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**Hygroscopic properties of
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Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol

**M. Gysel¹, E. Weingartner¹, S. Nyeki¹, D. Paulsen¹, U. Baltensperger¹,
I. Galambos², and G. Kiss³**

¹Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

²Department of Earth and Environmental Sciences, University of Veszprém, 8201 Veszprém, Hungary

³Air Chemistry Group of the Hungarian Academy of Sciences, University of Veszprém, 8201 Veszprém, Hungary

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Correspondence to: E. Weingartner (ernest.weingartner@psi.ch)

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Ambient continental-rural fine aerosol (K-pusztá, Hungary, $PM_{1.5}$) was sampled on quartz fibre filters in winter and summer 2001. Water-soluble matter (WSM) was extracted in MilliQ-water, and, in a second step, solid phase extraction was used to isolate the less hydrophilic fraction (ISOM) of the water-soluble organic matter (WSOM) from inorganic salts and remaining most hydrophilic organic matter (MHOM). This approach allowed to investigate a major fraction of WSOM isolated in pure form from ambient aerosols. Hygroscopic properties of both WSM and ISOM extracts as well as of aquatic reference fulvic and humic acids were investigated using a Hygroscopicity Tandem Differential Mobility Analyser (H-TDMA). ISOM deliquesced between 40–60% and 30–55% relative humidity (RH), in winter and summer, respectively, and hygroscopic growth factors at 90% RH were 1.08–1.11 and 1.16–1.17. The hygroscopicity of ISOM is comparable to secondary organic aerosols obtained in smog chamber experiments, but lower than the hygroscopicity of highly soluble organic acids. Hygroscopic behaviour of investigated fulvic and humic acids had similarities to ISOM, but hygroscopic growth factors were slightly smaller and deliquescence was observed at higher RH (75–85% and 85–95% RH for fulvic acid and humic acid, respectively). These differences probably originate from larger average molecular weight and lower solubility of fulvic and humic acids.

Inorganic composition data, measured ISOM hygroscopicity, and a presumable value for the hygroscopicity of the small remaining MHOM fraction were used to predict hygroscopic growth of WSM extracts. Good agreement between model prediction and measured water uptake was observed with differences (by volume) of +1% and –5% in winter, and –18% and –12% in summer. While deliquescence properties of WSM extracts were mainly determined by the inorganic salts (42–53 wt % of WSM), the WSOM accounted for a significant fraction of particulate water. At 90% RH, according to model predictions and measurements, about 80% (62%) of particulate water in winter (summer) samples are associated with inorganic salts and about 20% (38%) with WSOM.

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The relative contributions of both distinguished WSOM fractions, ISOM and MHOM, remains uncertain since MHOM was not available in isolated form, but the results suggest that the less abundant MHOM is also important due to its presumably larger hygroscopicity.

1. Introduction

Hygroscopic growth of atmospheric aerosol particles plays an important role in numerous atmospheric processes such as climate forcing, visibility degradation, cloud formation and heterogeneous chemistry. In recent years the influence of inorganic salts on these effects has been mainly investigated. Only several inorganic salts constitute the major part of the inorganic aerosol fraction (Heintzenberg, 1989), which is relatively well-characterised regarding its hygroscopic properties (Clegg et al., 1998; Ansari and Pandis, 1999). However, recent experimental and modelling studies strongly indicate that water-soluble organic matter (WSOM) contained in atmospheric aerosol particles is also important. It was also suggested, based on the partitioning of WSOM and water-insoluble organic matter (WINSOM) between fog droplets and interstitial aerosol particles, that WSOM plays an important role in the droplet nucleation process (Faccini et al., 1999). Furthermore organic species are potential candidates to delay or inhibit efflorescence (Choi and Chan, 2002a) of atmospheric aerosols.

WSOM, in contrast to the inorganic aerosol fraction, is composed of hundreds (or even thousands) of individual species (Saxena and Hildemann, 1996), where each contributes only a small mass fraction towards WSOM. Different approaches are generally used to determine the influence of WSOM on the hygroscopic behaviour under subsaturated RH conditions of ambient aerosols. Previous laboratory studies, investigating the hygroscopic properties of organic model substances, have mostly focused on pure and mixed low molecular weight organic acids such as carboxylic acids, dicarboxylic acids, and multifunctional organic acids or their salts (Na et al., 1995; Peng et al., 2001; Peng and Chan, 2001; Prenni et al., 2001; Choi and Chan, 2002b), and

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on their mixtures with inorganic salts (Cruz and Pandis, 2000; Lightstone et al., 2000; Choi and Chan, 2002a; Choi and Chan, 2002b; Hämeri et al., 2002). First theoretical models for the prediction of the hygroscopic growth of mixed inorganic/organic aerosols were recently introduced by several investigators (Clegg et al., 2001; Ming and Russell, 2001; Ming and Russell, 2002). The hygroscopic properties of artificial secondary organic aerosol obtained by oxidation of typical volatile organic precursors in smog chambers have also been investigated (Virkkula et al., 1999; Cocker III et al., 2001a; Cocker III et al., 2001b; Saathoff et al., 2003). Apart from the hygroscopic properties of organics under subsaturated conditions, their cloud condensation nuclei activity under supersaturated conditions has also been investigated in recent studies (Cruz and Pandis, 1997; Cruz and Pandis, 1998; Corrigan and Novakov, 1999; Prenni et al., 2001; Giebl et al., 2002).

It is more difficult to determine the influence of WSOM in real ambient particles. Towards this aim, hygroscopicity measurements are generally combined with chemical analysis of the inorganic and organic aerosol fractions. Excess water, which cannot be explained by the water uptake of the inorganic aerosol fraction, is then attributed to the organic aerosol fraction. Depending on the sampling location, considerable amounts of excess water have been reported in field studies by (Saxena et al., 1995; Swietlicki et al., 1999; Dick et al., 2000; Speer et al., 2003) when using this method.

The solid phase extraction method, recently developed and characterised by Varga et al. (2001), allows a major fraction of WSOM (so-called isolated organic matter, ISOM, mainly less hydrophilic compounds) to be isolated from total water-soluble matter (WSM). Several studies on ISOM from atmospheric aerosols at the high alpine site Jungfraujoch, Switzerland (Krivácsy et al., 2001) and at the continental-rural site K-puszta, Hungary (Varga et al., 2001; Kiss et al., 2002; Galambos et al., 2003) showed that ISOM mainly consists of humic-like substances and that it contributes up to 70 wt % to WSOM. The remaining smaller fraction of WSOM, which cannot be isolated from inorganic salts so far, consists of the most hydrophilic organic matter (MHOM). Figure 1 illustrates the classification scheme defined according to the chemical characterisa-

tion applied in this study. A complete list of acronyms and symbols is provided in the glossary (Sect. 6).

In order to further characterise the water-soluble organic aerosol fraction, WSM and ISOM were extracted from fine aerosol filter samples obtained during summer and winter field campaigns at the Hungarian Global Atmosphere Watch (GAW) site K-pusztá. These WSM and ISOM extracts were characterised by Galambos et al. (2003) and Nyeki et al. (2003) regarding their chemical properties and volatility, respectively, and their hygroscopic properties were investigated in this study using a Hygroscopicity Tandem Differential Mobility Analyser (H-TDMA) (Rader and McMurry, 1986). Hygroscopic properties of aquatic reference fulvic and humic acids were also investigated for comparison with ISOM, since ISOM has been shown to have many chemical similarities with humic substances. Furthermore, comprehensive chemical information about the WSM samples and measured ISOM properties were used to model the hygroscopic growth of WSM in order to assess the contribution of WSOM to the total particulate water. Apart from these main topics, these experiments revealed unusual hysteresis behaviour of the humic substances and ISOM samples, which was further investigated in specific hydration/dehydration experiments.

2. Experimental methods

2.1. Aerosol sampling, sample preparation and chemical characterisation

Details about aerosol sampling and may be found elsewhere (Galambos et al., 2003). Briefly, two winter and two summer fine aerosol Hi-Vol samples ($PM_{1.5}$, particulate matter with diameter $D \leq 1.5 \mu m$) were collected in 2001 at the continental-rural site K-pusztá, Hungary. Samples are defined here as “KPYMMDD”, indicating the sampling site and the start date of sampling. Aqueous WSM was obtained by soaking portions of the aerosol filters in MilliQ-water. Solid phase extraction (Varga et al., 2001) was used in a second step in order to separate water-soluble atmospheric humic matter

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(ISOM, less hydrophilic under acidic conditions) from inorganic salts. However, organic compounds that were very hydrophilic under acidic conditions (MHOM) could not be isolated from inorganic salts. Detailed chemical characterisation of PM_{1.5}, WSM, and ISOM was performed by Galambos et al. (2003).

Figure 1 illustrates the mean composition of the investigated aerosol samples as obtained by Galambos et al. (2003). A large fraction of PM_{1.5} is composed of WSM (~76 wt %), including inorganic salts (~36 wt %) as well as WSOM (~40 wt %). The water-insoluble fraction (~24 wt %) consists of WINSOM and black carbon (BC). The sum of all carbon containing species is defined as total carbonaceous matter (TCM).

Investigated reference materials were aquatic Nordic reference fulvic and humic acids (NRFA and NRHA, respectively, International Humic Substances Society IHSS, product No. 1R105F and 1R105H, isolated from Hellrudmyra tarn, Norway) and Aldrich humic acid sodium salt (NaHA, product No. H16752, isolated from crude lignite).

2.2. Aerosol generation

ISOM and WSM extracts had to be transformed into aerosol particles again in order to perform hygroscopicity measurements using the H-TDMA technique. WSM solutions were directly obtained in the form of aqueous extracts (see above) with concentrations of about 140–290 mg/l. Dry ISOM extracts were dissolved in MilliQ-water, by using an ultrasonic bath for about 20 min. Resulting concentrations were about 160–350 mg/l for the ISOM extracts. Dry NRFA, NRHA and NaHA samples were dissolved in MilliQ-water without using an ultrasonic bath. However, NRFA and NRHA could not be completely dissolved with this method. In order to remove suspended undissolved particles, all WSM, ISOM and reference solutions were filtered through a syringe membrane with a 0.22 µm pore size (Millex GV 13 mm, Millipore, USA). Artificial aerosol particles were then generated by nebulization of the solutions, and subsequently dried (RH < 25%) in a silica gel diffusion dryer with a residence time of about 300 s. The nebulizer (TSI 3076 type) was operated with artificial air (80% N₂ > 99.999%, 20% O₂ > 99.995%). Dried aerosol particles were neutralised and fed into the H-TDMA for the hygroscopic-

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icity measurement. Aerosols generated with this procedure are internally mixed, and the chemical composition of the individual particles is representative of the PM_{1.5} average WSM or ISOM composition. Scanning Electron Microscopy (SEM) micrographs of ISOM (KP010126) and NRFA particles with dry diameters of $D_0 \approx 100$ nm (selected using a Differential Mobility Analyser (DMA) and sampled on nucleopore filters) are shown in Fig. 2. Dry particles from all samples were found to be nearly spherical.

