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Jenny Rissler a, Joakim Pagels b, Erik Swietlicki a, Aneta Wierzbicka b, Michael Strand c, Lena Lillieblad c, Mehri Sanati b & Mats Bohgard b

a Div. of Nuclear Physics, Lund University, Lund, Sweden
b Div. of Ergonomics and Aerosol Technology, Lund University, Lund, Sweden
c Bioenergy Technology, Växjö University, Växjö, Sweden

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Hygroscopic Behavior of Aerosol Particles Emitted from Biomass Fired Grate Boilers

Jenny Rissler,1 Joakim Pagels,2 Erik Swietlicki,1 Aneta Wierzbicka,2 Michael Strand,3 Lena Lillieblad,3 Mehri Sanati,3 and Mats Bohgard2
1Div. of Nuclear Physics, Lund University, Lund, Sweden
2Div. of Ergonomics and Aerosol Technology, Lund University, Lund, Sweden
3Bioenergy Technology, Växjö University, Växjö, Sweden

This study focuses on the hygroscopic properties of submicrometer aerosol particles emitted from two small-scale district heating combustion plants (1 and 1.5 MW) burning two types of biomass fuels (moist forest residue and pellets). The hygroscopic particle diameter growth factor \( G_f \) was measured when taken from a dehydrated to a humidified state for particle diameters between 30–350 nm (dry size) using a Hygroscopic Tandem Differential Mobility Analyzer (H-TDMA). Particles of a certain dry size all showed similar diameter growth and the \( G_f \) at RH = 90% for 110/100 nm particles was 1.68 in the 1 MW boiler, and 1.5 in the 1.5 MW boiler. These growth factors are considerably higher in comparison to other combustion aerosol particles such as diesel exhaust, and are the result of the efficient combustion and the high concentration of alkali species in the fuel. The observed water uptake could be explained using the Zdanovski-Stokes-Robinson (ZSR) mixing rule. Agglomerated particles collapsed and became more spherical when initially exposed to a moderately high relative humidity. When diluted with hot particle-free air, the fractal-like structures remained intact until humidified in the H-TDMA. A method to estimate the fractal dimension of the agglomerated combustion aerosol and to convert the measured mobility diameter hygroscopic growth to the more useful property volume diameter growth is presented. The fractal dimension was estimated to be \( \sim 2.5 \).

1. INTRODUCTION

The supply of energy is one of the main issues in today’s society. Due to the increasing \( \text{CO}_2 \) concentrations in the atmosphere, authorities are promoting the use of renewable fuels such as biomass. In Sweden, for example, biofuels contribute to about 16% (98 TWh) of the total energy supply, increasing by \( \sim 4 \) TWh annually (Swedish Energy Administration 2003). A fraction of the increase is invested in moving grate plants between 0.5 and 10 MW used for local district heating.

While reducing the net \( \text{CO}_2 \) emissions, biomass combustion emits large amounts of fine particles if no particle removal technique is utilized. There is now a general consensus that elevated concentrations of both \( \text{PM}_{10} \) and \( \text{PM}_{2.5} \) are associated with adverse health effects (WHO 2003; WHO 2004). Although the exact mechanisms of the health effects are not known, chemical composition, size, morphology, and solubility are likely to be important parameters.

Aerosol particles emitted from combustion of biomass can also have an impact on regional and global climate through their influence on the Earth’s radiation budget and cloud microphysics. The role of atmospheric aerosols in cloud formation and lifetime along with the resulting global radiation balance currently constitute the largest source of uncertainty in our ability to predict future climate change resulting from human activities (IPCC 2001).

Several studies have been carried out on particle formation and emissions from woody biomass combustion for heat and power production. These range from large-scale (25–100 MW) CFB (Circulating Fluidized Bed) boilers (e.g., Valmari et al. 1999), to grate combustion in 0.5–12 MW boilers (Pagels et al. 2003; Lillieblad et al. 2004) to small (10–20 kW) residential wood stoves and boilers (Hedberg et al. 2002; Johansson et al. 2004). Emissions from other biomass fuels have also been studied, such as straw (Christensen et al. 1998) and olive residues (Jimenez and Ballester 2004), as well as co-firing of biomass and fossil fuels. Biomass burning in the open resulting from wildfires and deforestation has also attracted attention (Reid et al. 2004; Andreae and Merlet 2001).

During favorable combustion, ash components such as \( \text{K}_2\text{SO}_4 \), \( \text{KCl} \), and in some cases \( \text{K}_2\text{CO}_3 \) dominate the fine particle composition. Potassium is volatilized, and contributes to the formation of particles by homogeneous nucleation and subsequent condensation as the flue gases cool down. The concentration
of these ash components is mainly governed by the inorganic content of the fuel. If the combustion conditions are poor—as might be the case in forest fires and during the start-up phase in residential boilers—products of incomplete combustion, for example, Organic Carbon (OC) and Elemental Carbon (EC; i.e., soot) may dominate the chemical composition. The composition of fine particles from biomass combustion covers the full spectrum from almost pure KCl/K₂SO₄ particles in CFB boilers to almost pure OC/EC particles in forest fires. Although not studied in detail, the relative abundance of these two classes of particle components is expected to vary strongly over the combustion cycle. Some information is available on the variation in inorganic composition on a particle-by-particle basis from electron microscopy EDX analysis (Brunner et al. 2001), but more studies are needed to better understand the mixing status.

Combustion particles may be highly agglomerated. Park et al. (2004) have reported that the dynamic shape factor of diesel soot increased from 1.1 to 2.2 over the size range 50–220 nm. Valmari et al. (1999) suggested that fine mode particles from CFB combustion of biomass were compact and close to spherical based on Transmission Electron Microscopy (TEM) analysis.

