric acid concentration was calculated from the HSO_4^- and $(\text{HNO}_3)\text{HSO}_4^-$ signals. All ELVOCs were detected as clusters with the nitrate ion, and the total ELVOC concentration was calculated by summing up all the detected organic compounds in a mass range 260–622 Th. In order to get the concentrations of ELVOCs or sulfuric acid, the signals were divided by the reagent ion signals and multiplied by the calibration constant. The instrument was calibrated with a calibration setup described in Kürten et al. (2012).

Concentrations of trace gases (e.g. SO_2 , O_3) and meteorological conditions (temperature and solar radiation in UV-B wavelengths) were also measured at the Hyytiälä station. Additional information regarding these instruments can be found in Aalto et al. (2001) and in Hari and Kulmala (2005). The data for these parameters were arithmetically averaged to a 30 min time resolution. All instrumentation and measured parameters used in this study are summarized in Table 1.

2.2 Particle composition data analysis

Atmospheric particles consist of a large number of different organics and inorganic compounds with different water affinities (Swietlicki et al., 2008). By applying the Zdanovskii–Stokes–Robinson (ZSR) relation (Zdanovskii, 1948; Stokes and Robinson, 1966), i.e. assuming volume additivity, the hygroscopic growth factor of such a mixture can be estimated from the growth factor of each component of the particles and their

individual volume fraction by obtaining their respective dry densities and mass fraction from HR-AMS data (Gysel et al., 2007; Meyer et al., 2009).

$$GF_m = \left(\sum_i \varepsilon_i \cdot GF_i^3 \right)^{1/3}, \quad (2)$$

Here, ε_i is the volume fraction of component i , GF_i is the respective growth factor of i , and GF_m is the growth factor for the mixture. The properties of the compounds that are present in the particles are summarized in Table 2. Saathoff et al. (2003) and Varutbangkul et al. (2006) obtained the growth factor of around 1.11 at the RH of 85 % for the secondary organic aerosol (SOA) formed by photo-oxidation of monoterpene and for oxygenated terpene SOA, which corresponds to the growth factor of about 1.17 at the RH of 90 %. Hence, an ensemble mean growth factor of the organics (GF_{org}) as 1.17 was chosen for organic compounds to initialize the comparison between HTDMA measured HGF and HR-AMS derived HGF based on the ZSR mixing rule.

3 Results and discussion

3.1 Overview of measurements

The temporal evolution of particle number size distribution from DMPS, mass concentrations and mass fractions of chemical species (sulfate, nitrate, ammonium and organics) in submicron particles from the HR-AMS and the hygroscopic growth factor probability density function (GF-PDF) for particles of dry sizes 15, 20, 30, 60, 100 and 145 nm during the measurement period are plotted in Fig. 1. Based on DMPS data (Fig. 1a) and the classification method introduced by Dal Maso et al. (2005), 22 days were classified as new particle formation events (10 days during April and 12 days during May) and 15 days as non-event.

On average, the water uptake of particles of all sizes (Fig. 1d–i) was higher and more variable before the middle of May, when the NPF events were observed to take

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from morning to afternoon compared with nucleation mode particles, which was likely because of the Kelvin effect. If the Kelvin effect is taken into account, the increase in the HGF of 15 and 20 nm particles was comparable with that of 100 nm-sized particles. A similar behavior has also been observed in previous studies at our site (Ehn et al., 2007; Hämeri et al., 2001).

