

**Long-term volatility measurements of atmospheric aerosol in Hyytiälä**

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**Long-term volatility measurements of submicron atmospheric aerosol in Hyytiälä, Finland**

**S. A. K. Häkkinen<sup>1</sup>, M. Äijälä<sup>1</sup>, K. Lehtipalo<sup>1</sup>, H. Junninen<sup>1</sup>, J. Backman<sup>1</sup>, A. Virkkula<sup>1,2</sup>, T. Nieminen<sup>1</sup>, M. Vestenius<sup>2</sup>, H. Hakola<sup>2</sup>, M. Ehn<sup>3</sup>, D. R. Worsnop<sup>1,4</sup>, M. Kulmala<sup>1</sup>, T. Petäjä<sup>1</sup>, and I. Riipinen<sup>1,5</sup>**

<sup>1</sup>Department of Physics, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland

<sup>2</sup>Finnish Meteorological Institute, Erik Palménin aukio 1, 00560 Helsinki, Finland

<sup>3</sup>Institute for Energy and Climate Research (IEK-8), Forschungszentrum Jülich, 52425 Jülich, Germany

<sup>4</sup>Aerodyne Research, Inc., Billerica, Massachusetts, USA

<sup>5</sup>Department of Applied Environmental Science and Bert Bolin Centre for Climate Research, Stockholm University, 10691 Stockholm, Sweden

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Correspondence to: S. A. K. Häkkinen (silja.hakkinen@helsinki.fi)

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## Abstract

The volatility of atmospheric 20–500 nm aerosol particles was investigated at a boreal forest site in Hyytiälä, Finland. Measurements were performed continuously between January 2008 and May 2010. The ambient aerosol sample was heated step-wise to six temperatures ranging from 80 °C to 280 °C and the total mass concentration of aerosol particles was determined from the measured particle number size distributions before and after heating assuming particle density of 1.6 gcm<sup>-3</sup>. On average 19 % of the total aerosol mass stayed in the condensed phase even after heating to 280 °C. The observed non-volatile residual at 280 °C had a seasonal pattern; during winter the aerosol mass fraction remaining after heating was the highest and during summer the lowest. Black carbon concentrations correlated positively with the non-volatile fraction of the aerosol, but could not explain the presence of the non-volatile material completely: most of the time a notable fraction of the non-volatile residual was something else than black carbon. Using additional information on ambient meteorological conditions and trajectories, and results from an Aerodyne aerosol mass spectrometer (AMS), the chemical composition of the non-volatile residual and its seasonal behavior was further examined. During winter and spring months the non-volatile mass fraction had a marked positive linear correlation with pollutant trace gases, such as CO, SO<sub>2</sub> and NO<sub>x</sub>. This suggests an anthropogenic influence on the non-volatile fraction of the aerosol in winter and spring. The anthropogenic effect on the formation of the low-volatility material was furthermore supported by observed correlation between the non-volatile residual and the mass fractions of poly-aromatic hydrocarbons (PAHs) sampled simultaneously at the site. During the fall the aerosol particles had relatively more non-volatile material in them when the aerosol mass fractions of organic nitrate and organics in the AMS data were high, and when the measurement site was influenced by clean air masses passing over the forest. Thus, the existence of very low volatile organic nitrates in the aerosol phase can be speculated.

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## 1 Introduction

Aerosol particles, i.e. liquid or solid airborne particles, are ubiquitous in the earth's atmosphere. These particles affect our lives by reducing visibility (Cabada et al., 2004), causing adverse health effects (Davidson et al., 2005; Nel, 2005) and affecting the climate (Lohmann and Feichter, 2005; IPCC 2007). Aerosol particles reflect and absorb incoming solar radiation (Bohren and Huffman, 1983) and affect water circulation, precipitation and the earth's radiative balance via cloud formation (Ramanathan et al., 2001; Rosenfeld et al., 2008; Spracklen et al., 2008). Aerosol particles are either directly emitted into the atmosphere in the condensed or solid phase, for example pollen from vegetation or soot from combustion, or formed in the atmosphere from ambient vapors (Kulmala et al., 2004).

Volatility, i.e. the tendency of a molecule to evaporate from the aerosol phase, as compared with its flux to the particles, is among the most important factors determining if the molecule accumulates into the aerosol phase. Atmospheric aerosols are typically complex mixture of inorganic and organic compounds. The identities and thermodynamic properties of inorganic aerosols are relatively well-known – at least compared with the organic fraction of atmospheric aerosol. Ambient air contains thousands of organic compounds that have complex structures and formation mechanisms (Goldstein and Galbally, 2007). A large number of these compounds still remain unidentified. Depending on the location and season, 20–90 % of the aerosol mass consists of organics (Kanakidou et al., 2005; Zhang et al., 2007; Jimenez et al., 2009). A large fraction of the organics found in aerosol particles are semi-volatile under atmospheric conditions (Robinson et al., 2007), meaning that they can be present in both gaseous and particulate phases. In order to yield reliable estimates for the total aerosol budget and to understand how the semi-volatile compounds affect the formation and fate of atmospheric aerosols, the volatility of the aerosol constituents needs to be known. Information on aerosol volatility also gives indirect indications of the aerosol composition.

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The volatility of atmospherically relevant aerosol particles has recently been investigated extensively both in the laboratory (An et al., 2007; Faulhaber et al., 2009; Cappa and Wilson, 2011; Saleh et al., 2011) and in the field. Field measurements have been performed in various environments: in rural and urban background areas (Wehner et al., 2005; Ehn et al., 2007; Lee et al., 2010) as well as in polluted cities and roadsides (Wehner et al., 2004; Huffman et al. 2009; Birmili et al., 2010; Tiitta et al., 2010). In these studies, the general principle for measuring aerosol volatility has been similar: aerosol samples have been heated in a thermodenuder and the size (diameter, volume or mass) of aerosol particles determined before and after heating. Thermodenuders (TD) come in different designs, and the detected volatility depends on the temperature, residence time and total aerosol loadings in the TD (Cappa et al., 2010; Riipinen et al., 2010; Saleh et al., 2011; Fuentes et al., 2012) – making direct quantitative comparison of different volatility measurements challenging. One of the challenging aspects of the interpretation of TD data is the fact that time that it takes for the aerosol to reach equilibrium in a TD depends on the aerosol properties (Cappa et al., 2010; Riipinen et al., 2010; Saleh et al. 2011; Fuentes et al., 2012). This means that the ambient/laboratory generated aerosol does not necessarily achieve equilibrium in the currently available TDs – depending on the aerosol residence time in the TD (An et al., 2007; Riipinen et al., 2010; Saleh et al., 2011). Commercially available thermodenuders (TOPAS GmbH by TSI Inc, MN; Dekati TD by Dekati Ltd, Tampere, Finland) and the ones developed by Burtscher et al. (2001) and Wehner et al. (2002) have residence times of a few seconds. For measurement of semi-volatile organics TDs with longer residence times have been developed recently (An et al., 2007; Huffman et al., 2008). The TD used in this study is the same as described in Ehn et al. (2007) with a maximum heating temperature of 280 °C and a residence time around a second.

Atmospheric aerosols are typically a mixture of compounds with different volatilities. For individual compounds at a fixed residence time, the evaporation inside a thermodenuder typically happens around a specific temperature, while for complex atmospheric mixtures the temperature-dependence of the aerosol remaining after heating

is smoother (e.g., Riipinen et al., 2010). A large fraction of atmospheric organics and many inorganic aerosol compounds evaporate at temperatures below 300 °C (Turpin et al., 2000; Raatikainen et al., 2010), for example ammonium sulfate at around 200 °C and ammonium nitrate at around 60–75 °C even with residence times less than a second (Johnson et al., 2004; Philippin et al., 2004; Villani et al., 2007). However, some compounds, such as black carbon (BC), sea salt and crustal material, are not volatilized even at 300 °C.