2.3. Hygroscopicity measurement

The hygroscopic growth factor g of a particle is defined as

$$g(\text{RH}) = \frac{D(\text{RH})}{D_0}, \quad (1)$$

where D_0 is the particle dry diameter, and $D(\text{RH})$ is its diameter at a specific RH. The hygroscopic growth factor g indicates the relative size increase of particles due to water uptake. The H-TDMA system (Fig. 3) is described in detail by Weingartner et al. (2002) and Gysel et al. (2002). An additional prehumidifier was used in this study, and is described later. Briefly, a monodisperse fraction ($D_0 \approx 100$ nm) of dried neutralised (⁸⁵Kr bipolar charger) aerosol particles was selected with a first DMA (DMA1; TSI 3071). This monodisperse aerosol was then humidified, and the resulting particle size after humidification was measured by scanning the whole size range with a second DMA (DMA2) and a Condensation Particle Counter (CPC, TSI model 3022).

Mean diameter D_m and standard deviation σ (normal distribution) were obtained using an inversion algorithm based on the original TDMAFIT QBASIC program by Stolzenburg and McMurry (1988). The H-TDMA was kept at a constant temperature $T \sim 25^\circ\text{C}$ (DMA2 was submersed in a well-mixed water bath), and the relevant RH (RH_{DMA2}) was determined by measurement of the system temperature and DMA2 sheath air dew point using a dew point mirror (Edge Tech, Model DewPrime II). At constant conditions the RH accuracy is $\Delta\text{RH}_{\text{DMA2}} = \pm 1.2\%$ at 95% RH. Both DMAs were operated with a closed loop sheath air setup, which allowed the growth factor to be de-

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terminated with an accuracy of $\Delta g \approx \pm 0.003$. The humidification section consisted of an optional prehumidifier and a follow-on RH-conditioner. RH values after the prehumidifier (RH_P) and after the RH-conditioner (RH_C) were also monitored using capacitive RH sensors. Due to the closed loop setup, RH_{DMA2} equilibrates with RH_C after a time delay of a few minutes for small RH_C changes (cf. Fig. 4). Four measurement modes can be selected depending on the settings of RH_P and RH_C . Figure 4 shows a time series of RH_P , RH_C , and RH_{DMA2} during a complete measurement cycle (NRFA). The four different H-TDMA modes are:

- Dry reference diameter D_0 (Fig. 4a): This mode is used to measure the dry reference diameter D_0 of the particles selected with the first DMA. Both humidifiers are switched off. The RH throughout the whole H-TDMA equilibrates with the incoming dry aerosol air, i.e. RH_P , RH_C , and RH_{DMA2} are lower than 5%. In this case the particles do not undergo any change, and the diameter D_0 measured in DMA2 represents precisely the (electrical mobility) diameter of the dry particles selected with DMA1. D_0 is used as the reference diameter for all experimental growth factors g (cf. Eq. 1).
- Growth factors under decreasing RH conditions $g_{decr}(RH)$ (Fig. 4b): This mode is used to measure hygroscopic growth factors during dehydration. The prehumidifier is set to a high RH ($RH_P \geq 95\%$), and RH_C is successively increased. In this case $RH_P \geq RH_C \geq RH_{DMA2}$, i.e. the particles undergo strictly decreasing RH conditions, while passing through the instrument. Hence growth factors are labelled as $g_{decr}(RH_{DMA2})$. RH_{DMA2} increases slowly during the measurement of growth factors under decreasing RH conditions since the aerosol air introduces additional humidity in the closed-loop sheath air flow ($RH_C \geq RH_{DMA2}$).
- Growth factors under increasing RH conditions $g_{incr}(RH)$ (Fig. 4c): This mode is used to measure hygroscopic growth factors during hydration. The prehumidifier is bypassed ($RH_P \leq 5\%$), and RH_C is successively decreased. In this case is $RH_P \leq RH_C \leq RH_{DMA2}$, i.e. the particles undergo strictly increasing RH condi-

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tions, while passing through the instrument. Hence growth factors are labelled as $g_{incr}(RH_{DMA2})$. RH_{DMA2} decreases slowly during the measurement of growth factors under increasing RH conditions since the aerosol air reduces the humidity of the closed-loop sheath air flow ($RH_C \leq RH_{DMA2}$).

- 5 – RH-dependent restructuring of the particles $g_{restr}(RH)$ (Fig. 4d): This measurement provides the so-called restructuring factor $g_{restr}(RH_P)$, i.e. the size change of initially dry particles if they are exposed to a certain RH_P , and dried up again. The RH in the prehumidifier is varied, while the RH-conditioner is used as a dryer (RH_C and $RH_{DMA2} \leq 5\%$).

10 3. Theory

Three fundamentally different models are used in this study. The suitability of the theoretical ideal solution model and the empirical γ -model to provide parameterisations of the experimentally observed hygroscopic growth characteristics is compared and evaluated. In addition, the ideal solution model provides a rough estimate of the average molecular weight of the ISOM. The aim of the more sophisticated mixed particle model is to make a “hygroscopicity closure”, i.e. to investigate the individual contributions of the inorganic, ISOM, and MHOM fractions to the hygroscopic growth of the WSM samples.

3.1. Ideal solution model

20 The hygroscopic growth of soluble particles as a function of RH is described by the Köhler theory (Pruppacher and Klett, 1997; Seinfeld and Pandis, 1998). For an ideal solution the equilibrium RH above a flat surface is equal to the mole fraction x_w of water in the solution (Raoult’s law). Generally Raoult’s law is valid for diluted solutions, i.e. large growth factors close to or above water vapour saturation, while care has to be taken at lower RH. In this study the ideal solution model is used as the best possible

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approach to describe the hygroscopic growth of ISOM samples, since no information about real water activity values is available. For the case of a spherical droplet of diameter D , the Kelvin correction factor S_{Kelvin} accounts for the water vapour pressure increase over a curved surface. The resulting relation between the equilibrium RH and the droplet diameter D for an ideal solution is (Köhler equation):

$$RH = x_w(D) \cdot S_{Kelvin}(D) = x_w(D) \cdot \exp\left(\frac{4M_w\zeta}{RT\rho_w D}\right), \quad (2)$$

where M_w and ρ_w are the molar weight and the density of water, ζ is the surface tension of the solution, R is the ideal gas constant, and T [K] is the temperature. Due to lack of information the solution surface tension ζ is approximated by the surface tension of pure water. This has less effect on theoretical growth factors g_{th} under subsaturated RH conditions, but the use of Eq. (2) under supersaturated conditions to estimate critical supersaturation and diameter values would profit from more precise ζ values. Generally the mole fraction x_w is defined as:

$$x_w = \frac{n_w}{n_w + n_s}, \quad (3)$$

where n_w is the molar number of water molecules and n_s is the number of solute molecules (or ions if the molecules dissociate in aqueous solution). The mole fraction x_w of a droplet depends on g_{th} and the average molar volume per solute molecule (or ion) v_s :

$$x_w(g_{th}, v_s) = \frac{g_{th}^3 - 1}{g_{th}^3 - 1 + \frac{M_w}{\rho_w v_s}}. \quad (4)$$

Equation (4) includes the approximation, that the volume change due to mixing is zero, independent of solution concentration, i.e. the solute and solvent volumes are additive. Equation (2) determines the equilibrium mole fraction x_w of an ideal solution at a given RH, and Eq. (4) relates this concentration to the corresponding theoretical hygroscopic

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growth factor g_{th} . v_s , the only parameter determining the hygroscopicity of an ideal solution, is used to fit theoretical growth curves to experimental results obtained for ISOM. v_s depends on the solute average molar weight M_s , density ρ_s , and van't Hoff factor i_s of the solute:

$$v_s = \frac{M_s}{\rho_s \cdot i_s}. \quad (5)$$

The van't Hoff factor i_s is equal to the number of dissociated ions per molecule. Equation (5) was used to obtain an estimate of M_s from fitted v_s values, whereas values assumed for ISOM density ($\rho_{ISOM} = 1500 \text{ kg/m}^3$) and van't Hoff factor ($i_{ISOM} = 1$) are discussed below.

3.2. Empirical γ -model

The empirical γ -model is frequently used in literature (Swietlicki et al., 2000; Peng et al., 2001; Weingartner et al., 2002; Massling et al., 2003) to describe the hygroscopic growth of ambient as well as that of organic particles. It is a simple one-parameter relation:

$$g_{th} = (1 - \text{RH}/100\%)^{-\gamma}, \quad (6)$$

where γ is the model parameter. Even though this model is restricted to $\text{RH} < 100\%$, it is quite useful to quantify the hygroscopic growth of aerosol particles. γ was determined for all samples by fitting the model to experimental growth factors at 90% RH. The overall RH dependence of experimental growth factors measured in this study is generally better reproduced by the ideal solution model compared to the γ -model (see below), but nevertheless the latter is included here, since it allows a comparison with results from other studies.

3.3. Mixed particle model

The hygroscopic growth factor g_{WSM} of a mixed WSM particle can be estimated from the growth factors g_{Inorg} , g_{ISOM} , and g_{MHOM} of “pure” inorganic, ISOM, and MHOM particles, and from their respective volume fractions ε_{Inorg} , ε_{ISOM} , and ε_{MHOM} in the mixed particle:

$$g_{WSM} = \left(\varepsilon_{Inorg} g_{Inorg}^3 + \varepsilon_{ISOM} g_{ISOM}^3 + \varepsilon_{MHOM} g_{MHOM}^3 \right)^{1/3} \quad (7)$$

Equation (7) is equivalent to the Zdanovskii-Stokes-Robinson relation (ZSR relation, Chen et al., 1973), it includes the approximation of independent hygroscopic behaviour of the inorganic, ISOM, and MHOM fractions. Hygroscopic properties of mixtures of carboxylic, dicarboxylic, or multifunctional organic acids with single inorganic salts under subsaturated RH conditions have been previously investigated in laboratory experiments by Hansson et al. (1998), Cruz and Pandis (2000), Lightstone et al. (2000), Choi and Chan, (2002b), Hämeri et al. (2002), and Chan and Chan (2003). Experimental results often indicate fair agreement with ZSR predictions, but according to a more detailed analysis of literature data (Chan and Chan, 2003) positive or negative interactions between organic and inorganic compounds are likely, depending on mixed species and concentrations.

In this study, $g_{ISOM}(RH)$ is experimentally determined. The growth factor of the MHOM fraction is not known, but a value of $\gamma = 0.163$ (empirical γ -model) is representative of highly soluble organic acids (Peng et al., 2001) such as malonic acid (dicarboxylic acid), citric acid, malic acid and tartaric acid (hydroxy-carboxylic acids). Hence growth factors calculated with $\gamma_{MHOM} = 0.163$ are used as a best guess for $g_{MHOM}(RH)$. The composition of the inorganic fraction is known from the chemical analysis of the WSM samples (Galambos et al., 2003). Excess anions were compensated by H^+ to adjust the charge balance. The thermodynamic aerosol inorganics model (AIM) by Clegg et al. (1998; <http://www.hpc1.uea.ac.uk/~e770/aim/aim.htm>) for the $H^+ - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O$ system (AIM2-III) was used to determine

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corresponding growth factors g_{Inorg} . The minor cations Ca^{2+} and K^+ were replaced by a proper amount of Na^+ since they are not supported by AIM2-III.