The diel variation of the HGF was likely to be affected by both gas-phase chemistry (indirectly) and gas-to-particle partitioning (directly). More specifically, gas-phase concentration of condensable vapors, such as sulfuric acid that has a high water affinity and ELVOCs that are likely to be less hygroscopic despite their high O : C content, reached their maximum around noon (Fig. 3). Since the volume growth of newly-formed particles is caused by both sulfuric acid and organic vapor condensation (Riipinen et al., 2012), the increase of the HGF around noon was probably connected to the combination of, or competition between, the condensation of sulfuric acid and ELVOCs. Meanwhile, the ambient temperature was observed to increase from morning until afternoon (Fig. 3), which probably enhanced the evaporation of semi-volatile organics from the particle phase to the gas phase. The loss of these semi-volatile organics, which are less hygroscopic than sulfuric acid or sulfate in particles, may have also contributed to the enhancement in the hygroscopicity from morning until afternoon. Finally, the lifted boundary layer height during daytime, which mixed air masses of different histories, may also have influenced the daytime values of HGF.

A change in the chemical composition of an aerosol particle is the ultimate reason for the diurnal pattern of its HGF. Figure 4 shows the diurnal variation of the ratio of sulfate to organic material ($\text{SO}_4^{2-}/\text{Org}$) as well as the O : C ratio of the organic material in the particles obtained from the HR-AMS data. We observe that the $\text{SO}_4^{2-}/\text{Org}$ ratio started to increase in the late morning, causing the aerosol hygroscopicity to increase. The O : C ratio started to increase in the morning and peaked in the afternoon several hours later than the ratio $\text{SO}_4^{2-}/\text{Org}$ did. Since the hygroscopicity of organic particles has been observed to be larger for larger O : C ratios (Jimenez et al., 2009; Massoli et al., 2010; Duplissy et al., 2011), the increased O : C during the afternoon probably

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was higher than about 0.5, the chemically-derived values of HGF tended to be lower than the measured ones, while the opposite was true for the O : C ratios lower than about 0.5. This feature is strongly indicative of O : C dependence of the organic material hygroscopic properties in aerosol particles and suggests that the organic material with O : C > 0.5 is more hygroscopic than the average value of 1.17 used above.

Massoli et al. (2010) determined the hygroscopic growth factor of laboratory-generated secondary organic aerosol particles and found it to be a function of the oxidation level (O : C) of the organic materials. Their best-fit relation resulted in $HGF_{org} = (0.58 \pm 0.15) \cdot (O : C) + (0.85 \pm 0.08)$ at 90 % RH. We used this same O : C dependent growth factor as the input for the HGF of organic material in the accumulation mode particles. The resulting slope between the chemically-derived and measured HGF improved substantially, compared with assuming a constant HGF for the organic materials (Fig. 6, upper panel).

We also fitted the hygroscopic growth factor of organic material from our data by letting HGF_{org} vary as a function of measured O : C assuming a general formula of the form $HGF_{org} = a \cdot (O : C) + b$ for particles of each size, such that the sum of all residuals between each pair of measured and derived HGF became minimized (Sjogren et al., 2008). The corresponding results are shown for 100 and 145 nm particles in the lower panel of Fig. 6. Compared with the fit by Massoli et al. (2010), the slope of the relation between measured and derived HGF improved to a certain extent.

3.3.2 Organic–inorganic interactions

Besides the fact that the oxidation level of organic material can affect its hygroscopic properties, the interaction between inorganic and organic material can also influence (either reduce or enhance) the “apparent” HGF of organic matter in mixtures compared with their intrinsic HGF in the pure form (Sjogern et al., 2008; Suda et al., 2014; Hansen et al., 2015, 2015). In the Supplement (SI), Fig. S1 shows an illustration identical to Fig. 6, but colored according to the inorganic volume fraction. It is evident from Fig. S1,

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that also a parameterization based on the inorganic volume fraction would be able to improve the agreement between the AMS-predicted and measured HGF.