It has been observed that almost all submicron aerosol particles, even nucleated particles around 3–60 nm in diameter, have a non-volatile residual that does not evaporate at temperatures around 280–300 °C in similar setups as the one used in this study (Wehner et al., 2005; Ehn et al., 2007; Birmili et al., 2010). In polluted areas, the observed non-volatile aerosol material has been found to have a clear correlation with light-absorbing aerosol (Birmili et al., 2010). According to Kalberer et al. (2004), given enough time, some atmospheric organic compounds may form low-volatile polymers. Recently Smith et al. (2010) reported that aminium salt formation takes place in atmospheric nanoparticles and that these low-volatile salts contribute significantly to the growth of nanoparticles in various environments, also in boreal forests. Barsanti et al. (2009) suggested that amines may have a noticeable role in the formation of organic salts. All the aforementioned processes may be linked to the observations of low-volatility material in small atmospheric particles.

The evaporation properties of atmospheric submicron aerosol particles were investigated in this study by examining the mass reduction of aerosols due to evaporation at six temperatures ranging from 80 °C to 280 °C. Measurements were performed continuously during a period of two and a half years (January 2008 to May 2010) at the boreal forest site of Hyytiälä, Finland. The aerosol sample was heated and the aerosol size distribution before and after the heating were measured and compared. In order to interpret the evaporation patterns of submicron aerosol particles, the following data sets were included in the analysis: black carbon measurements, meteorological data and trajectory analysis as well as data from an aerosol mass spectrometer. Our main aims

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were to (1) determine the temperature dependence of aerosol volatility in Hyytiälä, (2) investigate the seasonality of aerosol volatility and its connection to other atmospheric variables, and (3) examine the chemical composition of the observed non-volatile residual found in atmospheric fine particles.

## 2 Materials and methods

### 2.1 Measurement site

Measurements for this study were performed at a rural background measurement station SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations II) located in Hyytiälä (61°51' N, 24°17' E, 181 m a.s.l.), in Southern Finland (Vesala et al., 1998; Kulmala et al., 2001; Hari and Kulmala, 2005). The SMEAR II station is surrounded by 48 yr old boreal conifer forest that covers an area spanning tens of kilometers to North and North-East. The nearest large cities are Tampere (around 60 km to South-West, 213 000 inhabitants) and Jyväskylä (around 100 km to north-east, 131 000 inhabitants). Ambient meteorological conditions such as temperature, relative humidity, solar radiation, wind speed and direction as well as concentrations of several trace gases, such as carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>), are measured continuously at the station. Also the fluxes of compounds such as water, ozone and several volatile organics are measured. In addition, measurements of aerosol properties such as aerosol particle number size distributions have been ongoing at the station continuously since 1996 (Mäkelä et al., 1997).

### 2.2 Instrumentation

#### 2.2.1 DMPS

The ambient aerosol number size distribution was measured with a twin-DMPS system (Aalto et al., 2001) consisting of two separate DMPSs (Hoppel, 1978; Winklmayr et al.,

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1991). The first DMPS determines the size distribution of small particles, 3–50 nm in diameter, and the other measures larger particles, 15 nm–1  $\mu$ m in size. Both DMPSs sheath flows are maintained using closed loop circulation (Jokinen and Mäkelä, 1997) and at a relative humidity below 20 %. Condensation particle counters (CPC, Stolzenburg and McMurry, 1991) used for particle counting are TSI-3025 and TSI-3010 (TSI Inc.), respectively. The time resolution of the combined system is ten minutes.

### 2.2.2 VDMPS

The evaporation of submicron aerosol particles was investigated using a volatility differential mobility particle sizer (VDMPS), which consists of two separate parts, a thermodenuder (TD, Ehn et al., 2007) and a DMPS. The thermodenuder heats up the sample air, after which the remaining aerosol material is directed to the DMPS system. In this study the term “non-volatile” refers to this material not evaporated in the oven. The heating temperature can be either held constant or scanned over several temperatures. The VDMPS used in this study measured the number size distribution of non-volatile particles of 20–500 nm in diameter. A TSI model 3010 CPC was used for particle counting. The thermodenuder was a 50 cm long tube fabricated from stainless steel with outer radius of 10 mm. The residence time, i.e. the time the aerosol sample spends in the oven, was around one second and the time resolution of the VDMPS was ten minutes. No absorptive material was used in the thermodenuder. The VDMPS and DMPS systems were located in the same measurement cottage and they used the same aerosol inlet (PM<sub>1,0</sub>).

The VDMPS was temperature-scanning during 1 January 2008 to 27 April 2009. The TD heated the aerosol sample to six temperatures, 80 °C, 120 °C, 160 °C, 200 °C, 240 °C and 280 °C, and data were acquired for each temperature with a time resolution of about one hour. From July 2009 onwards the aerosol sample was heated to a constant temperature, 280 °C (Fig. 1). Total data coverage for the measurement period (1 January 2008 to 24 May 2010) was about 75 %.

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The major loss processes in the heating tube are caused by thermophoresis and Brownian diffusion of small particles (Wehner et al., 2002). Due to these losses, VDMPs raw data underestimates the number concentration of submicron particles. Errors in particle number concentrations were corrected using experimentally derived particle losses presented by Ehn et al. (2007). The losses for aerosol particles above 15 nm in diameter were observed to be around 20 % of the total particle number concentration when heated to 280 °C. The same correction fit for particle penetration through the oven was used for all the six heating temperatures. The error resulting from this has been estimated to be only a few percent (Wehner et al., 2002).

### 2.2.3 Aethalometer

An aethalometer (Hansen et al., 1982) was used to measure the mass concentration of black carbon using a PM<sub>2.5</sub> inlet. In the data analysis it is assumed that black carbon mass concentration and light attenuation are linearly related, and black carbon mass is calculated from the change rate of light transmission through a filter at seven wavelengths. However, the presence of other light-scattering and absorbing particles, such as sulfate or brown carbon, on the filter can cause non-linearities in the relationship between light transmission and BC concentration (Reid et al., 1998; Bond et al., 1999). The aethalometer signal needs to be corrected for these effects (e.g., Weingartner et al., 2003; Arnott et al., 2005; Andreae and Gelencsér, 2006; Virkkula et al., 2007). The errors caused by brown carbon can be reduced by using higher light wavelengths, most preferably 880 nm (Weingartner et al., 2003).

In this study aethalometer data was corrected using the approach introduced by Weingartner et al. (2003), the resulting black carbon concentrations ( $M_{BC}$ ) being defined as

$$M_{BC} = \frac{M_{BC,raw} \sigma_{abs,0}(\lambda)}{\sigma_{abs}(\lambda) C(\lambda) R(ATN)}, \quad (1)$$

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where  $M_{BC,raw}$  is the black carbon concentration measured with an aethalometer (non-corrected),  $\sigma_{abs,0}$  is the wavelength-dependent absorption mass cross-section used by the manufacturer of the aethalometer,  $\sigma_{abs}$  is the absorption mass cross-section calculated using the absorption mass cross-section of MAAP (Multiangle Absorption Photometry, Petzold and Schönlinner, 2004) as a reference point ( $6.6 \text{ m}^2 \text{ g}^{-1}$  at 637 nm), and  $C$  and  $R(ATN)$  the calibration parameters. The calibration factor  $R(ATN)$  can be written as

$$R(ATN) = \left( \frac{1}{a(1 - \omega_0) + 1} - 1 \right) \frac{\ln(ATN) - \ln(10\%)}{\ln(50\%) - \ln(10\%)} + 1 \quad (2)$$

where  $a$  is 0.85 at 660 nm (Weingartner et al., 2003),  $ATN$  is light attenuation through the filter and  $\omega_0$  is a single-scattering albedo which can be derived from particle absorption and scattering measurements. Aerosol light scattering measurement data from a nephelometer (Anderson et al., 1996) was available for the period of interest. Values for absorption mass cross-sections and  $C$  factors are presented in Table 1. The  $C$  factors were calculated by using the average  $C$  value determined from Hohenpeisenberg MAAP-data by Collaud-Coen et al. (2010). Wavelength dependence of the  $C$  factor was gained from Arnott et al. (2005). Corrected black carbon data at 880 nm wavelength with a time resolution of five minutes was used in the analysis.