The aim of this study was to determine the hygroscopic properties of the flue gas particles emitted from biomass fired district heating units, using a Hygroscopic Tandem Differential Mobility Analyzer (H-TDMA). Hygroscopic properties in this study relate to how the particles absorb water vapor and grow into solution droplets as a function of the relative humidity (RH). The hygroscopic properties of aerosol particles are important for several reasons. The deposition pattern and deposition probability in the respiratory system is strongly dependent on the particle size in the actual airways. In the lower respiratory tract, the equilibrium RH is about 99.5% (Anselm et al. 1990). Under these conditions NaCl particles grow by a factor of five to six in diameter. Particle hygroscopic growth is also a crucial parameter for light scattering and for the selection of the sub-population of particles that act as cloud condensation nuclei. Furthermore, measurements of hygroscopic properties can provide size and time-resolved information regarding the mixing status of the aerosol, as well as proxy data on the chemical composition. These properties can be used for a better understanding of particle formation processes and to develop more efficient cleaning techniques.

Water vapor uptake of biomass combustion aerosol particles can be either due to the presence of water-soluble salts or to the presence of water-soluble organic compounds. As an example, pure KCl has a diameter growth factor of about 2 at RH = 90%. The water-soluble OC in biomass smoke consists of partly oxidized compounds originally present in the fuel. These compounds typically have lower growth factors. One abundant compound is levoglucosan—a pyrolysis product of cellulose (Simoneit et al. 1999)—which has a growth factor of about 1.3 at 90% RH (Svenningsson et al. 2005).

Previously, only a few measurements on hygroscopic diameter growth factors of biomass burning aerosols have been reported, some with regard to natural forest fires or clearing forest in the Amazon region (Vestin et al. 2004; Rissler et al. 2004), laboratory-scale experiments burning peat (Zeromskiene, 2004) and emissions to indoor air from wood stoves (Dua and Hopke 1996). Field studies of biomass burning smoke aerosol in the Amazon report low hygroscopic growth factors (∼1.1–1.3) at 90% RH (Vestin et al. 2004). For the laboratory-scale experiment burning peat the hygroscopic diameter growth, measured at 85% RH, was 1.04, corresponding to a growth of ∼1.06 at 90% RH (for 80 nm particles). For the indoor small-scale fires, measured at ∼99% RH, the growth was ∼1 for an open flame fire and 2 for particles from a smoldering fire, corresponding to a growth of ∼1–1.35 at 90% RH. The differences in results are likely due to highly variable burning conditions and combustion efficiency. To our knowledge, no measurements of hygroscopic diameter growth factors have been reported from combustion in biomass fired district heating, where the combustion conditions are favorable and water-soluble potassium salts tend to dominate the particle composition.

In this study, hygroscopic growth factor measurements are presented from two biomass fired moving grate boilers. The Zdanovski-Stokes-Robinson (ZSR) method was used to predict hygroscopic growth factors from chemical composition data partly reported previously (Pagels et al. 2003; Wierzbicka et al. 2005). A method is described that can be used to estimate the fractal dimension of agglomerated hygroscopic combustion aerosol and to convert the measured mobility hygroscopic growth factor to the more useful property volume growth factor. The study is a part of a larger national project (biofuels, health, and environment—emissions and air quality, Noone 2005), which aims to study the effects on environment and human health from increased utilization of biofuels combustion for energy production.

2. METHODS AND THEORY

2.1 Combustion System and Particle Sampling

The measurements were carried out in two biomass fired moving grate boilers used for local heat production in Sweden. The two boilers are a 1 MW boiler operating on moist forest residues (boiler 1) and a 1.5 MW boiler fired with dry pellets (boiler 2). During the measurements the two boilers were operated at 45–100% and 20–50% load, respectively.

The flue gas was sampled isokinetically downstream the multi-cyclone (the only flue gas cleaning device installed). Two different dilution systems were in use. For boiler 1 the flue gases were diluted (1:10) and cooled to room temperature using particle-free dry compressed air at ambient temperature. In this system, the flue gas sample experienced a high RH during dilution, which may to some extent simulate the dilution in and after the stack. Hygroscopic particles which go into water solution during dilution may recrystallize to a more compact
shape. The dew point of the undiluted flue gas is around 60°C. The cooled gas stream was further diluted (1:10) before being sampled with the H-TDMA.

For boiler 2, a two-stage ejector based dilution system was used. The first dilution stage used heated (110°C), particle-free air. This type of dilution system is often used in biomass combustion studies and prevents condensation of water and volatile components on the particles.

The boilers and the sampling systems are described in more detail by Pagels et al. (2003) and Wierzbicka et al. (2005). All reported concentrations are normalized to 13% CO₂, at 0°C and 101.3 kPa.

2.2 Hygroscopic Growth Measurements

2.2.1 Principle of the H-TDMA

The hygroscopic properties of aerosol particles, with dry sizes ranging between 20 and 350 nm, were studied with an H-TDMA. In principle the H-TDMA consists of three parts: a Differential Mobility Analyzer (DMA1) that selects a narrow, quasi-monodisperse size fraction of dry particles (RH < 10%); humidifiers conditioning the aerosol to a controlled humidified state; and a second DMA (DMA2) that measures the change in size caused by the imposed humidification. The aerosol and the sheath flows entering DMA2 were humidified separately. The DMAs used were of the Vienna type (Winklmayr et al. 1991).

The H-TDMA was operated in two different modes: (1) the size-scanning mode and (2) the RH-scanning mode. Using mode 1, humidity is kept constant while the selected dry size in DMA1 is varied. This gives information on how the hygroscopic diameter growth of the aerosol changes with particle size. Mode 2, instead, keeps the selected dry size constant while scanning the RH, here between 20–90%. This can be used to evaluate the deliquescent behavior of the aerosol particles. A more detailed technical description of the H-TDMA can be found in Svenningsson (1997) and Zhou (2001).