By considering both oxidation level and inorganic fraction, we further attempted to improve the agreement between predicted and measured HGF. We used a three-free parameterization scheme for 100 and 145 nm particles as the same fitting procedure as discussed above: $HGF_{org} = ([a \cdot (O : C)] + b)(1 + [c \cdot \varepsilon_{in}])$, where ε_{in} stands for the volume fraction of the total inorganics. The results, shown in the lower panel of Fig. 7, improved the slope of the correlation only slightly. This may be because the relation between the “apparent” growth factor of organics and inorganic volume fraction might be non-linear, non-addictive and species-dependent, thus making it complicated to unequivocally predict this growth factor (Hansen et al., 2015, manuscript in preparation). Although Fig. S1 suggests a relation between ε_{in} and HGF_{org} , we in fact found that there was a clear correlation between the O : C ratio of the organics and ε_{in} as shown in Fig. S2 in the SI. Therefore we cannot unambiguously determine whether the HGF_{org} dependence was due to O : C or ε_{in} . For reference, we also fitted the scaling factor from the inorganic volume fraction to the O : C dependent equation of Massoli et al. (2010) (upper panels in Fig. 7). However, the resulting slope was not improved, in addition to which we obtained a negative scaling factor (−0.3) from the inorganic fraction to HGF of organics for 100 nm particles and a positive one for 145 nm particles.

The above findings illustrate that it is highly complex to quantify the influence of the inorganic fraction on the HGF of organic matter. However, one needs to be careful with solute–solute interactions in deriving the additive HGF of an organic-dominated aerosol consisting of a highly complex mixture of some sparingly soluble organics (Hodas et al., 2015; Pajunoja et al., 2015; Virtanen et al., 2010), since the ZSR mixing rule assumes there is no solute–solute interactions. These sparingly soluble organics may undergo further dissolution when there are a certain amount of inorganic compounds exist in the solution (Suda et al., 2014) and thus these organics may appear to have a higher hygroscopic growth factor than in their pure form.

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3.4 Relation between the measured HGF and condensable vapor concentrations

Since the HGF of aerosol particles showed a clear diel variation, atmospheric photochemistry is very likely to play an important role. Vapor condensation from the gas phase to particles is the most important driver of the growth of atmospheric ultrafine aerosol particles, directly affecting the hygroscopicity of these particles. H_2SO_4 and ELVOCs are the major condensing vapor species at our measurement site (Kulmala et al., 2013; Ehn et al., 2014). We selected data during the time periods when particles originated from the regional NPF events in order to study the effect of gas phase composition on nucleation mode particle hygroscopicity.

Figure 8 shows the relation between the HGF and the measured gaseous sulfuric acid concentration for different-sized particles during NPF events, along with a linear fit to these data. We can see that these two quantities correlated moderately for 15 nm ($R^2 = 0.33$) and 20 nm ($R^2 = 0.39$) particles, but not for larger particles. This kind of behavior is expected, since the smaller the particles are, the larger the relative contribution from the immediate vapor condensation they will have and thus the more rapidly their bulk chemical composition responds to changing concentration of condensable vapors.

Besides H_2SO_4 , organic compounds, especially ELVOCs, are also considered as important condensing vapors to enhance new particle growth (Kulmala et al., 2013; Ehn et al., 2014). Therefore, we also explored the relationship between the measured HGF and ELVOC concentration, but no correlation between these quantities was observed. This is possibly because the hygroscopic properties of organics are expected to vary considerably from compound to compound (Kanakidou et al., 2005). Even though ELVOCs are likely to be more hygroscopic than many other types of organic vapors, their HGF is still expected to be much lower than that of H_2SO_4 , and therefore the net effect on HGF from ELVOC condensation will be less prominent. However, if we limited our data range to high ozone concentrations (higher than 45 ppb), the corre-

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lation coefficient between HGF and ELVOC concentration became relatively high for 15 nm ($R^2 = 0.46$), 20 nm ($R^2 = 0.42$), 30 nm ($R^2 = 0.41$) and 60 nm ($R^2 = 0.36$) particles (Fig. S3). It is hard to speculate over the reason for this behavior, as so little is still known about ELVOCs. However, the level of oxidant concentration and the relative roles of ozone and OH might be of importance for the ultimate hygroscopicity of ELVOCs. Aimed laboratory experiments should be attempted in the future in order to verify this finding.