### 2.2.4 AMS

The Aerosol Mass Spectrometer (AMS) used in this study was an Aerodyne Compact Time-of-Flight Aerosol Mass Spectrometer (C-ToF AMS, Aerodyne Research Inc., Billerica, US), which measures the chemical composition of submicron aerosol particles (Jayne et al., 2000; Drewnick et al., 2005).

A C-ToF AMS features an aerodynamic lens for concentrating the particles into a narrow beam, a particle time-of-flight (PToF) chamber for particle size distribution measurement, thermal vaporization of the sample particles in a 600 °C tungsten oven, 70 eV electron impact ionization (EI) of the produced vapor, and a compact ion-time-of-

fight mass spectrometer (C-ToF MS) to obtain a mass spectrum of the ions. The “hard” EI ionization method provides quantitative, yet highly fragmented ion spectra from the parent molecule.

The mass spectra of ions is interpreted, using knowledge of EI molecular fragmentation patterns, to assign the aerosol total mass loading into subgroups of different chemical composition: sulfates, organics, nitrates, ammonium and chlorides. The individual mass-per-charge signals and their relative ratios can be used to further characterize the composition of the sample aerosol. The final data is scaled with a collection efficiency factor (CE) to compensate for losses inside the AMS.

Because of the thermal vaporization method, the AMS does not quantitatively see “refractory compounds”, i.e. those that are not vaporized below 600 °C, such as sea salt and black carbon. Particulate water is also not quantitatively measured and is not included in the AMS-measured total aerosol mass.

Data used in this study was collected during two month-long AMS-campaigns: one in late spring 2008 and one in early fall 2008 (Fig. 1).

### 2.2.5 Meteorological parameters and PAH-data

Meteorological parameters as well as mass concentrations of polycyclic aromatic hydrocarbons (PAH) were also measured at SMEAR II. Ambient temperature, relative humidity, radiation and trace gas concentrations were continuously recorded at a 70-m-tall mast at different heights. In this study the radiation data was acquired from the height of 18 m whereas other meteorological data was from a lower measurement stage (4.2 m). All meteorological data was averaged over 30 min. Mass concentrations of PAHs were analyzed from filter samples (PM<sub>10</sub>) in Hyytiälä during 2008 (see Vestenius et al., 2011).

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### 3 Data analysis

#### 3.1 Volume fraction remaining

The volatility of 20–500 nm particles was studied by comparing the ambient and heated particle number and volume size distributions measured by the DMPS and VDMPS, respectively. The particle volume size distribution was calculated from number size distribution data assuming spherical particles. 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 ( $V_{\text{tot,DMPS}}$ ). Volume fraction remaining (VFR) can be written as

$$\text{VFR} = \frac{V_{\text{tot,VDMPS}}}{V_{\text{tot,DMPS}}}. \quad (3)$$

In this study VFR is equivalent to the aerosol mass fraction remaining (MFR) because particle density was assumed to be constant ( $1.6 \text{ g cm}^{-3}$ ).

#### 3.2 Black carbon fraction

The maximum mass fraction of black carbon in aerosol (black carbon fraction, BCF) was defined as

$$\text{BCF} = \frac{M_{\text{BC}}}{M_{\text{tot,DMPS}}}, \quad (4)$$

where  $M_{\text{BC}}$  is the corrected mass concentration of black carbon from the aethalometer data and  $M_{\text{tot,DMPS}}$  is the total mass concentration of ambient 20–500 nm aerosol as determined from the DMPS data. In order to investigate the minimum contribution of non-BC material to the MFR, black carbon mass was removed from the observed non-volatile residual. Mass fraction remaining without the effect of black carbon is then

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defined as follows

$$\text{MFR}_{\text{non-BC}} = \text{MFR} - \text{BCF} = \frac{M_{\text{tot, VDMPS}} - M_{\text{BC}}}{M_{\text{tot, DMPS}}}. \quad (5)$$

The aethalometer used for black carbon measurements determined the black carbon mass concentration of  $\text{PM}_{2.5}$  particles. The BCF, however, was calculated assuming that all the black carbon mass is distributed to particles smaller than 500 nm.  $\text{MFR}_{\text{non-BC}}$  thus provides a conservative estimate of the maximum BCF in the 20–500 nm aerosols, as probably a significant portion of the BC mass is in bigger, 500–2500 nm, particles.

### 3.3 Air mass trajectories

In order to investigate the relationship between atmospheric aerosol volatility and air mass properties, the air mass origin was determined with trajectory analysis. Back trajectories of air masses arriving to Hyttiälä were modeled with HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory model, Draxler and Hess, 1997), which runs via internet (Draxler and Rolph, 2011). In this study, we used hourly air mass trajectories at a 100 m arrival height above ground level. The trajectories were calculated 96 h backwards in time. In addition to the trajectories, HYSPLIT gives information on parameters such as the mixing (boundary) layer height. The average direction of the arriving air mass was determined using trajectories that were below twofold the mixing layer height.

## 4 Results and discussion

### 4.1 Ambient and non-volatile number and volume size distributions

Figure 2 shows the median ambient and heated (280 °C) number size distributions for winter (December–February), spring (March–May), summer (June–August) and fall

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(September–November). The median ambient number size distributions were bi- or tri-modal with Aitken and accumulation modes. The highest number concentrations were seen in the Aitken mode, and during summer and spring months the total particle number concentration was the highest – in agreement with previous observations (Dal Maso et al., 2005). Also nucleation mode (3–25 nm) particles are frequently observed in Hyytiälä. This mode cannot be clearly seen in Fig. 2 because of the averaging, as it has a distinct diurnal pattern. However, when examining aerosol number size distributions for days and nights separately, the nucleation mode was visible in day time number size distributions, especially during spring and fall months.

The median heated number size distributions were monomodal (Fig. 2). In general, the particle modes moved towards smaller sizes when heated, and the bimodal structure disappeared. Aerosol total number concentration after heating was noticeably lower than in the ambient air. There are at least two possible reasons for this, after the temperature-dependent losses are accounted for. First, it is likely that a large fraction of the smallest aerosols evaporate below the detection limit of the VDMPS system (20 nm). Second, the aerosol might be an external mixture of more and less volatile components, in which case some of the particles evaporate while others remain close to their original size. Based on earlier studies (Ehn et al., 2007) the former is more probable.

Figure 3 illustrates the median volume size distributions of particles in ambient conditions and after heating to 280 °C during different seasons. While the ambient and heated number and volume size distributions for the winter, spring and fall look relatively similar, the corresponding distributions for summer differ from the other seasons. During the summer the distinction between the ambient Aitken and accumulation modes is less clear and the average diameter of the heated aerosol smaller than during the other seasons.

## 4.2 Temperature-dependence of MFR

Figure 4 shows the time series of the MFR at different TD temperatures. The aerosol particles were more volatile during summer, whereas the highest values of the MFR occurred during winter months (Table 2). On average 19% of the aerosol mass was left after heating the aerosol to 280 °C. During winter and fall periods, the temporal variation of the MFR values was relatively similar independent on the TD temperature. During the spring and summer months, however, the MFRs below 200 °C seemed to show an increasing trend while the MFRs at higher temperatures were decreasing. This indicates an increase in the relative fraction of aerosol components that volatilize around 200 °C during the spring, as compared with the other months. These observations are in line with the results reported by Raatikainen et al. (2010), who studied the connection between aerosol composition and volatility during spring 2005 in Hyytiälä. They noted an anticorrelation between the MFR values between 50–150 °C and 150–280 °C, and concluded that the material volatilizing around 150 °C was mainly organic, while the mass remaining at the higher temperatures consisted of a mixture of organic and inorganic compounds. The MFR was generally slightly higher at night (0.21) as compared to daytime values (0.19).

Figure 5 shows the temperature dependence of the MFR of this study and a selection of other relevant studies. Our results are in qualitative agreement with the earlier research. Residence times and aerosol type varied from study to study. Ehn et al. (2007) and Wehner et al. (2005) investigated the volatility of nucleation mode particles in remote background sites by examining the change in aerosol mean diameter when heated. Other studies, including our study, determined the volume/mass decrease of particles.