2.2.2 Quality Assurance and Data Processing

The H-TDMA data were evaluated and assured for quality off-line, using a number of parameters logged by the H-TDMA software. An extensive description of the quality assurance procedure is given by Rissler et al. (2004) and Swietlicki et al. (2000). Certain criteria on the variations in concentration, RH and temperatures had to be fulfilled for data to be accepted. These criteria were used when calculating the instrumental error in Figure 5.

Each spectrum of the humidified aerosol size distribution was fitted with a computer program (Zhou 2001) based on the theory and algorithm of “TDMAFIT” (Stolzenberg and McMurry 1988). This program estimates the arithmetic mean mobility diameter growth factor, Gfb (defined as the ratio between the conditioned mobility diameter d_{b,wet}, and the dry mobility diameter, d_{b,dry}), the diameter growth dispersion factor (the broadening in addition to the ideal TDMA transfer function), and the number fraction of particles in each fitted hygroscopic particle group. For distributions fitted with two or more groups, the mean growth of the groups was calculated and presented as one Gfb. To present the broadening, which is related to the mixing status of the particles, an interval of the hygroscopic growth factor covering 90% of the wet distribution (fitted distribution) is given. This representation of the spectra were chosen since the fitted distributions were most often very close in growth and mainly dominated by one mode.

Hereafter we will distinguish between the mobility diameter growth factor, Gfb, and the volume diameter growth factor, Gfv. Since wet particles are spherical, d_{B,wet} = d_{V,wet} (d_{V} is the volume equivalent diameter) the difference between Gfb and Gfv is introduced due to non-spherical dry particles, i.e. d_{B,dry} ≠ d_{V,dry}.

Despite considerable efforts to stabilize the RH in DMA2, deviations from the nominal RH are difficult to avoid during operation. To facilitate comparisons, the growth factors of the size scans were corrected to the nominal RH of 90%. Corrections were made as described by Swietlicki et al. (2000) using KCl (Tang 1997) as model salt. Since the accepted variation in DMA2 RH is relatively small, the dependence on the type of salt applied in this correction is negligible.

2.3 Additional Measurements

A Scanning Mobility Particle Sizer (Wang and Flagan 1989) was operated in parallel with the H-TDMA during the two experiments. In addition, a Dekati 13 stage multi-jet low-pressure cascade impactor (LPI) was used to collect samples for gravimetric analysis, elemental analysis (PIXE), and analysis of major ions (IC). An Electrical Low-Pressure Impactor (ELPI) (Marjamäki et al. 2004) was used in the second boiler. These measurements are described in more detail by Pagels et al. (2003), Lillieblad et al. (2004) and Wierzbicka et al. (2005). In this article, some additional analysis is presented to identify the time and size variation of ash components like potassium salts and EC/OC. Such information is essential when interpreting the H-TDMA measurements.

2.4 Hygroscopic Growth and the ZSR Mixing Rule

The water uptake of a particle can be described using the Köhler equation (Köhler 1936). It combines the Kelvin curvature effect (C_k) and Raoult’s Law for water activity (a_w) as RH/100 = C_k · a_w. C_k takes into account the increase in equilibrium water vapor pressure caused by the droplet curvature, and the second term describes the depression in water vapor pressure due to soluble material in the particles.

2.4.1 The Zdanovski-Stokes-Robinson (ZSR) Method

A relatively simple way of estimating the volume growth factor of mixed particles is to use the Zdanovski-Stokes-Robinson (ZSR) method (Stokes and Robinson 1966). The ZSR method is defined by the equation:

\[ 1 = \sum \frac{m_v(a_w)}{m_{v,i}(a_w)} \]
where \( m_s \) is the molality of compound \( s \) in the mixture, and \( m_{w,s} \) the molality of the single electrolyte solution of the component \( s \), for which the water activity equals that of the solution mixture. This can also be expressed as a summation of the mass of water in an aqueous solution of a single solute, which contains the same mass of the solute as is dissolved in the mixture and, which has the same water activity as the mixture. It follows from the definition in Equation 1 that \( G_{ve}^{\text{Mix}} \) of the mixture, at a certain water activity, is given by:

\[
G_{ve}^{\text{Mix}} = \frac{3}{\sqrt{\sum \varepsilon_i \cdot G_{ve}^{3,s}}} \tag{2}
\]

where \( \varepsilon_i \) is the volume fraction of compound \( s \) in the dry particle, and \( G_{ve}^{3,s} \) is the hygroscopic growth factor of compound \( s \) at the specific water activity.

### 2.4.2 Water Activities of the Pure Salts

To calculate the hygroscopic diameter growth factor using the ZSR method, \( G_{ve} \) of the pure compounds needs to be known. The main components of the biomass combustion aerosol studied were \( \text{K}_2\text{SO}_4 \), \( \text{K}_2\text{CO}_3 \), and KCl. Since no data were found for the hygroscopic growth of \( \text{K}_2\text{CO}_3 \), this salt was further investigated in laboratory H-TDMA measurements. KCl has been characterized by Tang (1997). He measured the water activity (\( a_w \)) down to the point of crystallization (\( a_w = 0.62 - 1 \)). The deliquescence point is for KCl \( \approx 0.84 \) (Tang 1997), and the measured deliquescence point for \( \text{K}_2\text{CO}_3 \) is between 0.30–0.40 (when estimated from solubility: 0.54). For \( \text{K}_2\text{SO}_4 \), water activity data from Guendouzi et al. (2003) were used. However, they only measured the water activity for non-supersaturated (bulk) solutions. No water activity data were found for supersaturated solutions of \( \text{K}_2\text{SO}_4 \). Since the solubility of \( \text{K}_2\text{SO}_4 \) is low (0.12 g/cm\(^3\), from Lide 1991), resulting in a high deliquescence point, \( a_w \approx 0.97 \), it is impossible to measure the deliquescence branch using our H-TDMA system. In order to estimate the hygroscopic growth below the point of deliquescence, we use the fact that the hygroscopic growth for particles consisting of non-ideal subsaturated solutions can be approximated from classical Köhler theory (Köhler 1936), substituting the number of dissociating ions by a constant van’t Hoff factor. As a result of the variable degree of dissociation and non-ideal interactions in the electrolyte, the van’t Hoff factor varies with salinity. In the interval measured by Guendouzi et al. (2003) \( (a_w = 0.972 - 0.9958) \), a van’t Hoff factor of 2.05 can describe the measured water activity. This value was inserted into Köhler theory to extrapolate the hygroscopic behavior of \( \text{K}_2\text{SO}_4 \) down to supersaturated solutions. The errors introduced using a static van’t Hoff factor are, for our purpose, small.