4 Summary and conclusions

The hygroscopicity of nucleation, Aitken and accumulation mode particles in a boreal environment was studied. Concurrently, the non-size segregated aerosol chemical composition was also determined. The HGF of particles of all sizes showed a clear diel variation, with an increase in the HGF from morning until afternoon as a result of gas-phase chemistry producing condensing vapors and temperature dependent gas-to-particle partitioning. In addition to these, radiation/temperature-driven chemistry taking place in the aerosol phase and entrainment of particles from above the mixed layer during daytime may also have influenced the diel variation of the HGF.

The comparison between the HTDMA-measured and AMS-derived HGF showed a good agreement, especially for larger particles. This comparison also clearly indicated that the HGF of organic material in particles varies with the oxidation level of this material and possibly also due to its interaction with the inorganic compounds in particles. We found a similar dependence between the HGF of organic compounds and oxidation level as that reported by Massoli et al. (2010). The effect of O : C and volume fraction of inorganic species (ε_{in}) on the apparent HGF of organic compounds resulted in the following equation for 100 nm particles: $HGF_{org} = ([0.6 \cdot O : C] + 0.7) \cdot (1 + [0.2 \cdot \varepsilon_{in}])$. However, including the effect of inorganic compounds improved the closure between the measured and chemically-derived values of HGF only slightly. More lab work is needed to examine this effect thoroughly.

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Table 1. List of instrumentation and measured parameters that were used in this study.

Instruments	Measured Parameters
nano-HTDMA	Hygroscopic growth factor (HGF) of 15, 20 nm particles
HTDMA	Hygroscopic growth factor (HGF) of 30, 60, 100, 145 nm particles
DMPS	Particle size distribution 3–3000 nm
High resolution Aerosol Mass Spectrometer (HR-AMS)	Chemical composition of non-refractory material and O : C of submicron particles
Chemical Ionization Atmospheric Pressure interface Time-Of-Flight mass spectrometer (CI-API-TOF)	Sulfuric acid and extremely low volatile organic compounds concentration in gas phase
TEI 43 CTL fluorescence analyzer TEI 49C UV-light absorption analyzer (Thermo Fisher Scientific, Waltham, MA, USA)	SO ₂ O ₃
Pyranometers	Solar radiation in the UV-B wavelengths

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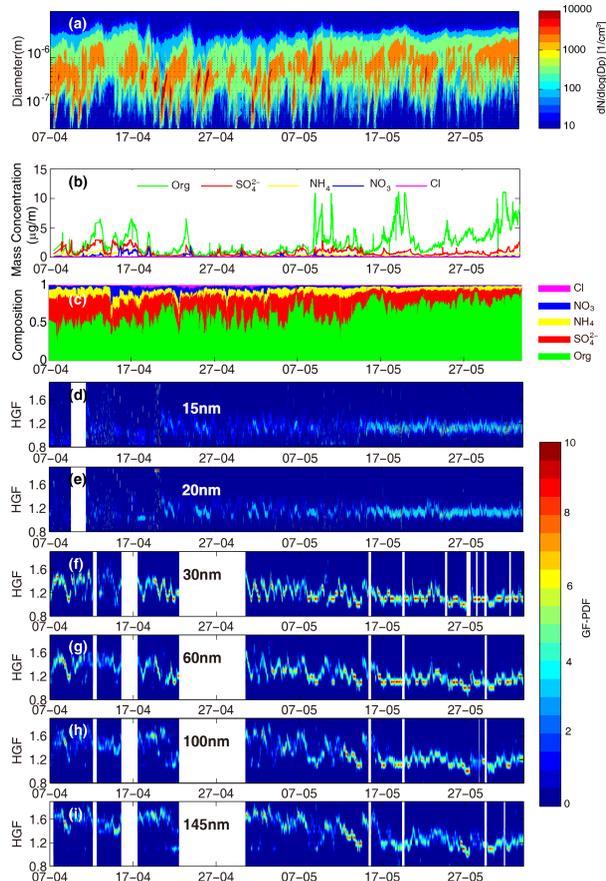


Figure 1. (a) Time series of particle number size distribution using DMPS. (b and c) Time series of mass concentrations and mass fractions of chemical species (sulfate, nitrate, ammonium and organics) in submicron particles from HR-AMS. (d–i) Time evolution of hygroscopic growth factor distribution for 15, 20, 30, 60, 100 and 145 nm particles using HTDMA.