In general the aerosol volatility measured in this study seems to fall close to the lower end of the literature values – although the different residence times and total aerosol loadings make the direct comparison challenging. More aerosol material is expected to evaporate when longer residence times are used. This can be seen when aerosol

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### 4.3 Contribution of black carbon to MFR

Although located in a rural remote area, polluted air masses drive black carbon aerosols to Hyytiälä. Seasonal behavior of the maximum black carbon fraction in aerosol particles (see Eq. 4) is presented in Fig. 4. The BCF was the highest during winter and fall, around 13–15%. In summer and spring months around 8–10% of the total aerosol mass consisted of black carbon.

The results presented in Fig. 6 support the assumption that black carbon is connected to aerosol volatility. The larger the BCF, the larger the observed MFR was on average. The same kind of observation was made by Birmili et al. (2010) in an urban environment. Best correlation between the BCF and the MFR was seen during spring time ( $r = 0.69$ ,  $p$ -value  $< 10^{-5}$ ). In general the correlation in summer was not as clear ( $r = 0.34$ ,  $p$ -value  $10^{-3}$ ), although specifically in summer the black carbon concentrations were often of similar magnitude than the concentrations of the non-volatile material. In most cases, however, the aerosol non-volatile mass could not be explained by black carbon only.

Neither crustal material nor sea salt is a significant contributor to submicron aerosol composition in Hyytiälä area (Saarikoski et al., 2005). As Kalberer et al. (2004) suggested, it is possible that e.g. some organic species form non-volatile compounds as particles age in the atmosphere. In order to get information of the chemical composition of aerosol non-volatile mass fraction,  $MFR_{\text{non-BC}}$  was correlated with a large number of atmospheric parameters, including radiation, relative humidity and trace gases (Table 3) as well as with aerosol composition measured with an AMS (Fig. 7). These results are discussed in more detail below.

### 4.4 Dependence of MFR on environmental variables

The Pearson correlation coefficients and  $p$ -values between the  $MFR_{\text{non-BC}}$  and a number of meteorological variables and trace gas concentrations are presented in Table 3. Over the whole measurement period the non-volatile particle mass fraction was higher

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at lower ambient temperatures ( $r = -0.46$  with  $p$ -value of  $< 10^{-5}$ ). In colder conditions the ambient vapor mixture is different, and a large fraction of the semi-volatile vapors condense, which may enable different kind of gas and aerosol phase chemistry than in warmer air masses. The SMEAR II sampling lines are at room temperature and aerosol spends more than 5 s in these lines before arriving to the TD. This should be sufficient for the sample to reach room temperature before being heated to the TD temperature. In addition, the temperature of the aerosol flow inside the TD was measured at the centerline. This suggests that the dependence of the  $MFR_{\text{non-BC}}$  on the ambient temperature is not likely to be due to e.g. residence time related artefacts in aerosol sampling.

Neither boundary layer height nor solar radiation affected the  $MFR_{\text{non-BC}}$  as strongly as the ambient temperature when looking at the correlations over the whole measurement period. This might also point to the direction that the observed dependence between the  $MFR_{\text{non-BC}}$  and temperature is not only due to correlation between temperature and boundary layer height, but some additional, perhaps chemistry-related, relationship between temperature and  $MFR_{\text{non-BC}}$  is needed. Even though relative humidity did not have a strong correlation with aerosol volatility, with lower concentrations of water vapor in the air, aerosol particles were more non-volatile. This is probably due to the effect of boundary layer height and ambient temperature on the water vapor concentrations.

A clear positive correlation was found between the concentrations of some anthropogenic trace gases, i.e.  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{CO}$ , and the non-volatile aerosol residual. In addition, the connection between atmospheric polycyclic aromatic hydrocarbons (PAHs), emitted from combustion processes (Anttila et al., 2005; Rissanen et al., 2006), and aerosol non-volatile residual was investigated. The monthly median values of  $MFR_{\text{non-BC}}$  as a function of the maximum mass fraction of PAHs in sub-500 nm particles are presented in Fig. 8. It can be clearly seen that particles were relatively more non-volatile with high PAH mass fractions. The correlation coefficient between aerosol non-volatile residual and the sum of PAH-fractions was as high as 0.79 with

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$p$ -value of 0.002 (Fig. 8). The results on PAH and trace gases indicate that aerosol volatility is connected to anthropogenic influence over the whole measurement period. It is possible that some of the PAHs having low saturation vapor pressures, around  $10^{-7}$  Pa, (Hytönen et al., 2009) will stay in the aerosol phase at high heating temperatures. However, it should be noted that the concentrations of anthropogenic pollutants vary strongly with boundary layer height and temperature – being higher during the winter so the different aspects of the meteorological and chemical data are difficult to distinguish.

Correlations between environmental variables and the  $MFR_{\text{non-BC}}$  varied with season. During winter months ambient temperature showed the strongest negative correlation with aerosol volatility, while in the spring the connection was somewhat weaker yet negative and thus following the overall trend. Unlike the other seasons, the  $MFR_{\text{non-BC}}$  correlated more clearly with solar radiation and boundary layer height than temperature during spring months: with low radiation and low mixing height particles were more non-volatile. Comparing trace gas concentrations with the non-volatile aerosol mass fraction after black carbon removal, winter and spring showed generally similar trends to the overall behavior of the data set – indicating a connection between the anthropogenic trace gases and  $MFR_{\text{non-BC}}$ .

In summer months comparisons with meteorology did not show strong correlations with any of the investigated meteorological parameters and trace gas concentrations – the significance of the correlation results are questionable, and the trends often opposite to the overall behavior of the data set. This can be partly explained by the fact that the amount of VDMPS data was the smallest for summer months. Also, there are more volatile organic (VOC) emissions in summer (Lappalainen et al., 2009) and a larger fraction of aerosol mass is secondary. That may affect the observed low  $MFR_{\text{non-BC}}$  values in summer. Meteorological parameters did not offer an unambiguous explanation to the fall  $MFR_{\text{non-BC}}$  values either. Determined correlations were similar to those calculated for spring but overall weaker and often statistically insignificant.

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## 4.5 Indications of the chemical composition of MFR

AMS data were available for two month-long campaigns: one in May–June and one in September–October 2008 (Fig. 1). The aerosol chemical composition, as determined from the AMS, is presented in Fig. 7 (upper panel). The mass fraction of the non-volatile material (non-BC) was compared with AMS measurements (Fig. 7, lower panel). During the spring campaign the  $MFR_{\text{non-BC}}$  (median 3 %) at 280 °C did not have a significant correlation with any of the AMS-compounds' mass fractions (Fig. 7, lower panel). However, AMS measurements during fall gave more insight to the chemical composition of the non-volatile residual. During this period the  $MFR_{\text{non-BC}}$  was very small (Fig. 4). However, not all of the non-volatile mass was black carbon during the campaign: the maximum value for the  $MFR_{\text{non-BC}}$  was 0.25 at its highest. In the following we will concentrate on the comparisons between the VDMPS data and the AMS data from the fall campaign.

The VDMPS was temperature-scanning during the AMS campaigns. This made it possible to study the correlation between the aerosol chemical composition and the  $MFR_{\text{non-BC}}$  at six different temperatures (see Fig. 9 for results from the fall campaign). Ammonia and sulfates correlated positively with the non-volatile residual only at temperatures below 160 °C. This is in line with previous studies reporting evaporation of ammonium sulfate at approximately 200 °C. Nitrates and organics, however, had a statistically significant positive linear correlation with  $MFR_{\text{non-BC}}$  at 280 °C. During the spring campaign the ammonium-sulfate behavior was similar to the fall campaign, whereas with organics and nitrates no clear correlation was found.