### 2.4.3 Solubility

The water solubility of the pure compounds must be taken into account when using the ZSR mixing rule. This is the case for \( \text{K}_2\text{SO}_4 \) and partly also for KCl. In Svenningsson et al. (2005) it was assumed that the constituents of the particle go partly into solution if other salts provide the water liquid phase, an assumption also used in this study. The water accessible for the solution is assumed to be \( V_{\text{droplet}} - V_{\text{non-sol.frac}} \), where \( V_{\text{droplet}} \) is the droplet volume and \( V_{\text{non-sol.frac}} \) is the volume of the not yet dissolved fraction of the particle. The solubilities in mixed particles were calculated from the solubility products, \( K_{sp} \), and take into account the common ion effect (McMurry and Fay 1998). The solubility products used were in turn calculated from the solubility of the pure salts taken from Lide (1991). The solubilities of the pure compounds (and the solubility products) are 1.12 g/cm\(^3\) \((2129 \text{ mol}^3/\text{dm}^9)\) for \( \text{K}_2\text{CO}_3 \), 0.344 g/cm\(^3\) \((21.3 \text{ mol}^2/\text{dm}^6)\) for KCl, and 0.12 g/cm\(^3\) \((1.31 \text{ mol}^3/\text{dm}^9)\) for \( \text{K}_2\text{SO}_4 \).

### 2.5 Non-Spherical Particles and Fractal Dimension

When dealing with freshly emitted combustion aerosols, the particles can be agglomerated. For agglomerated particles formed by coagulation, the mass-fractal dimension, \( D_f \), is often used to describe the shape of the particles. \( D_f \) is a parameter linking radius (length scale) and mass of the population of particles over a certain size range, defined as

\[
m = C_2 \cdot r_g^{D_f} \tag{3}
\]

where \( r_g \) is the agglomerate’s radius of gyration, \( m \) is the mass of the agglomerate and \( C_2 \) a constant. The radius of gyration is defined as the average distance from aggregate center of mass to each primary particle. This relation has been well established to describe fractal like agglomerates grown in diffusion-limited processes, in both simulations and experiments (Schmidt-Ott et al. 1990). According to Schmidt-Ott et al. (1990) the relation between the radius of gyration and the mobility diameter is linearly proportional in both the continuum regime and the free molecular regime, (for \( D_f > 2 \)). The present measurements were made in the intermediate regime, but a population of particles having coagulated under the same conditions will most often not have size distributions broader than the size range where \( D_f \) is expected to be approximately constant (Schmidt-Ott et al. 1990).

The mass of an aerosol particle can also be expressed as

\[
m = \rho_{\text{bulk}} \cdot \frac{\pi}{6} \cdot d_{ve}^3 \tag{4}
\]

where \( \rho_{\text{bulk}} \) is the inherent material density of the particle material and \( d_{ve} \) the volume equivalent diameter. Consequently (from Equation 3) \( d_{ve} \), \( r_g \) and \( d_B \) are related as:

\[
r_g \propto d_B^{D_f} \propto d_{ve}^{D_f}. \tag{5}
\]

The mass of the agglomerated particles is scaled by \( d_B \) raised to \( D_f (<3) \) instead of 3. Note that larger particles in a population have a more open structure than smaller ones, and consequently higher dynamic shape factors.
3. RESULTS AND DISCUSSION

3.1 Time and Size-Resolved Analysis of Concentrations

Size distribution data from the two boilers have been described in more detail previously (Pagels et al. 2003; Wierzbicka et al. 2005). The total number concentration of emitted particles was $5.1 \times 10^7$ and $6.3 \times 10^7$ particles/cm$^3$ for 50 and 100% load, respectively, in boiler 1 and $2.9 \times 10^7$ particles/cm$^3$ for a 30% load in boiler 2. Size distributions were essentially unimodal in the measured size range (15–300 nm). The geometrical mean diameters of the fitted lognormal size distributions were 117, 90, and 77 nm. The size distributions were, in principle, stable over time, with the exception of the largest particles in boiler 2. In Figure 1, the relative standard deviation (coefficient of variation) over time of the concentration in each SMPS size channel is given. Only size channels for which the variations due to counting statistics were less than 20% of the total standard deviation were included in Figure 1. The relative standard deviation is significantly larger than 0.3 only for particles larger than 150 nm in boiler 2.

The time variations in boiler 2 were studied with higher time-resolution using the ELPI. These measurements also showed a strong increase in temporal variation with increasing particle diameter. Often there was a clear periodicity in the time variations, typically on the order of 1 min, caused by grate movements.