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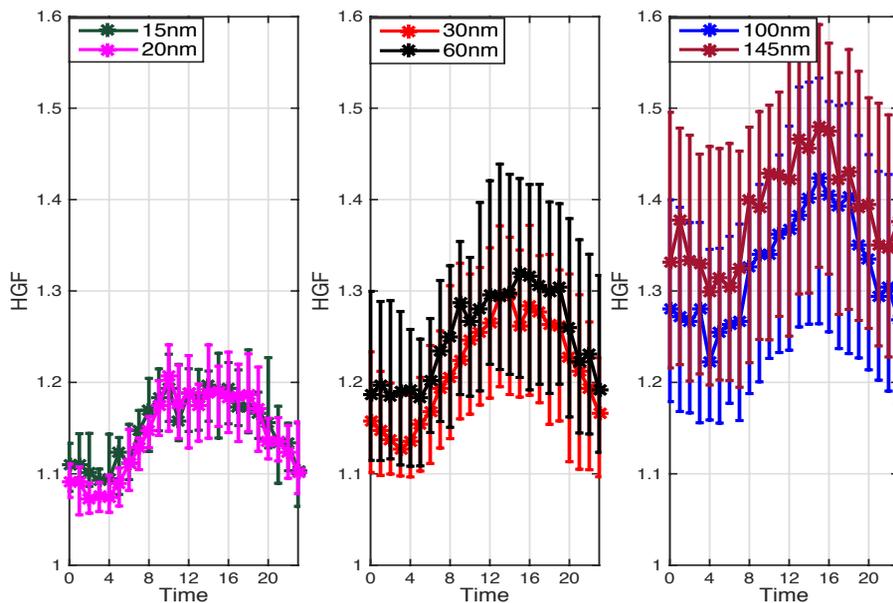


Figure 2. Diurnal variation of hygroscopic growth factor of particles with size of 15, 20, 30, 60, 100 and 145 nm during the measurement period.

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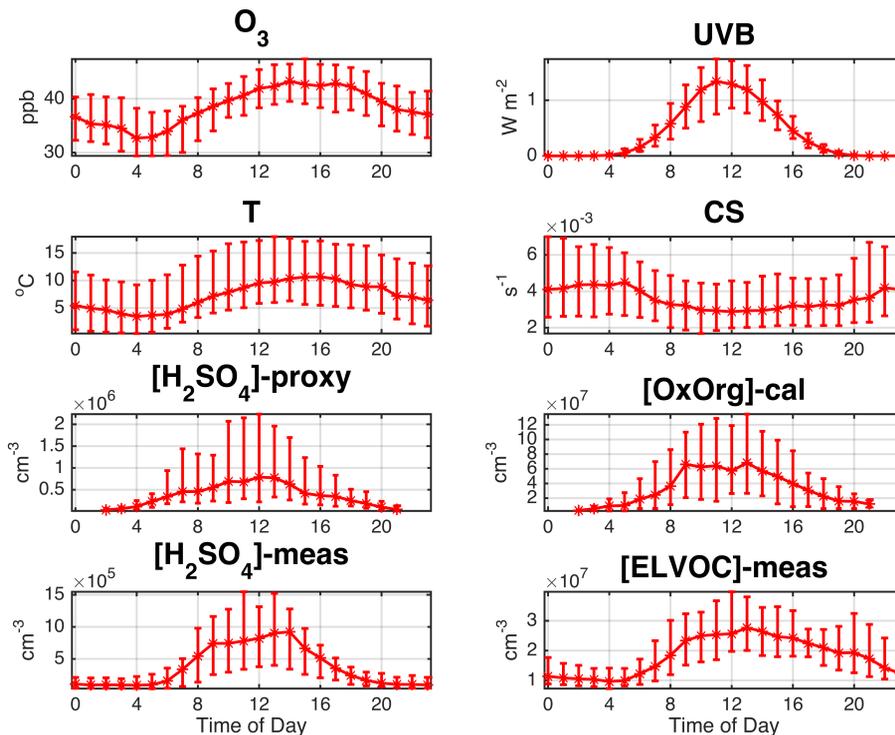