The relative importance of ammonium nitrate to organic nitrate was estimated by dividing the available ammonium to sulfate and the residual ammonium to nitrate. During the fall 2008 campaign the mass fraction of ammonium nitrate in the AMS nitrate was below 2 % suggesting that most of the nitrate present in the particles were organic nitrates. The presence of organic nitrates was also investigated by studying the  $\text{NO}_2^+ : \text{NO}^+$  ratio ( $\text{NO}_2^+$  ( $m/z46$ ),  $\text{NO}^+$  ( $m/z30$ )) in the AMS that describes qualitatively

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the relation between organic nitrate and inorganic nitrate (Fry et al., 2009). The results confirm that observed nitrate during fall 2008 was for the most part from organic origin. Our results thus indicate that the non-volatile fraction of aerosol probably had a connection to the presence of organic nitrates in the fall period, although additional studies are needed to verify this conclusion. However, our results also clearly indicate that the processes controlling composition of the non-volatile material in Hyytiälä vary depending on the season and probably no single explanation for the non-volatile residual can be found.

In the fall 2008 particles arriving at Hyytiälä from the clean sector (i.e. from the forest, Tunved et al., 2006) had relatively more nitrate and non-volatile material in them (Fig. 10) as compared with other air mass directions. According to Sogacheva et al. (2005) new particle formation is most probable when air masses arrive at Hyytiälä from the North Atlantic or arctic regions, i.e. from the clean sector. It has also been reported that low volatile secondary organic compounds participate in the growth of freshly nucleated particles (Kulmala et al., 1998; O'Dowd et al., 2002; Pierce et al., 2011; Riipinen et al., 2011). It may be that the nucleation mode particles grow by the same non-volatile materials, probably organic nitrates or salts of some form, as the larger submicron particles. However, the connection between wind direction and the  $MFR_{\text{non-BC}}$  was not apparent from the overall behavior, as for the other seasons no clear source region of non-volatile material was identified from the air mass trajectories.

## 5 Summary and conclusions

Chemical properties such as the composition of aerosol particles can be investigated indirectly by measuring the volatility of these particles. In this study measurements of evaporation of submicron particles, 20–500 nm in diameter, were analyzed. Measurements were performed in a boreal forest site in Hyytiälä at the SMEAR II station continuously during a two and a half year period from January 2008 to May 2010. The long time series of aerosol volatility as well as additional measurement data from the

SMEAR II station made it possible to examine the seasonal behavior of aerosol when heated, as well as to compare the data set with other atmospheric parameters, such as meteorological conditions, trace gas concentrations and aerosol composition.

During the first year and a half of the measurements the VDMPS system was in a temperature-scanning mode. Then aerosol was heated up to six temperatures, ranging from 80 °C to 280 °C. From July 2009 onwards the heating temperature in VDMPS was kept constant, at 280 °C. Temperature scanning yielded information on how the evaporation of aerosol particles depends on temperature. The higher the heating temperature was the more aerosol material was evaporated, the temperature response of the volatility being similar as in previous studies. At 80 °C 86 % of total aerosol mass remained after heating, whereas the mass fraction remaining (MFR) was 19 % at 280 °C.

It was found that the MFR varied with season. During winter, spring and fall months the relative amount of non-volatile material in aerosol particles was greater than that during summer. In order to explain the existence of the observed non-volatile residual as well as its seasonal behavior, additional measurements, such as black carbon data, were included in the analysis. Black carbon explained in maximum 55–90 % of the composition of the non-volatile aerosol mass fraction depending on season. The amount of black carbon in aerosol particles was slightly higher during winter and fall than other seasons, up to approximately 13–15 % of the aerosol mass. The relative amount of black carbon in aerosols was the highest during summer when on some days all non-volatile mass could have, in principle, been explained by black carbon. However, the correlation between the BC concentration and MFR was the poorest during summer months – this could be partly due to small amount of data from summer months, but also potentially linked to the contribution of other factors in defining the volatility of the aerosol in the summer as well.

Crustal material and sea salt are minor contributors to the total submicron aerosol mass in Hyytiälä, and the observed black carbon alone could not explain the existence of the non-volatile residual. Thus, roughly half of the aerosol non-volatile mass is explained by other compounds than the ones mentioned above. The properties of

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the non-BC compounds were analyzed further by comparing aerosol mass fraction remaining with modeled air mass trajectories, meteorological data as well as with results from aerosol mass spectrometry campaigns in spring and fall 2008. However, no single explaining factor was found.

In general ambient temperature had a marked correlation with  $MFR_{\text{non-BC}}$  whereas boundary layer height did not affect the aerosol non-volatile residual as significantly. However, during spring months the effect of boundary layer height was more notable than during other seasons. Our results did not show as strong correlation between non-volatile aerosol residual and boundary layer height as found by Birmili et al. (2010) who also showed that light-absorbing material, such as black carbon, is the main explaining compound of the observed non-volatile aerosols in urban areas. Clearly this was not the case in this study. Thus, volatility of boreal forest aerosols cannot be explained fully by the same parameters as in urban, more anthropogenic influenced, environment.

Results from the aerosol mass spectrometer in fall 2008 suggest the existence of compounds of organic origin in the MFR. With clean air masses, both the fraction of non-volatile material in aerosol particles and the mass fraction of nitrate (mainly organic origin) compounds in aerosol particles were higher than on average. This implies that the non-volatile nitrate compounds may contribute to the growth of submicron aerosol particles.

Especially during winter and spring the non-volatile residual correlated markedly with CO concentrations as well as with SO<sub>2</sub> and NO<sub>x</sub> concentrations. In addition, high PAH mass fractions corresponded to high values of the  $MFR_{\text{non-BC}}$ . Due to this, it can be speculated that the non-volatile aerosol fraction contains also other compounds from anthropogenic sources, e.g. low-volatile PAHs, in addition to black carbon. Additionally, Raatikainen et al. (2010) observed that aerosol nitrates, sulfates and ammonium correlated notably with low-volatile oxidized organic aerosol (LV-OOA) during spring time. LV-OOA was characterized as highly aged organic aerosol with anthropogenic origin. It is possible that some of these LV-OOA compounds may not evaporate at 280 °C due to organic polymerization (Kalberer et al., 2004). However, this was not supported in

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the publication by Raatikainen et al. (2010). It should be noted that Raatikainen et al. (2010) investigated aerosol volatility in Hyytiälä over a shorter time period and with different instruments than in this study.

As shown in this study, aerosol volatility in a boreal forest environment cannot be explained with any single parameter – but rather is dependent on several environmental factors, varies with season and is affected by both anthropogenic and biogenic factors.

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**Table 1.** Absorption mass cross-sections,  $\sigma_{\text{abs},0}$  (from the manufacturer) and  $\sigma_{\text{abs}}$  (calculated based on Petzold and Schönlinner, 2004), and  $C$  parameters for correcting the black carbon concentrations measured with an aethalometer.  $C$  factors given are determined from Hohenpeissenberg data (Collaud-Coen et al., 2010) but because of the similar forest environment, these factors were assumed to describe the Hyytiälä aerosol alike.

Wavelength $\lambda$ (nm)	$\sigma_{\text{abs},0}$ ( $\text{m}^2 \text{g}^{-1}$ )	$\sigma_{\text{abs}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$C$
370	39.53	11.36	2.64
470	31.12	8.95	2.75
521	28.07	8.07	2.81
590	24.79	7.13	2.87
660	22.16	6.37	2.93
880	16.62	4.78	3.09
950	15.39	4.43	3.13

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**Table 2.** Median total particle volume concentrations measured by the DMPS and VDMPS in different seasons as well as determined VFR (MFR) of 20–500 nm particles at 280 °C.

Season	Instrument	Total particle volume concentration ( $\mu\text{m}^3 \text{cm}^{-3}$ )	VFR
Winter	DMPS	1.72	0.25
	VDMPS	0.38	
Spring	DMPS	1.75	0.17
	VDMPS	0.25	
Summer	DMPS	1.99	0.09
	VDMPS	0.18	
Fall	DMPS	1.00	0.20
	VDMPS	0.18	

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**Table 3.** Correlation between  $\text{MFR}_{\text{non-BC}}$  and meteorological parameters: trace gas concentrations, ambient temperature, relative humidity and radiation for different seasons. Correlation coefficients ( $r$ ) and  $p$ -values in brackets describing the significance of the correlation are from 24 h median data.