The overall hygroscopic growth of the WSM samples was modelled (Eq. 7) with the growth factors g_{Inorg} , g_{ISOM} , and g_{MHOM} of the three WSM fractions (curves “Inorganic+ISOM+MHOM” in Figs. 6 and 7). The contribution of the inorganic fraction (curve “Inorganic”) was determined by treating the ISOM and MHOM fractions as inert with respect to water uptake (i.e. $g_{ISOM} = 1$ and $g_{MHOM} = 1$). Analogously, the curves “ISOM”, “MHOM”, and “Inorganic+ISOM” were calculated. A discussion of assumptions and approximations which affect all these model curves follows.

The conversion of measured carbon mass fractions into organic volume fractions (ε_{ISOM} , and ε_{MHOM}) depends on the organic matter to carbon mass conversion factors, determined by Galambos et al. (2003, see Sect. 4.1) and on the densities ρ_{Inorg} , ρ_{ISOM} , and ρ_{MHOM} . Due to a lack of information a value of 1500 kg/m^3 , which is appropriate for carboxylic and multifunctional organic acids (Saxena et al., 1995; Peng et al., 2001) was assumed for ρ_{ISOM} , and ρ_{MHOM} . The density ρ_{Inorg} was determined from the volume weighted average of the individual salts, which are present in the dry particle according to the AIM output. However, salts effectively present in the solid particle may differ from the thermodynamic AIM prediction, which is a Gibbs free energy minimization, but fortunately ρ_{Inorg} depends only slightly on the various salt combinations that are theoretically possible for a given ion composition. The solution density ρ_{sol} is approximated by the ratio of total mass to total volume of added inorganic, ISOM, MHOM and water fractions, assuming that the volume of mixing is zero. The replacement of Ca^{2+} and K^+ cations by Na^+ has little effect on g_{Inorg} due to their small abundance compared to the major ions. Apart from the unknown accuracy of the ZSR relation for these organic/inorganic WSM mixtures, modelled growth curves are most sensitive to the value of ρ_{ISOM} , since it directly changes the volume fraction of less hygroscopic ISOM (ε_{ISOM}) and that of distinctly more hygroscopic inorganic salts (ε_{Inorg}) in opposite direction.

3.4. Mobility correction factor f

Equations (2) and (4) (ideal solution model), Eq. (6) (γ -model), and Eq. (7) (mixed particle models) describe theoretical growth factors g_{th} in terms of volume equivalent diameters. Experimental results achieved with the H-TDMA are measured and presented in terms of electrical mobility diameters. To compare modelled growth factors g_{mod} with experimental results, a mobility correction factor f is introduced for g_{th} :

$$g_{mod} = f \cdot g_{th}. \quad (8)$$

Possible effects included in f are:

- Liquid particles at sufficiently high RH are spherical and compact, and hence volume equivalent and measured electrical mobility diameters are equal. Dry particles are also nearly spherical but cracks or cavities in the particle structure cannot be excluded (despite of the spherical shape seen in Fig. 2) and are possible, since large droplets leaving the nebuliser are suddenly exposed to very low RH in the diffusion dryer, leading to very fast water evaporation and crystallization of the particles. Such particles have dynamic shape factors larger than 1, resulting in dry mobility diameters, D_0 , larger than the corresponding volume equivalent diameters. Theoretical growth factors have to be adjusted with a correction factor $f \leq 1$ to account for such an overestimation of experimental dry diameters D_0 .
- The correction factor f also accounts for possible deficiencies of the assumption that the volume of mixing of deliquescent particles is zero, i.e. that the individual species volumes are additive in solution.

For the ISOM and the reference humic substances the correction factor f is chosen as the experimental value

$$f = g_{decr}(\text{RH}_{DMA2} \leq 5\%) \equiv (\text{RH}_p \geq 95\%), \quad (9)$$

since it is assumed that restructured particles at $\text{RH}_{DMA2} \leq 5\%$ are spherical and compact after the previous cycle of deliquescence ($\text{RH}_p \geq 95\%$) in the prehumidifier and

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subsequent drying in the RH-conditioner ($RH_C \leq 5\%$). Since no growth factors under decreasing RH conditions are available for the WSM samples, the correction factor f is chosen as the smallest measured growth factor under increasing conditions in this case. The mobility correction factor is always applied to the ideal solution model, the empirical γ -model, and the mixed particle model. However, modelled growth factors g_{mod} corrected with a RH independent mobility correction factor f are comparable only with experimental results of deliquescent particles at sufficiently high RH or under decreasing RH conditions, since the dynamic shape factor does not change substantially before deliquescence.

4. Results and discussion

4.1. Chemistry of atmospheric samples

A summary of $PM_{1.5}$ chemical composition as determined for the investigated samples by Galambos et al. (2003) is given in Table 1. It is assumed that $PM_{1.5}$ at K-pusztá is dominated by inorganic salts and carbonaceous matter (i.e. $PM_{1.5} = \text{inorganic salts} + \text{TCM}$), as it has been found in earlier mass closure experiments by Zappoli et al. (1999). Total mass concentrations of inorganic salts were directly measured using ion-chromatography while mass concentrations of carbonaceous species were determined by multiplication of the measured carbon mass concentration with mass conversion factors suitable for each class of compounds. ISOM mass conversion factors were between 1.81 and 1.91 as determined for each sample by elemental analysis (Galambos et al., 2003). General conversion factors of 2.3, 1.6 and 1.1 were applied for MHOM, WINSOM, and BC, respectively (Kiss et al., 2002). The apportionment of total water-insoluble carbonaceous matter into WINSOM and BC was not determined for all samples (Galambos et al., 2003), but this does not affect mass fractions of WSOM which are important for growth modelling (see below). Thus, only TCM (= WSOM + WINSOM + BC) mass concentrations are somewhat uncertain for KP010126 and

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KP010726. About 70% and 85% of $PM_{1.5}$ winter and summer samples, respectively, are water-soluble. The water-soluble mass itself is on average composed of 47% inorganic salts, 36% ISOM, and 17% MHOM with small seasonal differences except for a small trend towards a larger organic fraction in summer.

5 4.2. Hygroscopicity of atmospheric WSM and ISOM samples

Growth factors g , mobility correction factors f and model parameters γ of all investigated WSM and ISOM extracts are listed in Table 2. In the following, results will be discussed with respect to humidograms obtained for each summer and winter sample. The hygroscopic behaviour of the KP010816-ISOM and -WSM extracts under increasing RH conditions is illustrated in Fig. 5. WSM is seen to be distinctly more hygroscopic compared to ISOM. Starting at dry conditions, there is first a small size decrease at around 20% RH to a growth factor of $g_{WSM} = 0.96$. This small restructuring is attributed to a mobility effect, i.e. a reduction of the dynamic shape factor when a first fraction (supposably organic) of the WSM particle is dissolved and a spherical particle is formed, and possibly also to a negative volume of mixing with water (cf. discussion of Fig. 10). Hence the smallest detected growth factor at low RH is chosen as the mobility correction factor f for the WSM samples (see above). At $RH > 25\%$ there is continuous water uptake onto WSM particles, resulting in a growth factor of $g_{WSM} = 1.49$ at 90% RH. While the initial size decrease at low RH is common for all four WSM extracts, the two winter samples exhibited a more gradual growth characteristic between 40 and 80% RH in contrast to the continuous growth of both summer samples (cf. also Figs. 6 and 7). This different deliquescence behaviour between summer and winter samples probably arises from seasonal differences of the inorganic composition. For example ammonium nitrate is practically absent in summer due to its volatility (Galambos et al., 2003). At $RH > 70\%$ values, hygroscopic growth factors are comparable for summer and winter WSM extracts.

ISOM exhibits no distinct growth below 50%, but the particle size increases continuously at $RH > 50\%$, resulting in growth factors of $g_{ISOM} = 1.11$ and 1.17 at 85 and 90%

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RH, respectively. However, g_{ISOM} was slightly larger in summer than in winter (see Table 1). Possible reasons for this difference are varying precursor substances, i.e. more anthropogenic influence in winter, and faster (photo-)chemical oxidation in summer. Small differences were also observed in the chemical composition, as total mass to carbon mass ratios were slightly larger in the summer ISOM samples (Galambos et al., 2003). Hygroscopic growth factors of ISOM are comparable to the hygroscopicity of secondary organic aerosol mass, which was obtained in recent smog chamber studies by oxidation of α -pinene, β -pinene, limonene, m-xylene, or 1,3,5-trimethylbenzene (Cocker III et al., 2001a; Cocker III et al., 2001b; Saathoff et al., 2003; Virkkula et al., 1999), but it is distinctly lower than the hygroscopic growth of highly soluble organic acids such as malonic acid, citric acid, malic acid and tartaric acid (Peng et al., 2001).

An attempt to quantify the individual contributions of the inorganic, ISOM, and MHOM fractions to the overall hygroscopic growth of the WSM particles was done with the mixed particle model. Modelled and measured growth factors agreed well and comparison results are shown in Table 3, along with the percentages w of water associated with the individual WSM fractions at 90% RH for all four samples. Figures 6 and 7 illustrate the various mixed particle model results compared to experimental results for the KP010112-WSM and KP010726-WSM extracts, which are representative of investigated winter and summer samples, respectively. The inorganic fraction dominates the water uptake of WSM extracts in the RH range above deliquescence with a contribution of about $w_{Inorg} \approx 59$ –80% of total measured particulate water at 90% RH. Correspondingly, the contribution of the WSOM is about $w_{WSOM} \approx 41$ –20% at 90% RH. Within the WSOM, the contribution of the ISOM is about $w_{ISOM} \approx 6$ –9% and the contribution of the MHOM, determined as the difference $w_{MHOM} = w_{WSOM} - w_{ISOM}$, is about $w_{MHOM} \approx 14$ –32%. The partitioning of particulate water between different WSM fractions is quite constant in the range $75\% < RH < 95\%$.

Excess water w_{WSOM} concentrations obtained in this study for the continental-rural K-puszta aerosol are within the range of results of earlier studies on ambient particles using an H-TDMA (Saxena et al., 1995; Swietlicki et al., 1999; Dick et al., 2000) or a

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humidity controlled beta gauge (Speer et al., 2003) combined with chemical analysis. Saxena et al. (1995) attributed about $w_{WSOM} \approx 25\text{--}40\%$ of excess water at 80–88% RH to the organic fraction of non-urban aerosol in the Grand Canyon. At an urban site in Los Angeles, particulate water was in contrast reduced by the presence of organic substances, i.e. the effective water content was about 25–35% smaller at 83–93% RH than predicted from the inorganic fraction. Excess water amounts of about $w_{WSOM} \approx 0, 20, 44, 69\%$ were observed by Dick et al. (2000) for rural aerosol in the Smoky Mountains with organic mass fractions of about 32, 40, 58, 73%, respectively. In another study, Speer et al. (2003) estimated on average about $w_{WSOM} \approx 20\%$ of excess water associated with the organic fraction of a semi-rural aerosol. The hygroscopic growth of aged continental aerosol investigated at Great Dun Fell in northern England by Swietlicki et al. (1999) was explained by the water uptake of the inorganic fraction only, as long as there was only little or no photochemical activity. But they also detected excess water, probably associated with organic compounds, during a period with intense photochemical activity.