Figure 3. Diurnal variation of O₃, UVB, temperature, condensation sink (CS) and calculated sulfuric acid proxy and oxidation organics from monoterpene according to Nieminen et al. (2014) as well as the measured sulfuric acid and ELVOCs concentration in gas phase.

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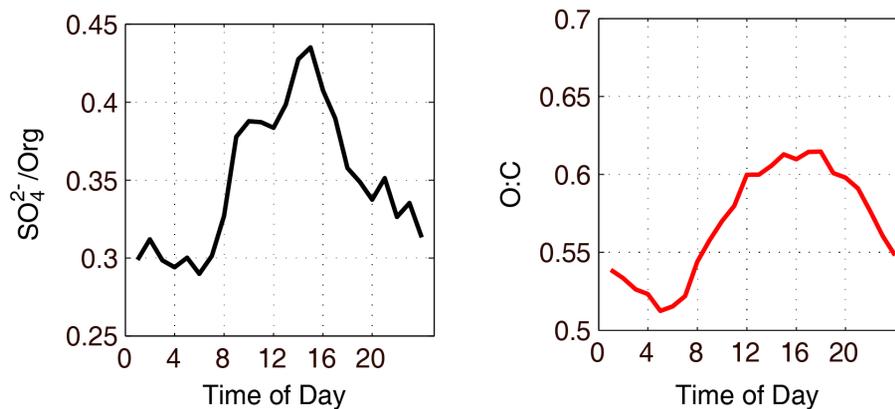


Figure 4. Diurnal variation of $\text{SO}_4^{2-}/\text{Org}$, O:C of non-size segregated particles.

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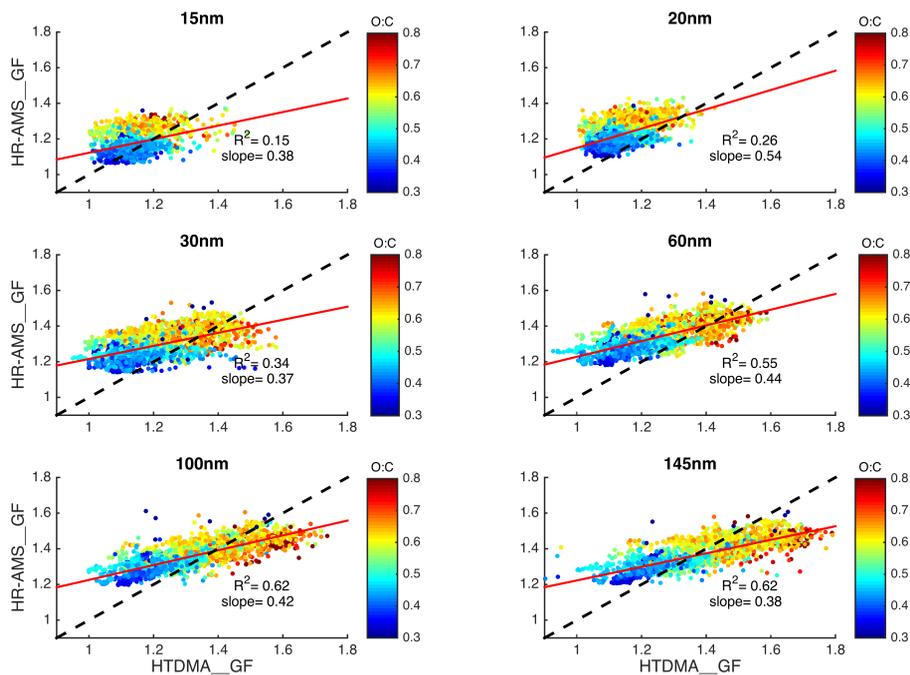


Figure 5. Comparison of HR-AMS-derived HGF with HTDMA-measured HGF of different-sized particles.