	Winter	Spring	Summer	Fall	All data
NO	0.10 ( $10^{-1}$ )	0.26 ( $10^{-4}$ )	-0.07 ( $10^0$ )	0.18 ( $10^{-2}$ )	0.07 ( $10^{-1}$ )
NO <sub>x</sub>	0.21 ( $10^{-3}$ )	0.38 ( $< 10^{-5}$ )	-0.18 ( $10^{-1}$ )	0.11 ( $10^{-1}$ )	0.33 ( $< 10^{-5}$ )
O <sub>3</sub>	0.08 ( $10^{-1}$ )	0.21 ( $10^{-2}$ )	0.01 ( $10^0$ )	0.09 ( $10^{-1}$ )	0.06 ( $10^{-1}$ )
SO <sub>2</sub>	0.39 ( $< 10^{-5}$ )	0.44 ( $< 10^{-5}$ )	0.14 ( $10^{-1}$ )	0.07 ( $10^{-1}$ )	0.44 ( $< 10^{-5}$ )
H <sub>2</sub> O	-0.36 ( $< 10^{-5}$ )	-0.18 ( $10^{-2}$ )	0.05 ( $10^0$ )	-0.26 ( $10^{-3}$ )	-0.45 ( $< 10^{-5}$ )
CO <sub>2</sub>	0.13 ( $10^{-1}$ )	0.36 ( $< 10^{-5}$ )	-0.31 ( $10^{-3}$ )	0.25 ( $10^{-3}$ )	0.42 ( $< 10^{-5}$ )
CO	0.24 ( $10^{-3}$ )	0.49 ( $< 10^{-5}$ )	-0.17 ( $10^{-1}$ )	0.13 ( $10^{-1}$ )	0.46 ( $< 10^{-5}$ )
RH	0.04 ( $10^0$ )	0.02 ( $10^0$ )	-0.14 ( $10^{-1}$ )	-0.01 ( $10^0$ )	0.18 ( $< 10^{-5}$ )
Temperature	-0.36 ( $< 10^{-5}$ )	-0.18 ( $10^{-2}$ )	0.23 ( $10^{-2}$ )	-0.26 ( $10^{-3}$ )	-0.46 ( $< 10^{-5}$ )
Global-radiation	0.02 ( $10^0$ )	-0.25 ( $10^{-3}$ )	0.04 ( $10^0$ )	-0.14 ( $10^{-1}$ )	-0.27 ( $< 10^{-5}$ )
Boundary layer height	0.06 ( $10^{-1}$ )	-0.33 ( $< 10^{-5}$ )	-0.03 ( $10^0$ )	-0.07 ( $10^{-1}$ )	-0.19 ( $< 10^{-5}$ )

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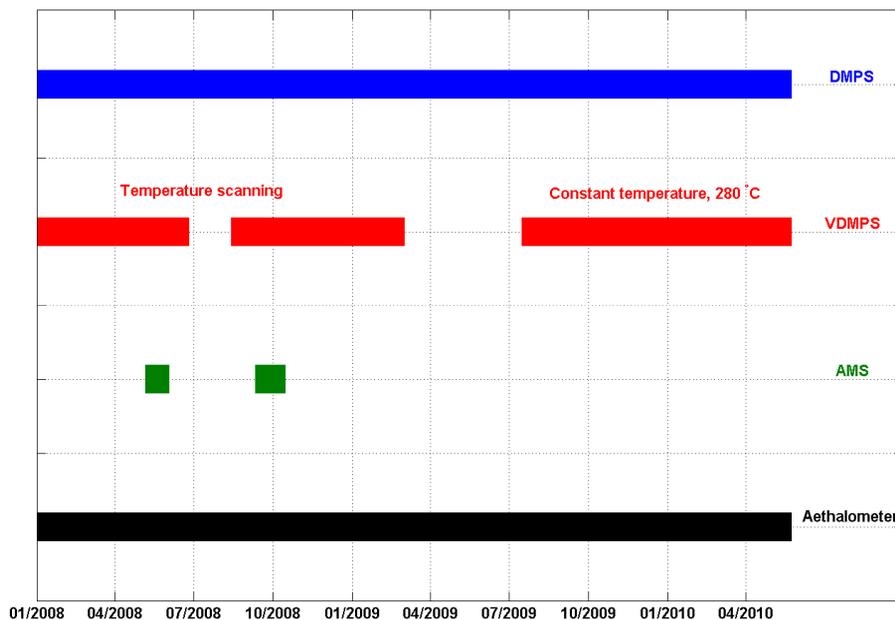
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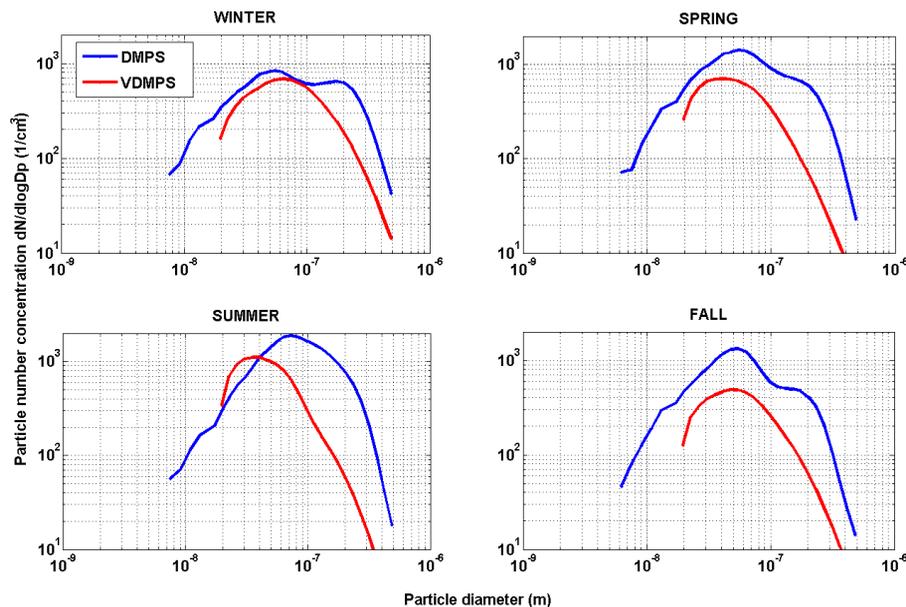


**Fig. 1.** Instruments used in this study and their functioning times during January 2008 to May 2010.

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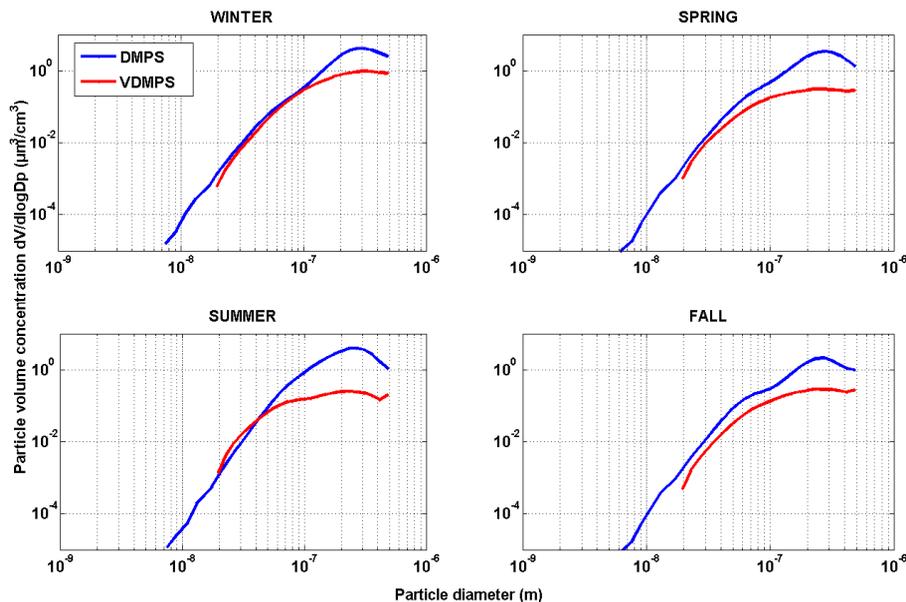