3.2 Size-Resolved Chemical Composition

Size-dependent information about the chemical composition is needed for comparison and interpretation of the hygroscopic properties measured on-line with the H-TDMA. Water-soluble ions detected by ion chromatography are given in Figure 2 as ion equivalent concentrations. The dominating ions were $\text{K}^+$, $\text{SO}_4^{2-}$, $\text{CO}_3^{2-}$, and $\text{Cl}^-$ in boiler 1 and $\text{K}^+$, $\text{SO}_4^{2-}$ and $\text{Cl}^-$ in boiler 2. The fraction of $\text{K}_2\text{CO}_3$ was estimated from an excess of positive ions found in the IC analyses (Pagels et al. 2003). More samples were analyzed with PIXE compared to IC. Also, the detection limit is lower, and thus, the variations in inorganic composition with particle size could be studied in more detail. The sulfur to chlorine mass ratio increased with particle size in boiler 1, while in boiler 2 it was essentially independent of particle diameter (Figure 3). The size-dependence in the S/Cl ratio seen in boiler 1 was possibly because KCl condenses later in the combustion process compared to $\text{K}_2\text{SO}_4$, and then mostly influences the composition of the smallest particles. The reason for the difference between boiler 1 and 2 is not known. We used the detected composition from IC as input to predict the hygroscopic growth with the ZSR rule. For boiler 1 a sensitivity test of the hygroscopic growth due to the size-dependent S/Cl ratio was made. The ratios were taken from the PIXE measurements.

The impactor substrates were first gravimetrically analyzed and then analyzed for IC. The mass fraction determined with IC for boiler 2, decreased from 0.7 in stages 2 and 3 (77 and 133 nm) to 0.2–0.3 in stages 5 and 6 (323 and 510 nm). The
detected fractions for both PIXE and IC increased to 0.50 for particles larger than 700 nm. However, neither PIXE nor IC can detect carbon. Wierzbicka et al. (2005) analyzed PM$_1$ samples for organic (OC) and elemental carbon (EC) in boiler 2 during the same measurement campaign. They found that OC and EC contributed, on average, to 8 and 34% of PM$_1$, respectively. The EC concentration varied by a factor of three in four different samples. The estimated SMPS mass concentration (assuming constant effective density) in the range 250–320 nm was highly correlated ($r^2 = 0.99$) with the EC concentration in individual samples. The correlation was significantly lower for 150–250 nm (0.66) and 25–150 nm particles (−0.28).

From the combined results of the different measurement techniques it was inferred that EC is enriched in particles between 150 and 700 nm. This is also in line with the observed fast temporal variations in concentrations observed with ELPI and SMPS for particles larger than 150 nm. Ash components (e.g., potassium) continuously evaporate and form smaller particles for which the temporal variations were small in both boilers.

In boiler 1, temporal variations were low for particle diameters between 150 and 400 nm. The total PAH concentration (particle and gas phase) of 29 analyzed compounds (Lillieblad et al. 2004) was very low (2.8 µg/m$^3$). Therefore, we expect the OC/EC contribution in boiler 1 to be small.

### 3.3 Hygroscopic Properties, Boiler 1

#### 3.3.1 RH Scan

In the 1 MW unit RH scans were performed for 120 and 200 nm particles at around 50% boiler load. The measured $G_{fB}$, is presented as a function of water activity in Figure 4. The particles started to take up water at low water activities and no clear deliquescent point was seen. The absence of a deliquescent point is not surprising since aerosol particles consisting of a mixture of many compounds, such as atmospheric aerosols, often display a continuous hygroscopic growth without deliquescence steps. Since the measurements do not show any indication of fractal-like behavior of the investigated particles within the H-TDMA, $d_B \approx d_{ve}$ and consequently $G_{fB} \approx G_{fve}$.

The IC analysis of the submicrometer flue gas particles showed the fine mode particles to mainly consist of KCl, K$_2$SO$_4$, and K$_2$CO$_3$. For the ZSR predictions we used a chemical composition of these compounds only, in ratios according to the IC analysis of filter samples collected in parallel with the RH scans. The composition used was in (dry) volume fractions 0.14, 0.44, and 0.42 (Figure 2).

Not taking solubility into account, the ZSR model predicts a water uptake that exceeds that observed with the H-TDMA (Figure 4). Comparing the slope of the experimental $a_w$ curve to that of the pure compounds, it can be seen that some of the particles constituents most likely go into solution as $a_w$ increases. Taking into account the low solubilities of K$_2$SO$_4$, and KCl in the ZSR prediction, the assumed mixture can reproduce the hygroscopic behavior of the flue gas particles reasonably well. Since it could be seen from the PIXE analysis that the sulfur to chloride ratio was changing as a function of size (Figure 3), a calculation was also performed doubling the fraction of KCl at the cost of K$_2$CO$_3$. The result is then even closer to the measured hygroscopic growth. KCl here goes completely into solution at a water activity of $\sim 0.80$, which can be discerned as a slight discontinuity in the calculated ZSR curve in Figure 4. Only 10% of the K$_2$SO$_4$ is in solution at $a_w \sim 0.9$.

![Figure 4](image_url) **FIG. 4.** Diameter growth factor for the RH scans performed in boiler 1 together with calculated diameter growth factor according to the ZSR mixing rule. In the model, chemical composition based on IC analysis of filter samples was used. The growth of the pure compounds is also shown.
For the time periods scanning in the RH mode, the hygroscopic behavior could thus be explained with the ZSR rule using only the inorganic compounds as main components of the particles. From the RH scans, no obvious difference in $G_{fe}$ was seen between the 120 and 200 nm particles.

### 3.3.2 Size Scan

The hygroscopic behavior was studied as a function of dry particle diameter using the size scanning mode of the H-TDMA, at 90% RH. A rather constant growth was observed, with slightly decreasing growth factors with increasing size, shown in Figure 5 and Table 1. During the scans, the boiler load was either 50 or 100%. A trend with somewhat higher hygroscopic growth at lower load was also observed.