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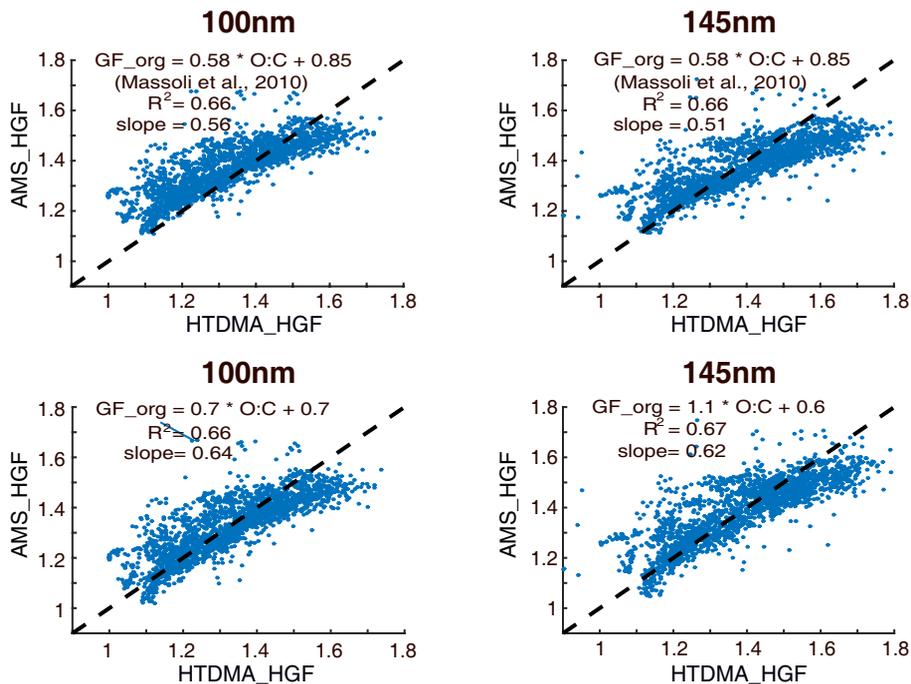


Figure 6. Comparison between AMS derived HGF with measured HGF when taking into account the influence of oxidation level of the organics on GF, with upper panels using the relation determined by Massoli et al. (2010), and lower panels by fitting the equation $GF = a \cdot O : C + b$ into our data.