**Fig. 2.** Median particle number size distributions from DMPS and VDMPS at 280 °C in different seasons.

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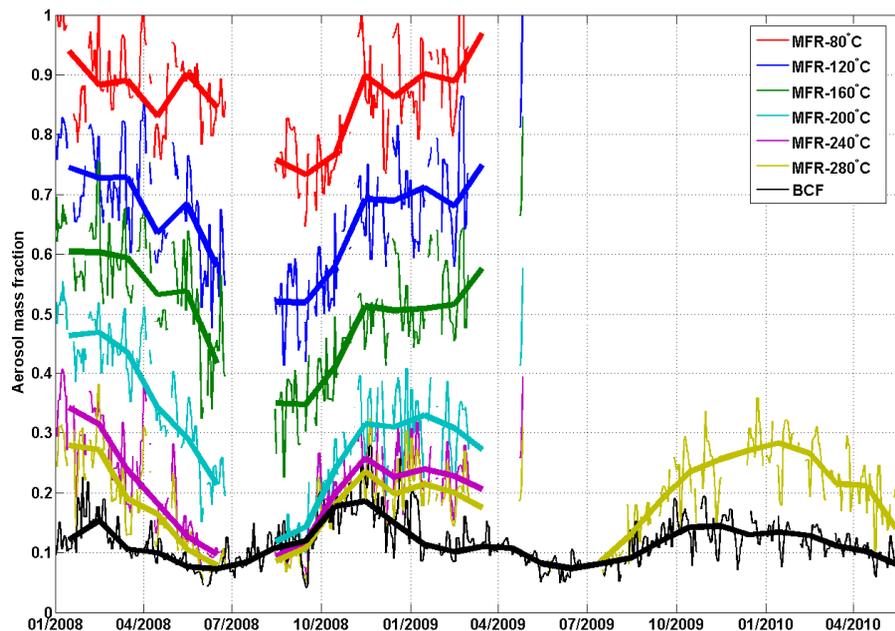


**Fig. 3.** Seasonal median volume size distributions from DMPS and VDMPS at 280 °C.

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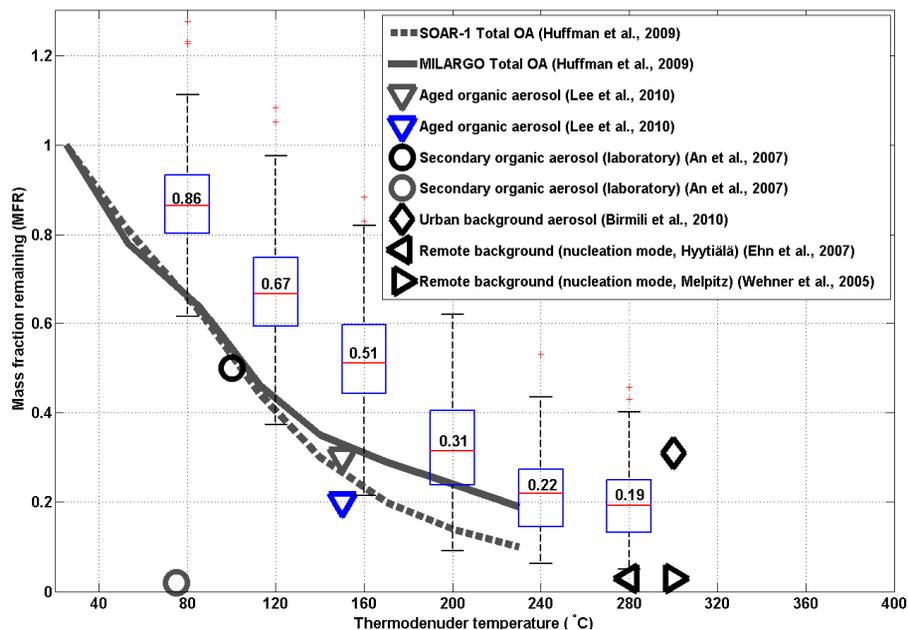


**Fig. 4.** Aerosol mass fraction remaining after heating in six temperatures from 80 °C to 280 °C is presented (colored lines). The black line describes the maximum mass fraction of black carbon in aerosol particles. Thicker lines show the monthly pattern of the parameters presented.

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**Fig. 5.** Comparison of thermograms between this study (the boxplot) and previous volatility studies. Coloring describes the residence times used (black: < 2 s, grey: 10–16 s, blue: > 100 s). SOAR-1 and MILAGRO campaign results are adapted from Huffman et al. (2009). Lee et al. (2010) investigated the volatility of aged organic aerosol during FAME-2008 campaign in Finokalia and volatility measurements of urban background aerosol were performed by Birmili et al. (2010) in Germany. Ehn et al. (2007) and Wehner et al. (2005) measured the volatility of nucleation mode particles in Hyytiälä and in Melpitz, respectively. Measurement results of laboratory generated secondary organic aerosol from An et al. (2007) are also presented.

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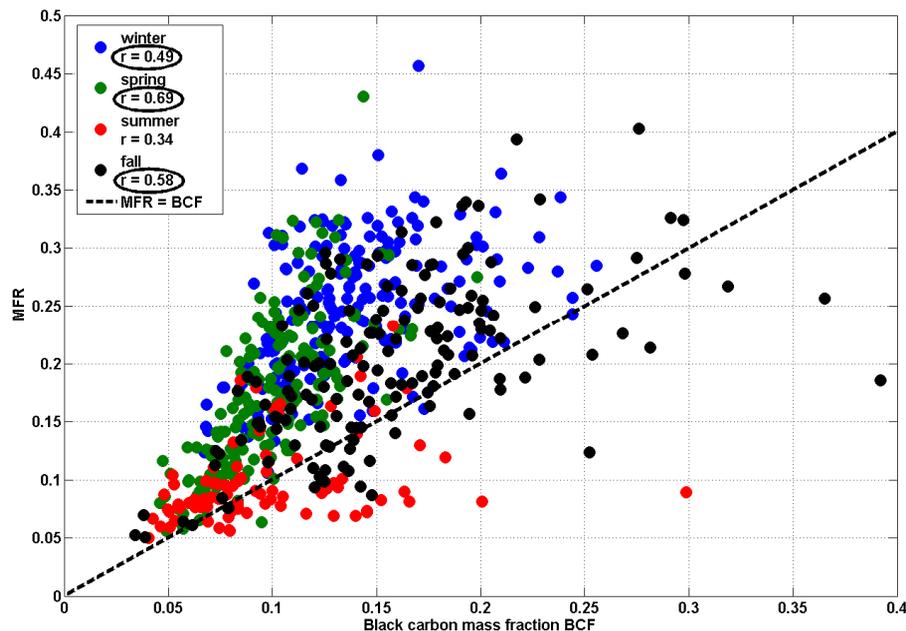
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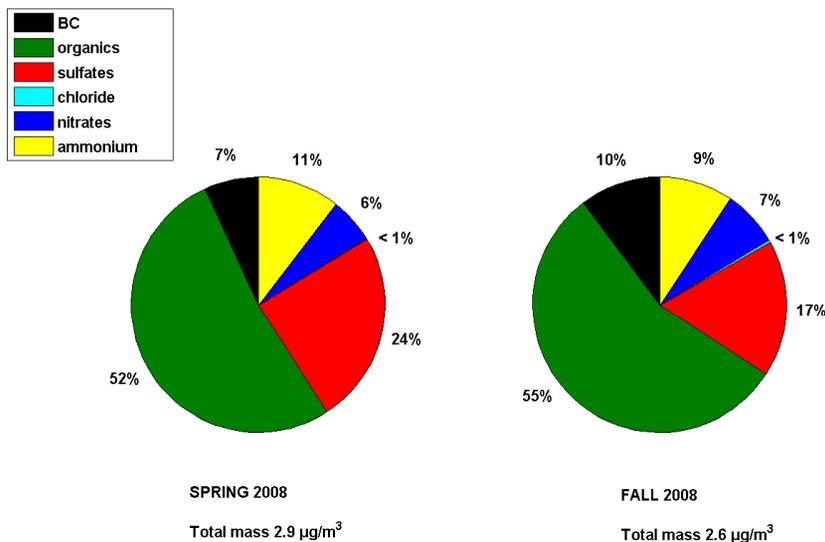
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**Fig. 6.** Mass fraction remaining at 280 °C as a function of black carbon mass fraction during different seasons. A clear correlation is seen during winter, spring and fall months ( $p$ -value  $< 10^{-5}$ ). The black line describes the situation where the entire non-volatile aerosol mass is black carbon. The existence of measurement points below this line most likely arise from the attribution of all  $PM_{2.5}$  BC to submicron aerosol.