Among the three mixed particle model versions used in this study, good agreement between measured and reconstructed hygroscopic growth of WSM extracts is obtained with the complete mixed particle model (“Inorganic+ISOM+MHOM”, see Figs. 6 and 7), which accounts for the water uptake by inorganic salts, ISOM, and uses an estimate ($Y_{MHOM} = 0.163$) for the hygroscopicity of MHOM, which is the only remaining undetermined WSM fraction (see above). Total modelled water uptake (by volume) is 1% larger to 5% smaller in winter and 12% to 18% smaller in summer compared to experimental results. The reason for this slightly lower model accuracy in summer is unclear, since the inorganic to organic mass ratio of WSM samples is quite independent of season. However, possible reasons could be greater effective MHOM hygroscopicity in summer analogous to greater ISOM hygroscopicity, higher average WSOM density, or stronger positive interactions between inorganic and organic solutes. As discussed above, modelled growth curves are most sensitive to the assumption of ISOM density ρ_{ISOM} , apart from uncertainties of the estimated MHOM hygroscopicity, the ZSR

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relation accuracy, and real solution densities. Hence ρ_{ISOM} was varied from 1000 to 1800 kg/m³ to indicate the model uncertainty at selected RHs (error bars of curve “Inorganic+ISOM+MHOM”). Despite a comprehensive characterisation of the K-pusztá aerosol, the estimated contribution of the MHOM fraction to the water uptake (i.e. the difference between “WSM experiment” and “Inorganic+ISOM”, Table 3) is still quite uncertain regarding all the model assumptions. Nevertheless the modelling results show that the hygroscopic growth characteristic of WSM is dominated by the inorganic fraction, but that a considerable amount of water is associated with WSOM, whereas contributions from the ISOM and MHOM fractions are probably of comparable relevance. At this point it has to be emphasized that the results of this study are representative of the average WSM composition of the fine aerosol mode PM_{1.5}, and that hygroscopic growth factors of WSM extracts are presumably slightly larger than growth factors of the original ambient aerosol particles since the ambient particles additionally contain a small fraction of WINSOM and BC. However, additional water-insoluble compounds in the particles do not affect percentages of water uptake associated with different WSM fractions, and growth factors of ambient particles could be deduced analogously to the mixed particle model (Eq. 7) by using $g_{WINSOM+BC} = 1$.

Besides particulate water associated with WSOM, another important topic of current research is the possible effect of WSOM on the deliquescence and efflorescence behaviour of inorganic salts (Cruz and Pandis, 2000; Choi and Chan, 2002a; Choi and Chan, 2002b; Hämeri et al., 2002). The AIM2-III model is not generally intended to be applied to calculating the properties of metastable (supersaturated) solutions, though this option is available. Nevertheless, approximate growth curves for decreasing RH conditions were calculated to obtain more information about the deliquescence behaviour of WSM extracts. The comparison of experimental results with modelled growth curves under increasing and decreasing RH conditions indicates that WSM extracts are fully deliquescent at around RH > 75–80%. The gradual deliquescence under increasing RH conditions is fairly well reproduced by the model, but the formation of hydrates (and also of letovicite in case of the KP010726-WSM extract) had to be sup-

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pressed in AIM2-III. However, it is not possible to decide which salt species were really present, but it can still be concluded that the large organic fraction contained in the WSM extract did not completely suppress the crystallisation of some inorganic salts under the very dry conditions ($RH < 5\%$ for ~ 300 s) in the diffusion dryer, nor was the deliquescence behaviour of the solid inorganic salts dramatically changed. This is in agreement with results obtained by Chan and Chan (2003) for mixtures of NaCl and $(NH_4)_2SO_4$ with humic substances.

4.3. Hygroscopicity of humic reference substances

Since ISOM has been characterised by different analytical techniques as primarily being composed of humic-like substances, hygroscopic properties of humic reference substances were also investigated. Growth factors (left ordinate) as a function of RH (upper abscissa) are shown in Fig. 8a–d for KP010112-ISOM, NaHA, NRFA, and NRHA, respectively. All four samples showed hysteresis behaviour basically similar to KP010726-ISOM (Fig. 9, detailed discussion below). Growth factors at 90% RH of NaHA, NRFA, and NRHA are 1.18, 1.13, and 1.06, respectively, which is in the same range as atmospheric ISOM samples. These results show that there are qualitative similarities between the hygroscopic behaviour of ISOM and humic reference substances, but the deliquescence transition of the reference substances is at higher RH, indicating a lower solubility. The growth factors and deliquescence RHs of NRHA and NRFA could even be somewhat biased towards larger growth factors and lower RH, respectively, if residuals filtered after initial sample dissolution (see above) consisted mainly of the least soluble and possibly least hygroscopic molecules.

4.4. Deliquescence and hysteresis of organic samples

A closer analysis of ISOM growth characteristics highlights some uncommon hysteresis features. Figure 9 shows hygroscopic growth factors (left ordinate) of the KP010726-ISOM extract on an enlarged growth scale. Under increasing RH conditions (cf. curve

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“ g_{incr} ”) the particle size increases continuously from $RH < 5\%$ to $RH = 30\%$, followed by a decrease of the particle diameter during deliquescence between 30 and 45% RH. Above 45% there is again distinct particle growth up to 95% RH. Experimental growth factors under decreasing RH conditions (cf. curve “ g_{decr} ”) are equal to g_{incr} between 95 and 45% RH. Below 45% evaporation with decreasing RH continues, ending with a particle size that is smaller than initially selected. However, at the very lower end of the g_{decr} measurement ($RH < 5\%$ RH) the particle size increases again towards the initially selected diameter. This indicates that crystallisation occurs under these very low RH conditions. The uncommon hysteresis behaviour, i.e. the size reduction during deliquescence, was detected for all ISOM extracts and it was highly reproducible.

Each growth factor measured with a H-TDMA is an average value of all particles of the monodisperse aerosol fraction, since it is determined from modal diameters under dry and humid conditions. In parallel, the trend of the modal standard deviation, σ (normal distribution), during hygroscopic growth indicates the mixing state of the aerosol. σ remains constant (increases) during hygroscopic growth, if growth factors of individual particles are equal (different). Figure 10 illustrates the changes of the monodisperse size distribution at different RH for NaHA (cf. corresponding g and σ in Fig. 8b). The line “RH = 2%” corresponds to the initially selected monodisperse aerosol fraction ($D_0 = 104$ nm). Under increasing RH conditions the particles grow homogeneously to a mean diameter of $D = 110$ nm at 51% RH, i.e. there is no change of the standard deviation σ . From 51 to 79% RH the mean particle size increases only slightly to $D = 112$ nm, but there is a distinct broadening of the monodisperse size distribution. Between 79 and 89% RH there is again homogeneous growth up to a diameter of $D = 121$ nm. Under decreasing RH conditions the modal diameter decreases continuously without any further change of the size distribution shape, ending with a diameter of $D = 99$ nm at 5% RH (line “RH = 5% (decreasing RH)”). Thus the hygroscopic growth of NaHA particles is always homogeneous, except for the deliquescence transition between 60 and 75% RH, where there is a broadening of the monodisperse aerosol. ISOM (cf. Figs. 8a and 9) as well as NRFA (Fig. 8c) and NRHA (Fig. 8d) ex-

hibit this characteristic decrease of the electrical mobility diameter accompanied by a parallel increase of σ during deliquescence, too.

A priori one would expect no broadening of the monodisperse aerosol fraction during growth for these internally mixed aerosols composed of particles with identical composition (see above). But how can the broadening during deliquescence be explained? Concluding from the continuous evaporation under decreasing RH conditions, particles are most probably liquid solution droplets once they were exposed to high RH, which may also exist at low RH as metastable supersaturated solutions. Accordingly, the transition under increasing RH conditions identified by the size reduction and the broadening of σ , corresponds to deliquescence, i.e. the dissolution of the solid particles. There are mainly two possible reasons (cf. also section “mobility correction factor”) explaining a mobility diameter decrease during deliquescence despite the parallel water uptake: a) the dynamic shape factor of the solid particles is larger than 1, i.e. they are not perfectly spherical and they have cracks or cavities, leading to a decrease of the electrical mobility diameter only when the particles are transformed into compact spheres during dissolution b) the volume of mixing of humic-like substances with water is negative causing a real size decrease in terms of electrical mobility and volume equivalent diameters. Variations of the solid particle density and of the initial dynamic shape factor between individual particles then lead to the observed broadening of the monodisperse aerosol fraction during deliquescence despite identical chemical composition. However, at this point it has to be mentioned, that the hysteresis of all humic-like substances is small compared to the hysteresis of inorganic salts (e.g. $(\text{NH}_4)_2\text{SO}_4$), and could only be detected due to the high instrument resolution (cf. KP010726 in Fig. 9). This uncommon decrease in mobility diameter at deliquescence is most probably not of atmospheric importance, but it should be kept in mind as a potential source of discrepancies between results obtained with different techniques, e.g. if mobility diameter growth factors are compared with mass gains.

The relatively small growth below deliquescence is attributed to a surface effect, where the most soluble compounds might form a liquid solution shell. Water adsorption

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alone is not sufficient to explain this growth, since a growth factor of 1.05 (e.g. NRFA at 52% RH, Fig. 8c) corresponds to an equivalent of 6 monolayers of water.

For all WSM samples a small size decrease in parallel with a broadening of the monodisperse aerosol was observed under increasing RH conditions somewhere between 10 and 40% RH (cf. Figs. 5–7). This indicates that WSOM and possibly also some inorganic salts of the WSM particles already dissolve at this low RH.

4.5. Restructuring

The restructuring $g_{restr}(RH_P)$ of ISOM, NaHA, and NRFA particles as a function of prehumidifier RH (RH_P) was also measured (Figs. 8e–g). In this instrument mode (cf. Fig. 4d) particles are selected under dry conditions in DMA1, exposed to a certain RH_P , dried again in the RH-conditioner and the restructured dry size is measured in DMA2. No restructuring or broadening below deliquescence RH was detected for ISOM and NaHA, i.e. the hygroscopic growth under increasing RH conditions in the range $RH < DRH$ is reversible. Through the deliquescence transition there is continuous restructuring (decrease of g_{restr}) accompanied by a broadening of the standard deviation. This indicates that the reduction of the electrical mobility diameter during dissolution is irreversible on this timescale (~ 5 s residence time after the RH-conditioner), which is in agreement with the observation of supersaturated solutions and growth factors $g_{decr} < 1$ at low RH under decreasing RH conditions. There is no further restructuring or broadening above the deliquescence transition, confirming that in this RH range, size changes under increasing or decreasing RH conditions are only a result of water condensation or evaporation. While the restructuring behaviour of NRFA is similar to ISOM and NaHA during deliquescence and at higher RH, it is different below deliquescence. Restructuring factors g_{restr} larger than 1 in the RH range below deliquescence indicate that the hygroscopic growth of NRFA is to some extent irreversible on this time scale.