The average hygroscopic growth factors at 90% RH are also plotted in Figure 4, here recalculated into water activity. Consequently, the higher activities in the figure correspond to the growth of the larger particles. The PIXE analysis showed that the sulfur to chlorine mass ratio increased with size (Figure 3), indicating that the smaller particles had a slightly different chemical composition (e.g., a larger fraction of KCl). Using the ZSR method and taking limited solubility into account, an increased fraction of KCl at 90% RH would result in higher hygroscopic growth factors, which is in agreement with this observation.

Overall, we can conclude that there was no larger fraction of elemental or insoluble organic carbon present, except from possibly in the larger sized particles. This is in agreement with the results presented in section 3.2.

#### 3.3.3 Internal Mixture and Temporal Variation

For the 1 MW boiler, the humidified size distribution mainly revealed unimodal growth. When multiple modes were present, they were close in growth. The variation of the hygroscopic growth within each scan is presented as the interval in $G_{fe}$ that covers 90% of each spectrum. For 110 nm particles the interval was $\pm 0.12$, to be compared to that of pure ammonium sulfate (similar growth factor), which is $\pm 0.06$. That means the broadening of each humidified size distribution was slightly larger than if the particles of one scan were perfectly internally mixed (i.e., all individual particles had similar hygroscopic growth). This suggests that the processes of nucleation, condensation and coagulation create an internally well-mixed aerosol, or that compounds of similar hygroscopic growth composed the particles. An example of a humidified size distribution at ~90% RH of 100 nm particles is shown in Figure 6. The average spread in growth factor at each dry diameter is presented together with the average growth in Table 1.

The standard deviation of $G_{fe}$ in time, presented in Table 1, indicates variations in the combustion process in time (leading to a slight variation in chemical composition), especially for the smallest and the largest particles.

#### 3.4 Hygroscopic Properties, Boiler 2

During the measurements in boiler 2 (1.5 MW pellets boiler) the load was more stable than for boiler 1, typically around 30%. The number of scans was higher. Since the time resolution of one H-TDMA scan was ~3–4 minutes, the fast events with high concentrations of EC were largely sorted out with the quality...
assurance procedure and no details of mixing status of single particles at these events could be determined.

### 3.4.1 RH Scan

For boiler 2, RH scans were made for 100, 200, and 300 nm particles. The concentrations were low and changed rapidly in the measurements for 200 and 300 nm particles. Therefore only a few spectra passed the quality criteria.

For the 100 nm particles the RH scans showed no hygroscopic growth up to \( \approx 0.5 \) in \( a_w \). At \( a_w \) around 0.5 and up to 0.78, the humidified mobility diameter decreased below the dry value (Figure 7), with a minimum in \( G_f^B \) at \( a_w \approx 0.73 \). For \( a_w \) higher than 0.8 the hygroscopic growth factor was > 1.

Since \( d_B \) of agglomerated particles is larger than \( d_{ve} \), the “shrinking” behavior between \( a_w \) 0.5 and 0.78 could be explained by restructuring of agglomerated particles into a more spherical shape while taking up only small amounts of water, when humidified within the H-TDMA. For agglomerated particles \( G_f^B < G_f^{ve} \), and the approximation \( G_f^B \approx G_f^{ve} \) would lead to a substantial underestimation of the water uptake. Since the particles tend to show a decrease in mobility diameter until \( a_w \approx 0.73 \); the particles below this water activity are not yet spherical (i.e., not liquid droplets). At higher water activities the \( G_f^B \) starts to increase, indicating that the particles above this \( a_w \) are likely to be liquid spherical droplets.

For 200 and 300 nm particles the number of accepted scans was low, as was the hygroscopic growth factor. However, these particles followed the same trend, with a somewhat stronger reshaping behavior (Figure 7). This is consistent with larger particles of a population having a more open structure (section 2.5). The reason for the hygroscopic growth below the deliquescence point of KCl can be explained by the inverse Kelvin curvature effect or the presence of other compounds, not contributing much to the growth, but still providing a small liquid phase. Previously it has been reported that agglomerate spark-discharge carbon particles, and to a smaller extent diesel soot particles, restructure to more compact particles at RH below the deliquescent point due to the inverse Kelvin effect (Weingartner et al. 1997).

The ZSR method was also applied to the boiler 2 measurements. The chemical composition used in the calculations was in volume fractions 0.70 K2SO4 and 0.30 KCl estimated from the IC analysis (chemical composition taken from the impactor...
stage with geometric mean aerodynamic diameter of 130 nm, as shown in Figure 2). However, for a meaningful comparison between \( G_f \) calculated with the ZSR method and experimental data, the measured \( G_f \) has to be converted to \( G_v \) taking into account the particle agglomerate structure. This was done using a fractal dimension, \( D_f \) of 2.49 and \( C_3 = 0.563 \) (Equation 6). The estimation of \( D_f \) and \( C_3 \) was made from the size scans as described in section 3.5.

Taking into account the limited solubility of the salts, the ZSR method can reproduce the measured growth well, as shown in Figure 7. KCl is completely in solution at 0.83 a\( _w \). Due to the limited solubility of K\( _2 \)SO\( _4 \) only 6% of K\( _2 \)SO\( _4 \) is in solution at a\( _w \sim 0.9 \).

The RH scans performed for particles from boiler 2 clearly showed a reshaping behavior while this was not seen for particles from boiler 1. The difference can be attributed to the dilution system. For boiler 2, the primary diluting air was heated, and the RH was kept low until humidification within the H-TDMA.