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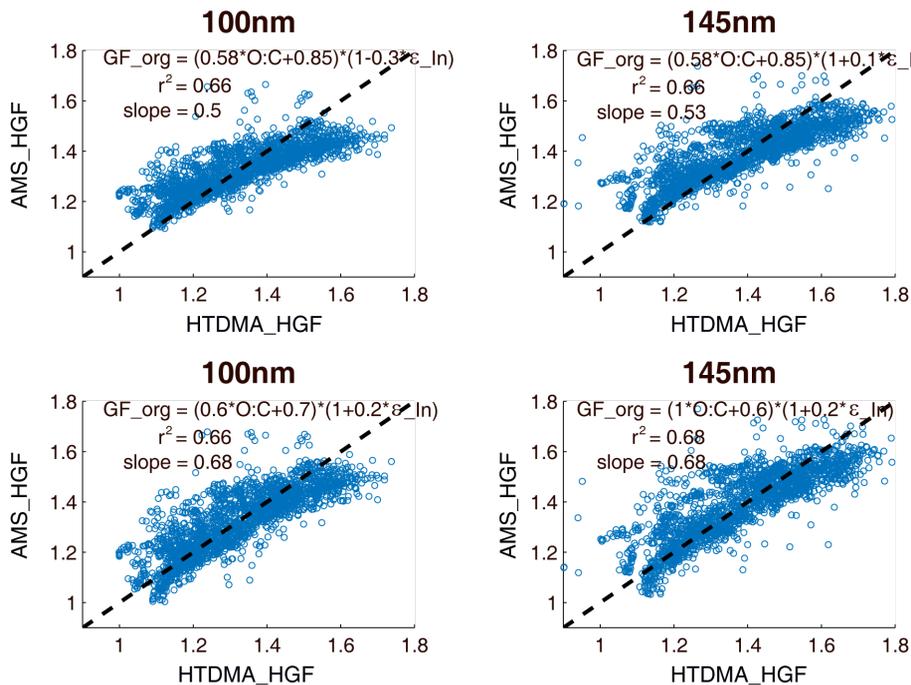


Figure 7. Comparison between AMS derived HGF with measured HGF when taking into account of both oxidation level and inorganic volume fraction on GF of the organics.

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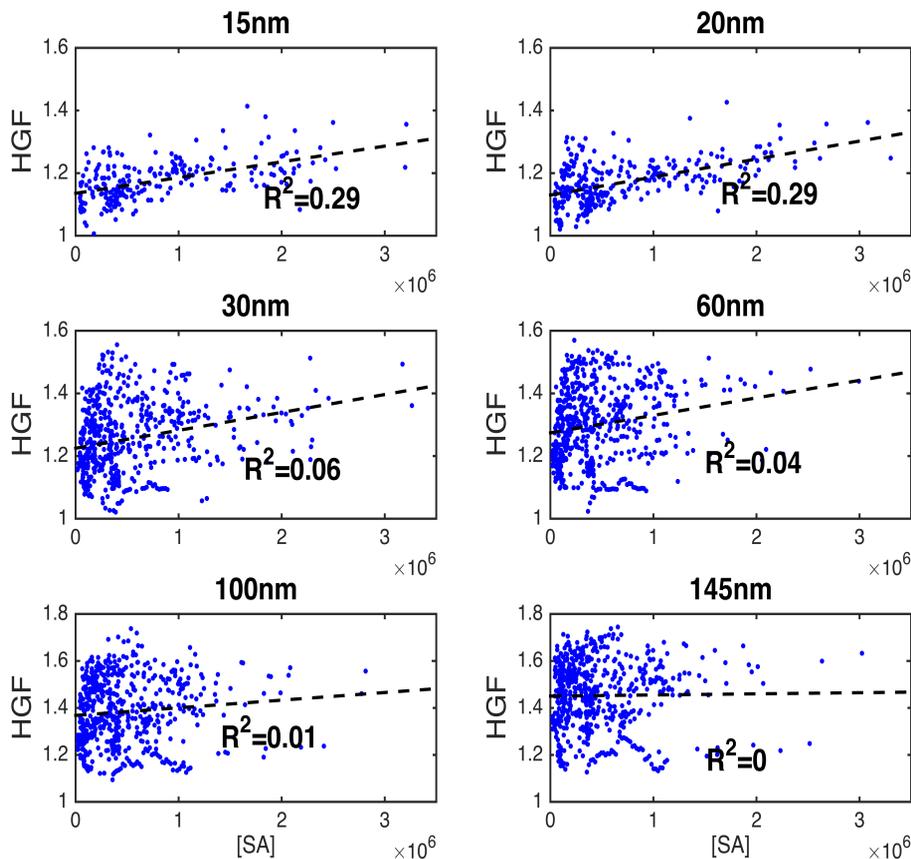


Figure 8. HGF of 15, 20, 30, 60, 100 and 145 nm particles with sulfuric acid concentration in gas phase during the time of NPF.

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