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4.6. Empirical γ -model and ideal solution model

Empirical growth curves (γ -model) were fitted to experimental growth factors at 90% RH of WSM, ISOM and humic reference substances (see Figs. 5, 8, and 9). The empirical γ -model is not able of reproducing the observed hygroscopic growth factors very precisely. Nevertheless, the relative agreement between fitted and measured growth factors under decreasing RH conditions is better than $\pm 6\%$ in the range from 60 to 90% RH for all WSM samples, and better than $\pm 4\%$ and $\pm 3\%$ in the entire RH range for all ISOM samples and humic reference substances, respectively. The γ -model is hence a simple but useful tool to describe the hygroscopic growth of WSM, ISOM, and humic reference substances.

The ideal solution model was applied to describe the hygroscopic growth of ISOM and humic reference substances, where v_s was used to fit theoretical growth curves to experimental results (cf. Eq. 4). It reproduces the experimental growth characteristic of ISOM and humic reference substances much better compared to the empirical γ -model (see Figs. 5, 8, and 9). The relative agreement between measured and modelled growth factors in the entire RH range is better than $\pm 1\%$ and $\pm 2\%$ for all ISOM samples and humic reference substances, respectively. This does not essentially mean that the solution behaviour is in reality ideal, but this model is at least suitable to describe the hygroscopic behaviour and to get a rough estimate of the average molar weight M_{ISOM} of the ISOM, according to the approach described in Sect. 3.1. For the latter purpose ρ_{ISOM} and the van't Hoff factor i_{ISOM} were assumed to be 1500 kg/m^3 (cf. above) and 1, respectively. The van't Hoff factor of acidic compounds is in principle always > 1 , but since the pK_a of ISOM ranges from 3 to 9, i_{ISOM} is in fact expected to be smaller than 1.03 for a solution droplet at $\text{RH} \leq 95\%$ (conc. $\geq 1.8 \text{ M}$). M_{ISOM} values obtained with the ideal solution model under the above-mentioned assumptions are between 300 and 495 kg/kmol (see Table 2). M_{ISOM} estimates are proportional to ρ_{ISOM} and ρ_{ISOM} for a given v_s (see Eq. 5), i.e. assuming a lower ISOM density of $\rho_{ISOM} = 1000 \text{ kg/m}^3$, results in M_{ISOM} estimates between 200 and 330 kg/kmol . As discussed in Sect. 3.1,

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solution surface tension ζ was approximated by the surface tension of pure water. However, measurements of the influence of other ISOM samples on the surface tension of water and $(\text{NH}_4)_2\text{SO}_4$ -solution (Kiss et al., 2003b) samples showed that ISOM reduces the surface tension typically by about 40% at a moderate concentration of 1 g/l. On the other hand, M_{ISOM} estimates increase only about 10% if one assumes a 50% reduction of surface tension by ISOM. Kiss et al. (2003a) determined the average molar weight of ISOM extracted from filters sampled at K-pusztá between March 1999 and June 2000. They reported values of 200–300 and 215–345 kg/kmol using liquid chromatography mass spectrometry and vapour pressure osmometry, respectively. This is good agreement between these three approaches regarding the fact that molecular weight estimates of humic substances often vary more than an order of magnitude depending on the applied experimental technique.

Molar weight estimates, also assuming a density of $\rho_{\text{humic}} = 1500 \text{ kg/m}^3$ and a van't Hoff factor of $i_{\text{humic}} = 1$, for NaHA, NRFA, and NRHA are 216, 510, and 765 kg/kmol, respectively. M_w estimates for the NRFA and NRHA samples are thus larger than estimates for ISOM. This is in agreement with the stronger refractory character of NRFA and NRHA during volatilisation compared to ISOM (Nyeki et al., 2003). Distinctly larger molar weights (number averaged) of 2180 kg/kmol and 4410 kg/kmol for NRFA and NRHA, respectively, have previously been reported by Pettersson et al. (1994). However, they used size exclusion chromatography which has been reported to give higher average molecular weight estimates for humic substances than other techniques (Leenheer et al., 2001). A value of $M_{\text{NaHA}} \approx 3300 \text{ kg/kmol}$ (average by weight) was reported by Wolf et al. (2001) for NaHA. The molar weight estimate of 216 kg/kmol, obtained in this study for NaHA, is most probably too low, since the sodium ions are expected to dissociate, and the van't Hoff factor is hence > 1 . If one considers a sodium mass fraction of $\sim 9 \text{ wt} \%$ (Aldrich product analysis) and assumes that all sodium ions dissociate, one would end up with a van't Hoff factor of $i_{\text{NaHA}} \approx 6.5$ and an average molar weight (before dissociation) of $M_{\text{NaHA}} \approx 1400 \text{ kg/kmol}$, but also these corrected values are not reliable since the deduction is highly sensitive to small uncertainties of

the initial value.

5. Conclusions

Ambient continental-rural fine aerosol was sampled on quartz filters and WSM was extracted in MilliQ-water. Solid phase extraction was subsequently used to isolate ISOM, constituting the major (less hydrophilic) fraction of WSOM, from inorganic salts and the remaining MHOM. Extensive chemical characterisation of these extracts was carried out by Galambos et al. (2003), while hygroscopic properties were investigated here using a H-TDMA instrument. ISOM hygroscopicity was comparable to secondary organic aerosols, which were obtained in smog chamber studies by oxidation of typical gaseous precursors, but lower than the hygroscopicity of highly soluble organic acids. Deliquescence was already observed at moderate RH between 30 and 60% for different ISOM samples. Differences between summer and winter samples were small, but there is a trend towards larger hygroscopicity and lower deliquescence RH in summer. Köhler theory for ideal solutions was used to estimate the average molar weight of ISOM. Resulting M_w estimates of 300–495 kg/kmol assuming a van't Hoff factor of $i_{ISOM} = 1$ and a density of $\rho_{ISOM} = 1500 \text{ kg/m}^3$ are in good agreement with earlier investigations of K-pusztá ISOM using liquid chromatography mass spectrometry and vapour pressure osmometry. Aquatic fulvic and humic acids were also investigated for comparison with ISOM. Although some similarities in hygroscopic behaviour were observed, fulvic and humic acids were slightly less hygroscopic and deliquescence occurred at higher RH compared to ISOM. This indicates a lower average molecular weight and higher solubility of ISOM. Deliquescence of ISOM, fulvic acid, and humic acid was characterised by a small but nevertheless uncommon decrease in mobility diameter. This behaviour is probably not of atmospheric importance, but it is a potential source of discrepancy between different techniques to measure hygroscopic growth of particles.

Comprehensive chemical information and measured hygroscopic properties of ISOM were used to model the hygroscopic growth of the WSM. Good agreement between

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model predictions and measurements was obtained. The analysis of modelled and measured WSM growth factors showed furthermore that between 20 and 40% of total particulate water is associated with WSOM. This finding confirms results from earlier studies that, apart from inorganic salts, organic compounds are also actively involved in atmospheric processes in which particle hygroscopic properties are crucial. The relative contributions of the distinct WSOM fractions, ISOM (67–71 wt %) and MHOM (29–33 wt %), remains uncertain since MHOM was not available in isolated form, but the results suggest that the less abundant MHOM was also important due to its presumably larger hygroscopicity.

6. Glossary

Abbreviations were generally adopted from literature. However, an “M” (matter) instead of a “C” (carbon) as the last letter (e.g. WSOM instead of WSOC) is used to clearly distinguish between the mass of carbonaceous compounds and their carbon mass content.

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6.1. Acronyms

AIM	aerosol inorganic model
BC	black carbon
CPC	condensation particle counter
DMA	differential mobility analyser
DRH	deliquescence relative humidity
H-TDMA	hygroscopicity tandem differential mobility analyser
ISOM	isolated organic matter
KPYYMMDD	sample labels indicating the site K-pusztá and the sampling date
MHOM	most hydrophilic organic matter
NaHA	Aldrich humic acid sodium salt
NRFA	nordic reference fulvic acid
NRHA	nordic reference humic acid
PM _{1.5}	particulate matter with diameter $D \leq 1.5 \mu\text{m}$
SEM	scanning electron microscopy
TCM	total carbonaceous matter
WINSOM	water-insoluble organic matter
WSM	water-soluble matter
WSOM	water-soluble organic matter
ZSR relation	Zdanovskii-Stokes-Robinson relation

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6.2. Symbols

D	particle diameter
D_0	dry reference diameter
f	mobility correction factor
g	hygroscopic growth factor (D/D_0)
g_{decr}	hygroscopic growth factor under decreasing RH conditions (dehydration)
g_{incr}	hygroscopic growth factor under increasing RH conditions (hydration)
g_{restr}	restructuring factor
g_{th}	theoretical hygroscopic growth factor
i_s	van't Hoff factor of the solute
M_w	molar weight of water
M_s	molar weight of the solute
n_w	molar number of water molecules
n_s	molar number of solute molecules (or ions)
R	ideal gas constant
RH_C	relative humidity in the RH-conditioner
RH_{DMA2}	relative humidity in the second DMA
RH_P	relative humidity in the prehumidifier
S_{Kelvin}	Kelvin correction factor
T	temperature
x_w	mole fraction of water
γ	model parameter of the γ -model
ε	volume fraction
v_s	molar volume per solute molecule (or ion)
ρ	mass density
ρ_w	density of water
ζ	surface tension
σ	standard deviation (normal distribution) of the monodisperse aerosol

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References

- Ansari, A. S. and Pandis, S. N.: Prediction of multicomponent inorganic atmospheric aerosol behavior, *Atmos. Env.*, 33, 745–757, 1999.
- Chan, M. N. and Chan, C. K.: Hygroscopic properties of two model humic-like substances and their mixtures with inorganics of atmospheric importance, *Environ. Sci. Technol.*, accepted, 2003.
- Chen, H., Sangster, J., Teng, T. T., and Lenzi, F.: General method of predicting water activity of ternary aqueous-solutions from binary data, *Can. J. Chem. Eng.*, 51, 234–241, 1973.
- Choi, M. Y. and Chan, C. K.: The effects of organic species on the hygroscopic behaviors of inorganic aerosols, *Environ. Sci. Technol.*, 36, 2422–2428, 2002a.
- Choi, M. Y. and Chan, C. K.: Continuous measurements of the water activities of aqueous droplets of water-soluble organic compounds, *J. Phys. Chem. A*, 106, 4566–4572, 2002b.
- Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{H}_2\text{O}$ at 298.15 K, *J. Phys. Chem. A*, 102, 2155–2171, 1998.
- Clegg, S. L., Seinfeld, J. H., and Brimblecombe, P.: Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds, *J. Aerosol Sci.*, 32, 713–738, 2001.
- Cocker III, D. R., Clegg, S. L., Flagan, R. C., and Seinfeld, J. H.: The effect of water on gas-particle partitioning of secondary organic aerosol. Part I: α -pinene/ozone system, *Atmos. Env.*, 35, 6049–6072, 2001a.
- Cocker III, D. R., Mader, B. T., Kalberer, M., Flagan, R. C., and Seinfeld, J. H.: The effect of water on gas-particle partitioning of secondary organic aerosol: II. m-xylene and 1,3,5-trimethylbenzene photooxidation systems, *Atmos. Env.*, 35, 6073–6085, 2001b.