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	Spring 2008	Fall 2008
Sulfates and $\text{MFR}_{\text{non-BC}}$	0.08 ( $10^{-1}$ )	-0.27 ( $10^{-2}$ )
Chloride and $\text{MFR}_{\text{non-BC}}$	-0.02 ( $10^0$ )	0.05 ( $10^0$ )
Nitrites and $\text{MFR}_{\text{non-BC}}$	-0.06 ( $10^0$ )	0.41 ( $10^{-5}$ )
Ammonium and $\text{MFR}_{\text{non-BC}}$	0.05 ( $10^0$ )	-0.18 ( $10^{-1}$ )
Organics and $\text{MFR}_{\text{non-BC}}$	-0.05 ( $10^0$ )	0.29 ( $10^{-3}$ )

**Fig. 7.** Aerosol chemical composition during AMS measurement campaigns in spring and fall 2008 is illustrated in the upper panel. Black carbon mass measured with an aethalometer is included in the total aerosol mass and the median total mass concentrations of particles are provided. The correlation ( $r$  and  $p$ -value in parenthesis) between  $\text{MFR}_{\text{non-BC}}$  at 280 °C and mass fractions of AMS-compounds is presented in the lower panel.

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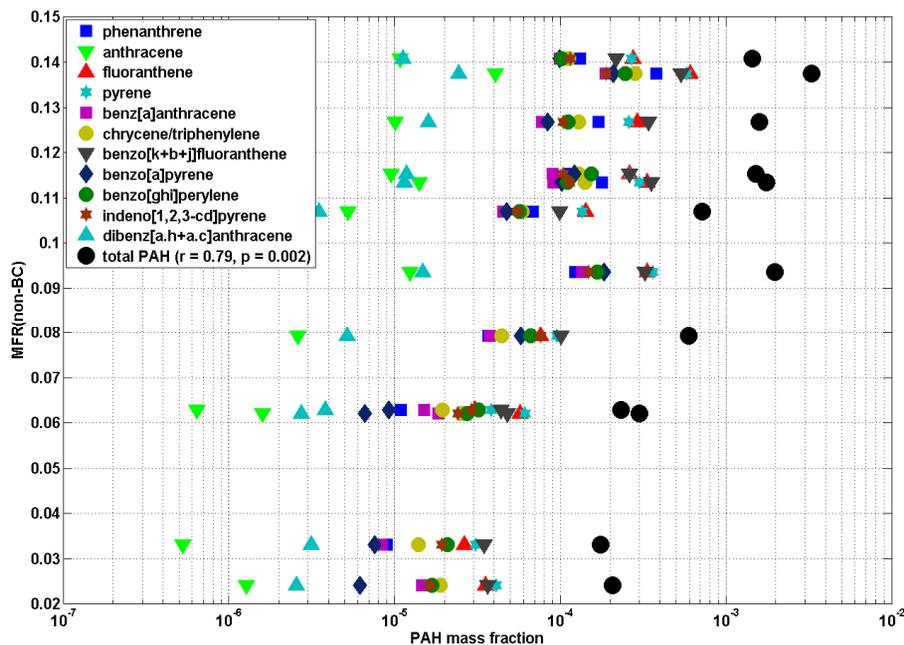
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**Fig. 8.** Aerosol mass fraction remaining (non-BC) as a function of PAH mass fractions. Monthly means have been used. Note the logarithmic scale.

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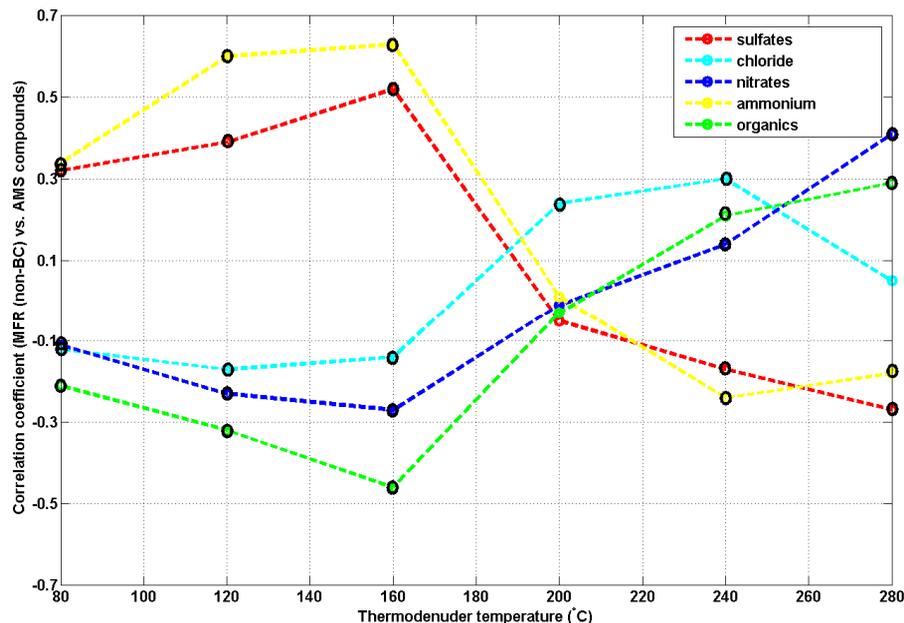
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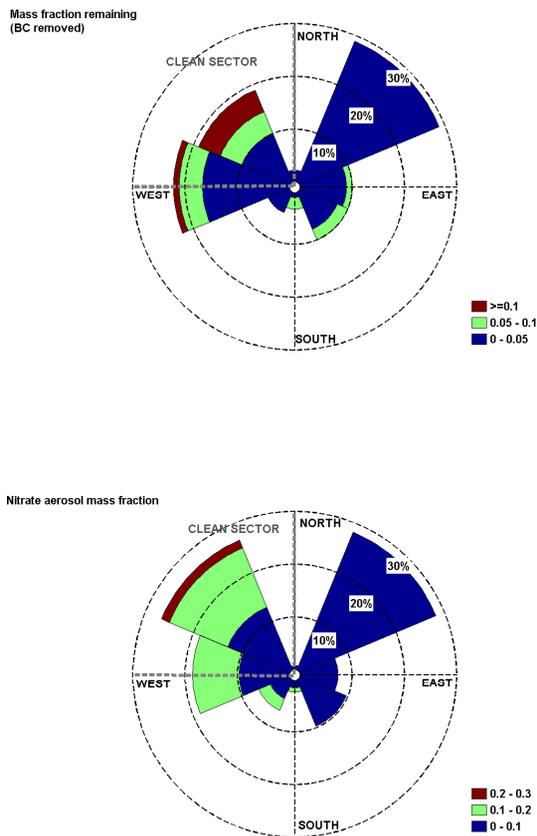
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**Fig. 9.** Calculated correlation coefficients between  $\text{MFR}_{\text{non-BC}}$  and mass fractions of AMS-compounds at six different temperatures. Correlation values with black circle on them are statistically significant with  $p$ -value < 0.05.

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**Fig. 10.** Wind roses of aerosol mass fraction remaining (non-BC) after heating to 280 °C (upper panel) and nitrate mass fraction during AMS measurement campaign in fall 2008 (lower panel). The colors represent the mass fractions, and the percent values correspond to the amount of data from each direction bin.

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