### 3.4.2 Size Scan

Scanning DMA 1 in size at 90% RH revealed a strong decrease in \( G_f \) from 1.46 for the 30 nm particles to 0.99 for the 350 nm particles. This decrease was observed despite the fact that the chemical composition obtained from IC analysis and the S/Cl ratio obtained from PIXE data was essentially independent of particle diameter. For particles larger than 150 nm, the decreasing growth might have been affected by the presence of EC (discussed in sections 3.1 and 3.2). For particles 100 nm and smaller the size-dependent growth is likely to be caused by the fractal-like shape of the particles. It follows from the definition of fractal dimension that larger particles have a more open structure (higher dynamic shape factors) and consequently, the observed reduction in \( G_f \) as a function of size is explained by the increasing ratio of \( d_B \) and \( d_v \) as a function of size.

### 3.4.3 Internal Mixture and Temporal Variation

The humidified size distribution in boiler 2 was in general narrow with a slight modal structure. On some occasions, often in connection with higher loads, a clearly distinguished modal structure was seen—generally clearer for the smaller sized particles. This means that the aerosol on these occasions was externally mixed, i.e., particles of the same size had different chemical composition (or morphology). Examples of humidified distributions for 100 nm particles at \( \sim 90\% \) RH are given in Figure 6.

The temporal variation of the measured hygroscopic growth was prominent, but still smaller than for boiler 1. This may be explained by smaller load changes or the use of the more homogeneous pellets fuel in boiler 2. The variation in time is presented as standard deviation of the growth factor in Table 1.

### 3.5 Fractal Dimension from H-TDMA Measurements

Often when calculating the volume equivalent diameter growth factor (\( G_{ve} \)), \( d_{ve,dry} \) is approximated by the measured \( d_{B,dry} \) (i.e. \( G_f \approx G_{ve} \)). In the case of processed atmospheric aerosols, this approximation most often only introduces minor errors. However, for agglomerated particles, such as those measured here, the errors introduced are large. In order to correctly calculate \( G_{ve} \) for agglomerated aerosol particles that can be described by a fractal dimension, the relation in Equation 5 is used, and the hygroscopic growth factor can be calculated according to:

\[
G_{ve} = \frac{d_{ve, wet}}{d_{ve, dry}} = \frac{d_{B, wet}}{\sqrt[3]{d_{B, dry}^{D_f}} \cdot C_3}
\]

where \( C_3 \) is a constant.

Assuming that the chemical composition is constant over the considered size range, then for a constant \( a_w \), \( G_{ve} \) is also...
constant over this size range. Rearranging Equation 6, an expression by which \( Df \) can be determined from the relative change in \( Gf_B \) over dry size can be derived:

\[
Df = 3 \cdot \frac{\Delta \log(d_{B, wet})}{\Delta \log(d_{B, dry})}. \tag{7}
\]

This equation is valid when the fractal dimension \( Df \) is constant over the size interval in question, and for a hygroscopic aerosol so that the particles are spherical at the \( a_w \) used. Note that \( Df \) determined with Equation 7 does not depend on the absolute \( Gf_{ve} \). For a particle population with a fractal dimension lower than 3 and chemical composition constant over size, the relation between \( Gf_B \) and \( Gf_{ve} \) (i.e., the absolute \( Gf_{ve} \)) is determined by the primary particle size (which affects the value of \( C_3 \) in Equation 6).

The size scans performed during this study were made at 90% RH, corresponding to an \( a_w \) ranging from 0.86 for the smallest particles, to 0.89 for the largest. Correcting the measured \( Gf_B \), to a constant \( a_w \) (0.88, the average in the interval of interest) a weak dependence on assumed primary particles size is introduced. From the H-TDMA measurements, we see that the primary particle size is smaller or equal to 30 nm. In the correction to a constant water activity, a primary particle size of 30 nm was used. The sensitivity to this was investigated using a primary particles size of 10 nm. The correction to \( a_w = 0.88 \) was made as described in the methods section using KCl as a model compound.

The estimation of fractal dimension from H-TDMA data was made using least squares regression analysis, fitting \( Df \) to get a constant \( Gf_{ve} \) as a function of size. The fit was performed in the range 30–100 nm since constant chemical composition over size was restricted to apply only to particles smaller than 150 nm (section 3.2). The fractal dimension was estimated to be 2.49 (2.54 not including the 100 nm particles). Using a primary particle size of 10 nm decreased the fractal dimension by 0.02.

As discussed, the fitted fractal dimension only weakly depends on the absolute \( Gf_{ve} \). However, to determine \( Gf_{ve} \) we have to assume a primary particle size. The lower limit of \( Gf_{ve} \) is set by the growth of the 30 nm particles. Assuming spherical 30 nm particles, \( C_3 \) was fitted to 0.563 (0.592 using 30–75 nm). Inserting \( C_3 \) and \( Df \) in Equation 6, \( Gf_{ve} \) was calculated and is shown together with \( Gf_B \) in Figure 8. It is worth noting that if the 30 nm particles also had an agglomerated structure, the real water uptake would be underestimated and our estimate of \( Gf_{ve} \) would be a lower limit. The estimated \( Df \) and \( C_3 \) result in dynamic shape factors (Hinds 1999) of 1.42, 1.65, and 1.84 (mobility diameters) for 100, 200, and 300 nm particles, respectively. In Figure 8 it can be seen that when the larger particles (>150 nm) were corrected to the same fractal dimension as particles <150 nm in diameter, these larger particles had a somewhat lower \( Gf_{ve} \) than expected if the chemical composition was constant over size; not as low, however, as for an aerosol dominated by soot. This is either because the intermittent events with high soot concentration are sorted out by the quality assurance procedure (restrictions in the variation in concentration during one scan) or due to a different fractal behavior of these particles.

The estimated \( Df \) and \( C_3 \) were also applied to the RH scans, to recalculate the hygroscopic growth. The recalculated growth was used in the comparison with the result from the ZSR method. The agreement was good when using the recalculated growth (see previous section and Figure 7) indicating that the primary particle size may be close to 30 nm.