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- Corrigan, C. E. and Novakov, T.: Cloud condensation nucleus activity of organic compounds: a laboratory study, *Atmos. Env.*, 33, 2661–2668, 1999.
- Cruz, C. N. and Pandis, S. N.: A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei, *Atmos. Env.*, 31, 2205–2214, 1997.
- 5 Cruz, C. N. and Pandis, S. N.: The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol, *J. Geophys. Res.*, 103D, 13 111–13 123, 1998.
- Cruz, C. N. and Pandis, S. N.: Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol, *Environ. Sci. Technol.*, 34, 4313–4319, 2000.
- Dick, W. D., Saxena, P., and McMurry, P. H.: Estimation of water uptake by organic compounds
10 in submicron aerosols measured during the Southeastern Aerosol and Visibility Study, *J. Geophys. Res.*, 105D, 1471–1479, 2000.
- Facchini, M. C., Fuzzi, S., Zappoli, S., Andracchio, A., Gelencsér, A., Kiss, G., Krivácsy, Z., Mészáros, E., Hansson, H. C., Alsberg, T., and Zebühr, Y.: Partitioning of the organic aerosol component between fog droplets and interstitial air, *J. Geophys. Res.*, 104D, 26 821–26 832,
15 1999.
- Galambos, I., Kiss, G., Horváth, E., Molnár, á., Gysel, M., Nyeki, S., Weingartner, E., and Baltensperger, U.: Chemical characterisation of water-soluble matter and humic-like organics in atmospheric fine aerosol, manuscript in preparation, 2003.
- Giebl, H., Berner, A., Reischl, G., Puxbaum, H., Kasper-Giebl, A., and Hitzenberger, R.: CCN
20 activation of oxalic and malonic acid test aerosols with the University of Vienna cloud condensation nuclei counter, *J. Aerosol Sci.*, 33, 1623–1634, 2002.
- Gysel, M., Weingartner, E., and Baltensperger, U.: Hygroscopicity of aerosol particles at low temperatures, 2. Theoretical and experimental hygroscopic properties of laboratory generated aerosols, *Environ. Sci. Technol.*, 36, 63–68, 2002.
- 25 Hämeri, K., Charlson, R., and Hansson, H. C.: Hygroscopic properties of mixed ammonium sulfate and carboxylic acids particles, *AIChE J.*, 48, 1309–1316, 2002.
- Hansson, H.-C., Rood, M. J., S., K.-V., Hämeri, K., Orsini, D., and Wiedensohler, A.: NaCl aerosol particle hygroscopicity dependence on mixing with organic compounds, *J. Atmos. Chem.*, 31, 321–346, 1998.
- 30 Heintzenberg, J.: Fine particles in the global troposphere, A review, *Tellus*, 41B, 149–160, 1989.
- Kiss, G., Varga, B., Galambos, I., and Ganszky, I.: Characterization of water-soluble organic matter isolated from atmospheric fine aerosol, *J. Geophys. Res.*, 107D, 8339,

doi:10.1029/2001JD000603, 2002.

Kiss, G., Tombácz, E., Varga, B., Alsberg, T., and Persson, L.: Estimation of the average molecular weight of humic-like substances isolated from fine atmospheric aerosol, *Atmos. Env.*, 37, 3783–3794, 2003a.

5 Kiss, G., Tombácz, E., Gelencsér, A., Krivácsy, Z., Molnár, á., Mészáros, E., and Hansson, H.-C.: Surface tension effects of water-soluble organic matter in nucleating cloud droplets, manuscript in preparation, 2003b.

Krivácsy, Z., Gelencsér, A., Kiss, G., Mészáros, E., Molnár, A., Hoffer, A., Mészáros, T., Sárvári, Z., Temesi, D., Varga, B., Baltensperger, U., Nyeki, S., and Weingartner, E.: Study on the chemical character of water soluble organic compounds in fine atmospheric aerosol at the Jungfraujoch, *J. Atmos. Chem.*, 39, 235–259, 2001.

10 Leenheer, J. A., Rostad, C. E., Gates, P. M., Furlong, E. T., and Ferrer, I.: Molecular resolution and fragmentation of fulvic acid by electrospray ionization/multistage tandem mass spectrometry, *Anal. Chem.*, 73, 1461–1471, 2001.

15 Lightstone, J. M., Onasch, T. B., Imre, D., and Oatis, S.: Deliquescence, efflorescence, and water activity in ammonium nitrate and mixed ammonium nitrate/succinic acid microparticles, *J. Phys. Chem. A*, 104, 9337–9346, 2000.

Massling, A., Wiedensohler, A., Busch, B., Neusüß, C., Quinn, P., Bates, T., and Covert, D. S.: Hygroscopic properties of different aerosol types over the Atlantic and Indian Oceans, *Atmos. Chem. Phys. Discuss.*, 3, 135–185, 2003.

20 Ming, Y. and Russell, L. M.: Predicted hygroscopic growth of sea salt aerosol. *J. Geophys. Res.*, 106D, 28259–28274, 2001.

Ming, Y. and Russell, L. M.: Thermodynamic equilibrium of organic-electrolyte mixtures in aerosol particles, *AIChE J.*, 48, 1331–1348, 2002.

25 Na, H. S., Arnold, S., and Myerson, A. S.: Water activity in supersaturated aqueous-solutions of organic solutes, *J. Cryst. Growth*, 149, 229–235, 1995.

Nyeki, S., U. Baltensperger, G. Coulson, I. Galambos, M. Gysel, G. Kiss, Z. Krivácsy, and I. Colbeck (2003). Properties of humic-like organics isolated from atmospheric fine aerosol. Aerosol volatility. Abstracts of the European Aerosol Conference 2003, Madrid, 31 Aug. – 05 Sept. 2003, *J. of Aerosol Science*, S225–S226, 2003.

30 Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions, *Environ. Sci. Technol.*, 35, 4495–4501, 2001.

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- Peng, C. G. and Chan, C. K.: The water cycles of water-soluble organic salts of atmospheric importance, *Atmos. Env.*, 35, 1183–1192, 2001.
- Pettersson, C., Ephraim, J., and Allard, B.: On the composition and properties of humic substances isolated from deep groundwater and surface waters, *Org. Geochem.*, 21, 443–451, 1994.
- 5 Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Sherman, D. E., Russell, L. M., and Ming, Y.: The effects of low molecular weight dicarboxylic acids on cloud formation, *J. Phys. Chem. A*, 105, 11 240–11 248, 2001.
- Pruppacher, H. R. and Klett, J. D.: *Microphysics of Clouds and Precipitation*, Kluwer Academic Publishers, Dordrecht, 1997.
- 10 Rader, D. J. and McMurry, P. H.: Application of the tandem differential mobility analyzer to studies of droplet growth or evaporation, *J. Aerosol Sci.*, 17, 771–787, 1986.
- Saathoff, H., Naumann, K.-H., Schnaiter, M., Schöck, W., Möhler, O., Schurath, U., Weingartner, E., Gysel, M., and Baltensperger, U.: Coating of soot and $(\text{NH}_4)_2\text{SO}_4$ particles by ozonolysis products of α -pinene, *J. Aerosol Sci.*, 34, 1297–1321, 2003.
- 15 Saxena, P. and Hildemann, L. M.: Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, 24, 57–109, 1996.
- Saxena, P., Hildemann, L. M., McMurry, P. H., and Seinfeld, J. H.: Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, 100D, 18 755–18 770, 1995.
- 20 Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics. From Air Pollution to Climate Change*, John Wiley & Sons, Inc., New York, 1998.
- Speer, R. E., Edney, E. O., and Kleindienst, T. E.: Impact of organic compounds on the concentrations of liquid water in ambient $\text{PM}_{2.5}$, *J. Aerosol Sci.*, 34, 63–77, 2003.
- 25 Stolzenburg, M. R. and McMurry, P. H.: TDMAFIT user's manual, University of Minnesota, Department of Mechanical Engineering, Particle Technology Laboratory, Minneapolis, 1988.
- Swietlicki, E., Zhou, J. C., Berg, O. H., Martinsson, B. G., Frank, G., Cederfelt, S. I., Dusek, U., Berner, A., Birmili, W., Wiedensohler, A., Yuskiewicz, B., and Bower, K. N.: A closure study of sub-micrometer aerosol particle hygroscopic behaviour, *Atmos. Res.*, 50, 205–240, 1999.
- 30 Swietlicki, E., Zhou, J. C., Covert, D. S., Hämeri, K., Busch, B., Vakeva, M., Dusek, U., Berg, O. H., Wiedensohler, A., Aalto, P., Makela, J., Martinsson, B. G., Papaspiropoulos, G., Mentes, B., Frank, G., and Stratmann, F.: Hygroscopic properties of aerosol particles in the north-eastern Atlantic during ACE-2, *Tellus*, 52, 201–227, 2000.

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Varga, B., Kiss, G., Ganszky, I., Gelencsér, A., and Krivácsy, Z.: Isolation of water-soluble organic matter from atmospheric aerosol, *Talanta*, 55, 561–572, 2001.

Virkkula, A., Van Dingenen, R., Raes, F., and Hjorth, J.: Hygroscopic properties of aerosol formed by oxidation of limonene, α -pinene, and β -pinene, *J. Geophys. Res.*, 104D, 3569–3579, 1999.

Weingartner, E., Gysel, M., and Baltensperger, U.: Hygroscopicity of aerosol particles at low temperatures. 1. New low-temperature H-TDMA instrument: Setup and first applications, *Environ. Sci. Technol.*, 36, 55–62, 2002.

Wolf, M., Buckau, G., Geckeis, H., Thang, N. M., Hoque, E., Szymczak, W., and Kim, J.-I.: Aspects of measurement of the hydrodynamic size and molecular mass distribution of humic and fulvic acids, in *Humic Substances. Structures, Models and Functions*, edited by Ghabbour, E. A., and Davies, G., pp. 51–61, The Royal Society of Chemistry, Cambridge, 2001.

Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M. C., Gelencsér, A., Kiss, G., Krivácsy, Z., Molnár, á., Mészáros, E., Hansson, H.-C., Rosman, K., and Zebühr, Y.: Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, *Atmos. Env.*, 33, 2733–2743, 1999.

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Table 1. Aerosol chemical composition of Hi-Vol atmospheric filter samples

sample	PM _{1.5} [*] μg/m ³	TCM μg/m ³	inorg. salts μg/m ³	WSM of PM _{1.5} wt %	inorg. salts of WSM wt %	ISOM of WSM wt %	MHOM of WSM wt %
KP010112	33.5	23.4	10.1	65	47	36	17
KP010126	13.7	8.5	5.2	72	53	33	14
KP010726	11.7	7.4	4.3	89	42	40	18
KP010816	21.4	13.4	8.0	80	47	36	17

* PM_{1.5} was calculated under the assumption that the aerosol is composed of exclusively carbonaceous matter and water-soluble inorganic salts.