Recently De Carlo et al. (2004) distinguished between two different values of the fractal dimension in a single aerosol population, depending on the number of primary particles in the agglomerate. The fractal dimension was 2.46 for fewer primary particles than 60 and 1.79 for larger agglomerates. For diesel soot with a primary particle size of 33 nm, the break point between the two regions was around 165 nm. The value for agglomerates of less than 60 primary particles is in agreement with our estimation for 30–100 nm particles (2.49). We also found a lower fractal dimension for larger particles (2.37) in the size range 100–300 nm.

Pagels (2005) varied the temperature in a similar ejector sampling system in a larger boiler operated with moist forest residue. It has been found that dried particle samples decreased their mobility diameter on average 20% when the particles experienced high RH during sampling. Larger particles shrank more than smaller ones. The fractal dimension of dry sampled particles was estimated to be 2.5–2.6 (and that of humid sampled particles 3.0–3.1) with the SMPS-ELPI distribution fitting method. In that study the elemental carbon concentration was negligible. A partial restructuring process occurred at temperatures above 400°C in experiments incorporating a thermodesorber.

In previous electron microscopy analyses (Valmari et al. 1999) it was concluded that particles from CFB combustion are spherical or compact. This was explained by transformation
through condensation in preference to coagulation. The agglomerated structure found in in-situ measurements suggests that coagulation is a strong transformation process and that the nucleation rate and the initial number concentrations are higher in the moving grate boiler than what would be the case for an aerosol mainly formed by condensation. In-situ measurements performed on airborne particles avoid uncertainties caused by sample storage or exposure to the electron beam in an electron microscope. Krämer et al. (2000) used an H-TDMA to show that NaCl particles generated from the gas phase in a laminar flow reactor were highly agglomerated and that even at an RH significantly below the deliquescent point, particle compaction occurred (NaCl has a vapor pressure similar to KCl). Dynamic shape factors assessed from mobility changes and hygroscopic growth models were in the order of 4–5.

4. SUMMARY AND CONCLUSIONS

The flue gas particles emitted from two biomass combustion units had, in contrast to other combustion aerosols such as diesel exhaust particles, relatively high hygroscopic growth factors. This is explained by the particle composition dominated by potassium salts (KCl, K2SO4, and K2CO3). The average volume equivalent diameter growth factor at RH = 90%, for 110/100 nm particles, was 1.68 in boiler 1 and ∼1.5 (uncorrected growth 1.24) in boiler 2. For both boilers the particles were internally well-mixed, except on some occasions in boiler 2, when a second more hygroscopic mode appeared. The temporal variation in growth factor for the 110/100 nm particles was 0.10 (1 std. dev.) and 0.07 for boilers 1 and 2, respectively.

The volume equivalent diameter growth factor could be reproduced surprisingly well by the modeled growth using the ZSR method, where the chemical composition was assumed on the bias of IC and only inorganic ions were considered. The consistency between measured and modeled hygroscopic growth was found for both boilers.

Fast temporal variations in the size spectrometer (both ELPI and SMPS) measurements identified as EC enriched particles were observed for particles larger than 150 nm in the 1.5 MW boiler. These observations were consistent with filter measurements of EC/OC published previously (Wierzbicka et al. 2005) and size-resolved recovered mass fractions from ion chromatography. The mixing status at these occasions is not known since events with fast variations were sorted out in the H-TMDA quality procedure.

In boiler 2 the measured \( Gf_B \) decreased strongly with increasing particle size, while the chemical composition was largely independent for particle sizes in the range 30–100 nm. Furthermore, 100 nm particles decreased their mobility diameter by around 10% at RH ∼75% before growing to solution droplets. These results were attributed to particles changing the morphology from agglomerated structures to droplets when humidified, leading to an underestimation of the water uptake if assuming \( Gf_B = Gf_{ve} \). A method was developed to estimate and correct for the fractal dimension of hygroscopic agglomerated particles. From our H-TDMA data, the fractal dimension was estimated to ∼2.5, which is somewhat higher than the value of 2.35 for diesel engines (Park et al. 2004), indicating more compact particles. No indication of agglomerate particles shape was seen for boiler 1. This was attributed to a different sampling system used, where the particles experienced high RH already during sampling.

Since the solubility of K2SO4, a salt often formed in biomass combustion, is limited, it is important to take the low solubility into account when extrapolating the hygroscopic growth from water vapor saturations to supersaturations relevant for cloud processes or the humidity in our lungs. Estimating the number of soluble ions from the hygroscopic growth at 90% RH would lead to a significant underestimation of the hygroscopic growth, since at 90% RH only ∼60% (boiler 1) and 35% (boiler 2) of the particle was in solution even though the soluble volume fraction was close to 1. This is, however, most likely only a problem when dealing with an aerosol constituted of only a few compounds and of low solubility.

The environmental importance of the observation with high hygroscopic growth of the flue gas particles is mainly related to the atmospheric residence time of the emitted particles. Hygroscopic particles are more easily incorporated in cloud and raindrops, leading to a higher probability of wet deposition and thus a shorter residence time in the atmosphere, compared to a hydrophobic particle of the same dry size. From a human health aspect, the deposition pattern of the particles in the humid environment of the human respiratory system (RH close to 99.5%) is strongly affected by the hygroscopic properties of the inhaled aerosol particles. The growth in diameter inside the lungs for 100 nm particles from both boilers would be ∼4.5 leading to an increase in volume of 90 times (assuming ideal solutions). For the number size distribution, a reduction in total respiratory deposition of a factor of 2–3 is obtained for the aerosols considered in this paper according to the ICRP model, by assuming RH = 99.5% throughout the respiratory tract.

REFERENCES