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Table 2. Deliquescence relative humidity and model parameters

	growth factor	deliquescence	mobility correction	γ -model	ideal solution model
sample	g(90%) (–)	DRH [°] (%)	f (–)	γ^* (–)	M^\dagger (kg/kmol)
KP010112-ISOM	1.08	50–60	0.96	0.050	495
KP010126-ISOM	1.11	40–55	0.97	0.059	405
KP010726-ISOM	1.16	30–45	0.98	0.073	315
KP010816-ISOM	1.17	45–55	0.98	0.075	300
KP010112-WSM	1.48	n.a. [‡]	0.96	0.189	n.a.
KP010126-WSM	1.52	n.a.	0.95	0.203	n.a.
KP010726-WSM	1.52	n.a.	0.96	0.199	n.a.
KP010816-WSM	1.49	n.a.	0.96	0.193	n.a.
NaHA	1.18	60–75	0.94	0.097	n.a.
NRFA	1.13	75–85	1.01	0.049	510
NRHA	1.06	85–95	0.98	0.034	765

[°] The given RH values indicate the range between deliquescence onset and completion.

^{*} The model parameter γ was fitted to the experimental growth factor at 90% RH.

[†] M is obtained by fitting the ideal solution model to experimental results. The given M estimates are only valid under the following assumptions: The density of the organic solute is $\rho = 1500 \text{ kg/m}^3$, and the van't Hoff factor of the organic molecules is $i = 1$ (see text for the discussion of these assumptions).

[‡] Not applicable.

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Table 3. Model accuracy at 90% RH (mixed particle model) and attribution of particulate water w to the different fractions of WSM

sample	model accuracy*	inorganic salts w_{Inorg}	WSOM w_{WSOM}	ISOM w_{ISOM}	MHOM [†] w_{MHOM}
KP010112-WSM	1%	80%	20%	6%	14%
KP010126-WSM	−5%	79%	21%	6%	15%
KP010726-WSM	−18%	59%	41%	9%	32%
KP010816-WSM	−12%	65%	35%	9%	26%

* Difference between prediction of the complete inorganic+ISOM+MHOM model and measured water uptake.

[†] Estimate from difference between measured value and model prediction for the inorganic+ISOM fraction.

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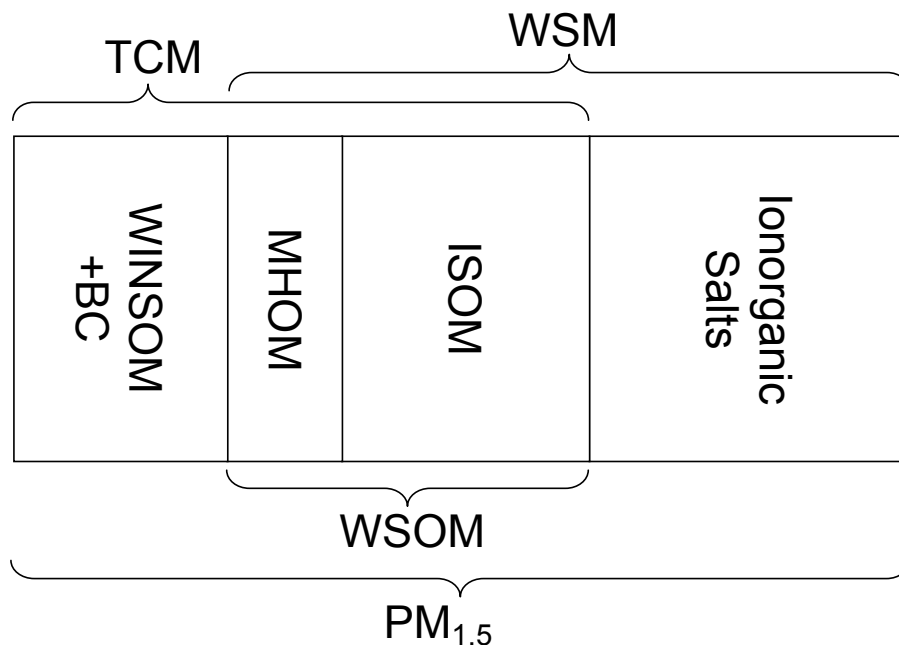


Fig. 1. Compound classification of total particulate matter with diameter $D \leq 1.5 \mu\text{m}$ ($PM_{1.5}$): i) Water-insoluble organic matter (WINSOM) and black carbon (BC), ii) most hydrophilic organic matter (MHOM), iii) isolated organic matter (ISOM), iv) inorganic salts, v) water-soluble matter (WSM), vi) water-soluble organic matter (WSOM), and vii) total carbonaceous matter (TCM). The box widths are proportional to the corresponding average mass fractions of all samples (see Table 1).

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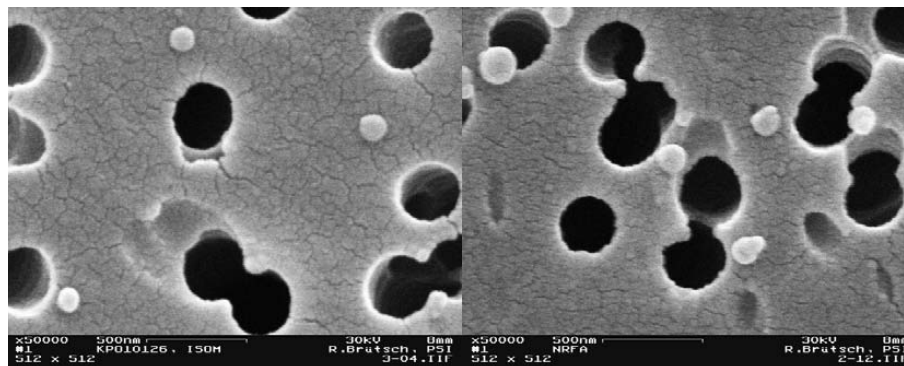


Fig. 2. SEM micrographs of $D_0 \approx 100$ nm particles, which were produced by atomising ISOM (on the left) and NRFA solution (on the right). Dark holes are the filter pores.

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Fig. 3. Hygroscopicity Tandem Differential Mobility Analyser with optional prehumidifier.

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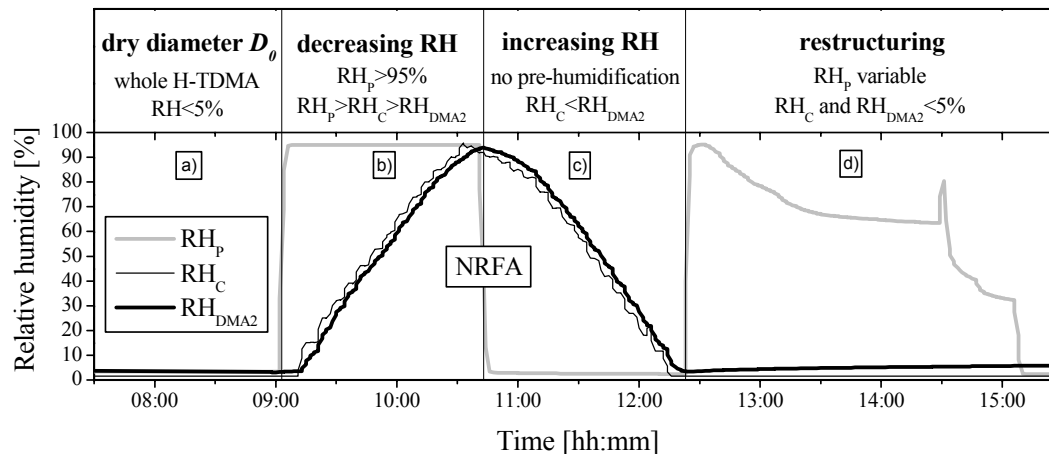


Fig. 4. Typical measurement cycle with the H-TDMA (NRFA sample). Abbreviations are RH after prehumidifier (RH_P), RH after RH-conditioner (RH_C), and RH in DMA2 (RH_{DMA2}). Dry, monodisperse particles initially selected in DMA1 are then successively exposed to RH_P , RH_C , and RH_{DMA2} . **(a)** Measurement of dry diameter D_0 , **(b)** growth factor $g_{decr}(RH_{DMA2})$ under decreasing (!) RH conditions, **(c)** growth factor $g_{incr}(RH_{DMA2})$ under increasing (!) RH conditions, and **(d)** restructuring $g_{restr}(RH_P)$.

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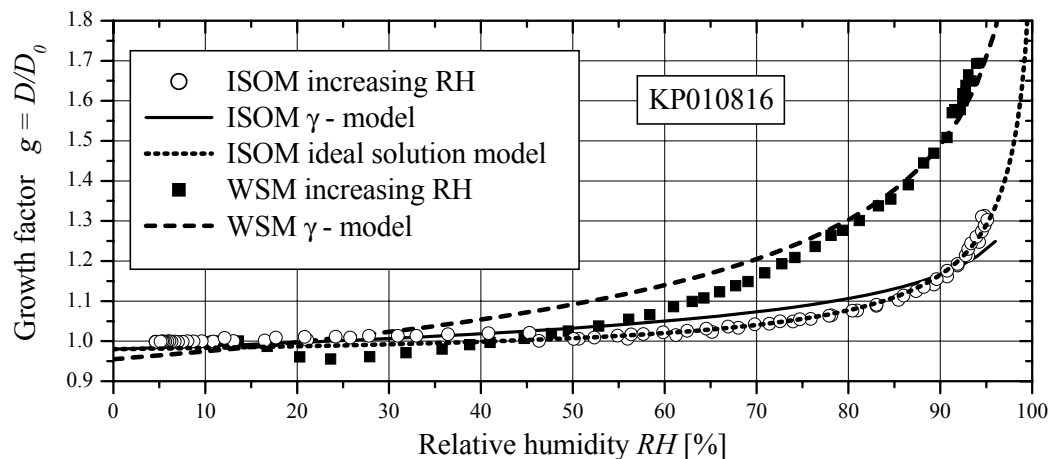
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**Fig. 5.** Hygroscopic growth factors of KP010816-ISOM and -WSM samples.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

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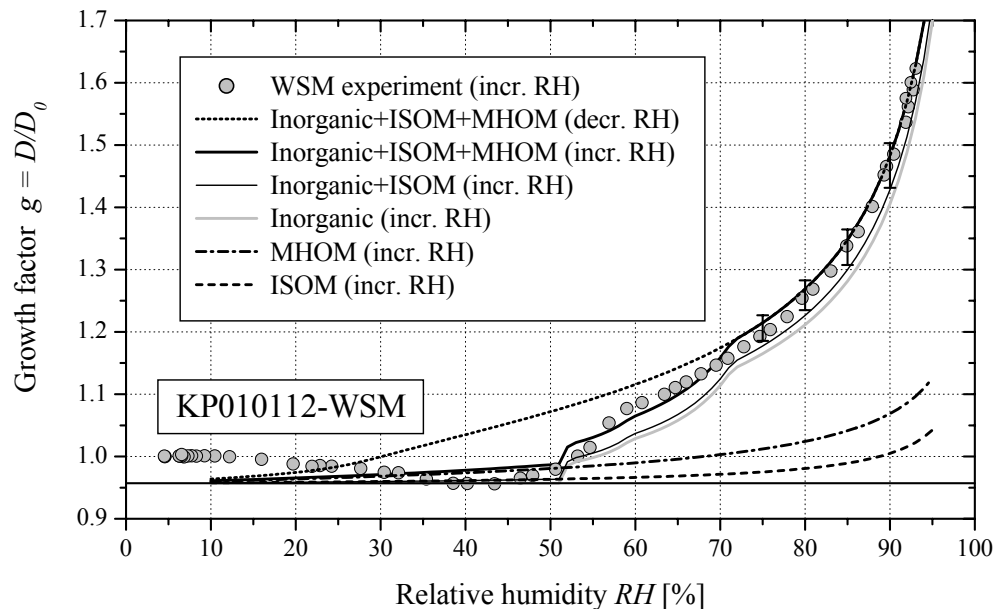


Fig. 6. Contributions of the inorganic, ISOM, and MHOM (according to $\gamma_{MHOM} = 0.163$) fractions to the hygroscopic growth of the KP010112-WSM sample.

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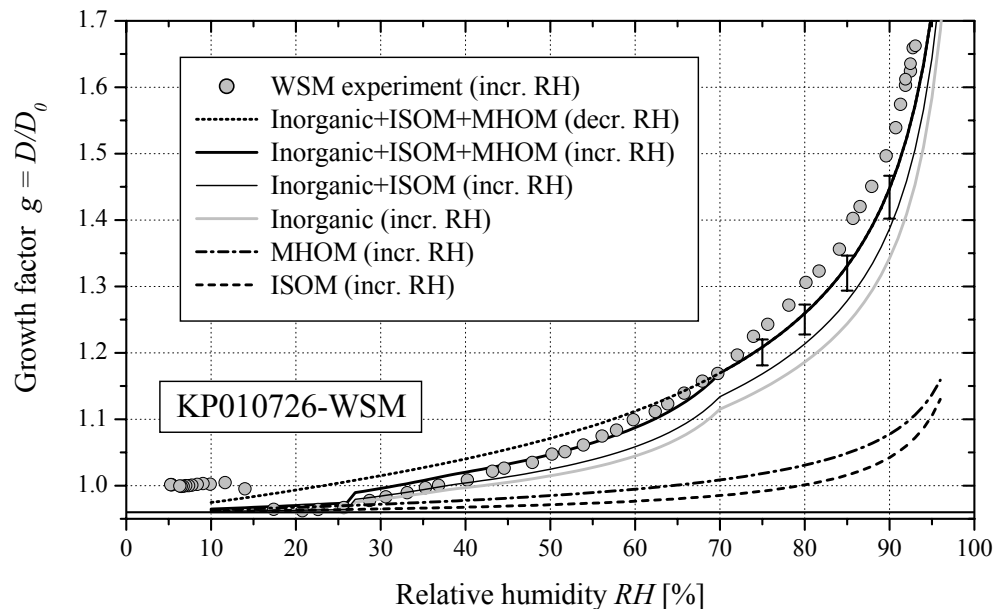


Fig. 7. Contributions of the inorganic, ISOM, and MHOM (according to $\gamma_{MHOM} = 0.163$) fractions to the hygroscopic growth of the KP010726-WSM sample.

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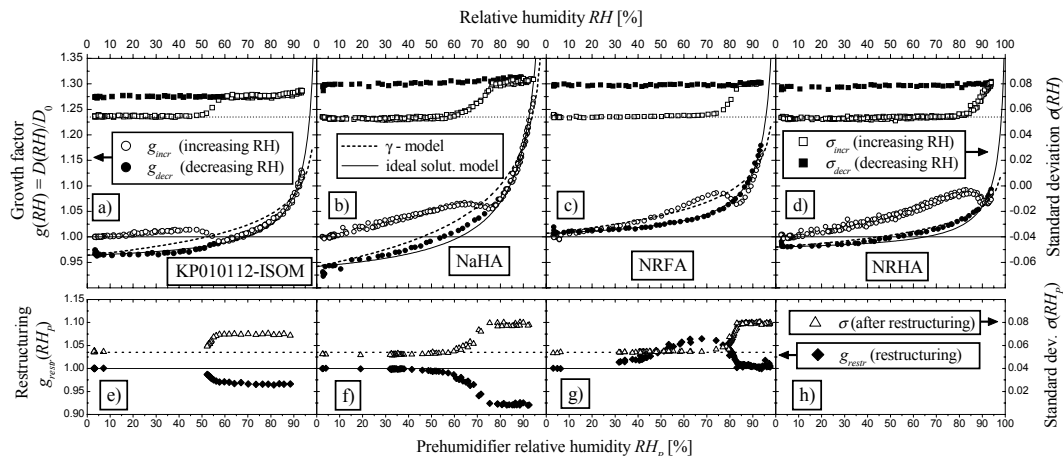


Fig. 8. Hygroscopic properties of particles generated from ISOM, NaHA, NRFA and NRHA solutions: **(a)–(d)** Hygroscopic growth factors (left ordinate) and broadening (right ordinate) of the monodisperse aerosol as a function of RH (upper abscissa). **(e)–(h)** Restructuring (left ordinate) and standard deviation (right ordinate) after restructuring as a function of prehumidifier RH (lower abscissa).

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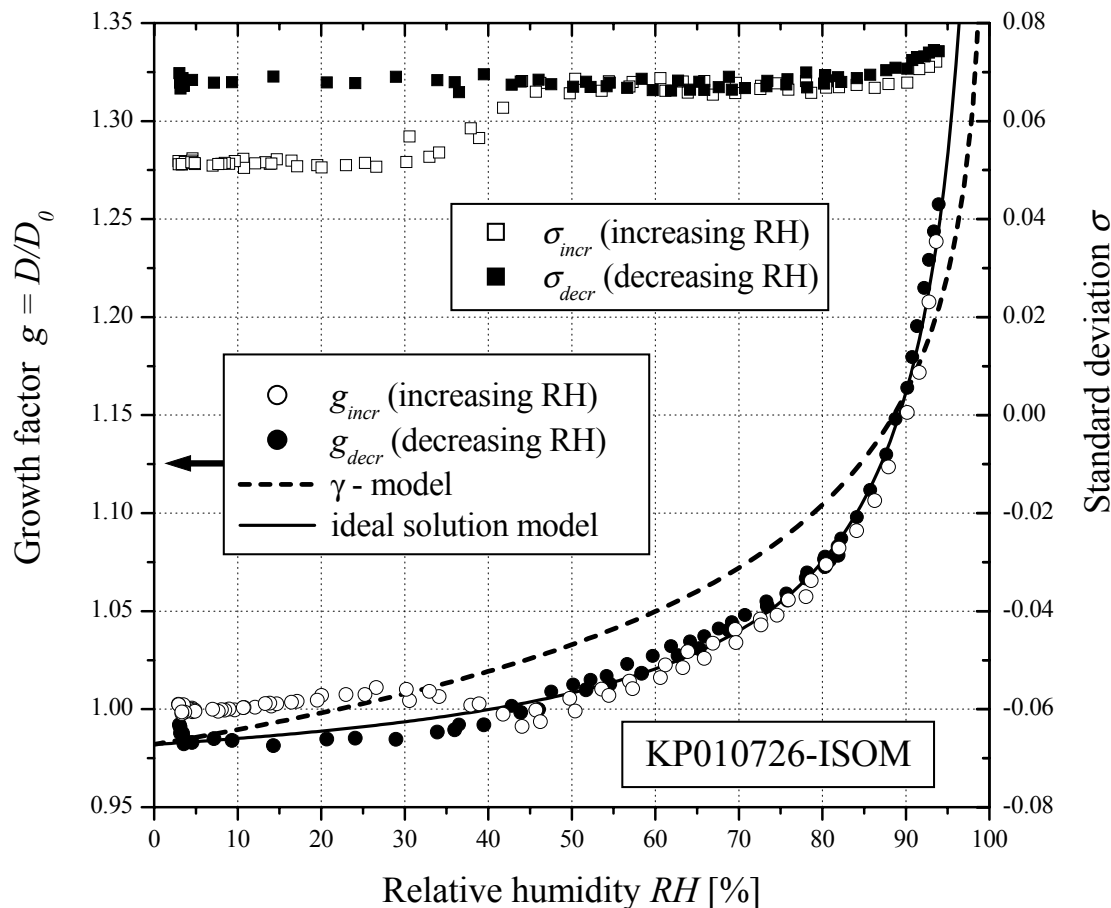


Fig. 9. Hygroscopic growth factors (left ordinate) and corresponding standard deviations (right ordinate) of the KP010726-ISOM sample under increasing and decreasing RH conditions.

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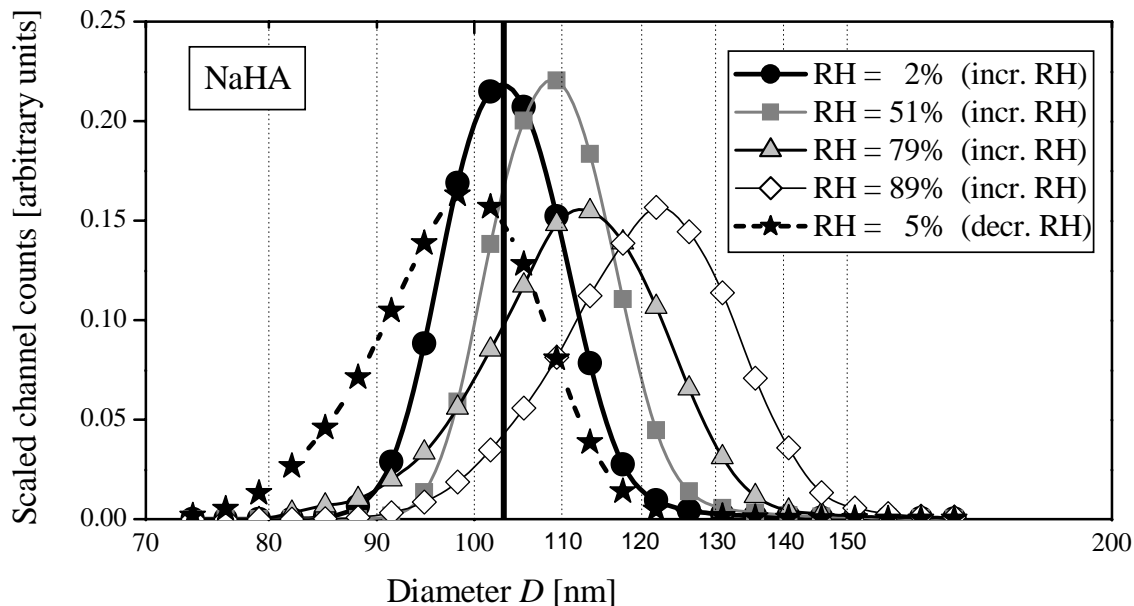


Fig. 10. Size changes and broadening of the monodisperse NaHA-aerosol at different RH. Initial dry size ($D_0 = 103$ nm) marked with a vertical line.

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