**Atmospheric
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Discussions**

Influence of semi-volatile species on particle hygroscopic growth

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Abstract

The hygroscopic properties of aerosol particles are often related to their content of soluble material, on the basis of the Kohler theory. Recent studies, however, seem to indicate that the role of aerosol particle semi-volatile fraction properties has been underestimated. In this study, we use a novel method based on a Tandem Differential Mobility Analyser (TDMA) system combining particle volatilization and humidification conditioning (VH-TDMA) to test the effect of the gentle volatilization of a small fraction of the atmospheric particles on the particle hygroscopic growth in several environments (urban to remote). Results show that the particle hygroscopic properties can either be enhanced or decreased after thermal conditioning of the particle at moderate temperatures (50 to 110°C). The hygroscopic growth factor changes induced by volatilization indicate that some volatile compounds, although present at low concentrations, drastically influence the hygroscopic growth of particles in the way that can not be predicted by the Kohler theory at equilibrium.

1 Introduction

Knowledge of hygroscopic properties of atmospheric particles is important to better quantify the role of aerosols in the climate system. Uptake of water by atmospheric particles not only modifies the mass of aerosol particle but also increases the particle size and therefore its ability to diffuse solar radiation. An increase of the relative humidity from 40 to 80% for the global mean aerosol would, for example, result in an increase of the radiative forcing by a factor of 2.1 (Pilinis et al., 1995). In addition, because hygroscopic growth is linked to the particle chemical composition, measurement of water uptake reveals the degree of mixing of an aerosol population. In turn, the way in which the various constituents are externally or internally mixed influences the optical properties of atmospheric aerosols (Lesins et al., 2002). Hygroscopic growth is also a key parameter linking aerosol particles to the number of cloud condensation

nuclei (CCN) potentially forming a cloud, which in turn influences climate through the so-called indirect effect (Twomey, 1977). A certain number of studies have therefore investigated water uptake by atmospheric aerosols in order to provide a unambiguous and reliable link between aerosol hygroscopic properties and the number of particles
5 of an aerosol population activating to cloud droplets in a humid environment (Rissler et al., 2004; Kreidenweiss et al., 2005).

   The Kohler theory (1936) is often used to describe the critical supersaturation at which a Cloud Condensation Nuclei (CCN) of known size is activated, i.e. grows into a cloud droplet. The reliability of the model calculation strongly depends on the input
10 parameters of the model, e.g. the surface tension, the molality of the solution formed on the aerosol particle, the fraction of soluble material, the protonation constants, Van't Hoff factor, etc. Most of these properties are often not measurable in the field and input parameters are often simplified to a reduced number of compounds.

   The Kölher theory appears well-suited to describe the activation of pure inorganic
15 particulate matter (e.g. Ammonium Sulphate, Sodium Chloride etc.), but not always of the behaviour of more complex mixtures including organic material (Svenningsson et al., 2006). Organic compounds tend to have limited water solubility, which implies that they are less CCN active, and not detected in the sub saturation region. Some studies (Saxena et al., 1995; Raymond and Pandis, 2002) have shown that organic
20 material can affect the hygroscopic behaviour of aerosol particles and activate particles more easily than the Kohler theory predicts from inorganic salts. In other cases, however, the Kohler theory tends to overestimate droplet number concentration (Snider and Brenguier, 2000). The hygroscopic growth for organic-inorganic mixtures has also been compared to growth models, with various degrees of agreement. While several
25 studies have successfully predicted hygroscopic growth of some mixtures using the Zdanovskii-Stokes-Robinson (ZSR) relation (Stokes and Robinson, 1966), deviation from this theory has also been encountered even for simple mixtures (Svenningsson et al., 2006).

One of the reasons for the limitation of both the Kölher and ZSR theories may be linked to non-adequate representation of interactions within mixtures. Theoretical calculations of the hygroscopic growth mainly involves the solubility of the particle bulk, but the presence of organics should also be taken into account through the surface tension of the solute, and through the accommodation coefficient of water on the hydrated surface (Pruppacher and Klett, 1997). A certain number of laboratory studies investigated hygroscopic growth of inorganic salts coated with condensable organic material. Results generally revealed a limitation of the growth rate due to the presence of the hydrophilic material (Hansson et al., 1998). However, it is not yet known how all organics compounds influence the particle growth rate when they are exposed to a humid environment. Moreover, synthetic particles do not properly simulate the chemical complexity of natural aerosols. In this study, we investigate how natural volatile organic compounds affect the particle ability to grow in a humid environment using a novel Volatility-Humidity tandem differential mobility analyzer (Villani et al., 2008).

2 Instrument and methods

2.1 Description of the VH-TDMA unit

The need to gain some insight into the chemical nature of sub micrometer aerosols has previously lead to the development of hygroscopic growth and volatility methods for aerosol research. Because the hygroscopic growth depends on the chemical properties of the aerosol, sized particles of different composition can be distinguished through their differing growth response to humidification. Frequently, these properties are investigated using tandem differential mobility analyser (TDMA) systems (Rader and McMurry, 1986). Furthermore, volatile compounds can often be distinguished by the differences in their volatilisation temperatures (i.e. with a V-TDMA system). In this study, the method is based on a TDMA system combining volatilisation and humidification conditioning of the particles (Volatility Hygroscopicity Tandem Differen-

tial Mobility Analyser, VH-TDMA). The VH-TDMA is composed of two DMAs and CPCs (TSI 3010), separated by a thermo-desorbing unit and a hydration device in series. Measuring particle concentration on both DMAs with two CPC is useful for an absolute comparison of the evolution of the four spectra with time. A complete description of the instrument can be found in Villani et al. (2007) for the V-TDMA unit and Villani et al. (2008) for the VH-TDMA. The operation procedures alternate a DRY scan (bypassing thermo-desorption and humidity conditioning units) to control proper functioning of the 2 DMAs, one conventional H-TDMA scan to measure the hygroscopic growth factor (Hgf) of monodispersed dry aerosol, one conventional V-TDMA scan to measure size reduction of monodispersed dry aerosol after thermal treatment at specified temperature, and one Volatility-Humidity scan to measure the Hgf of thermally treated monodispersed aerosol.

The Hygroscopic growth factor (Hgf) at 90%RH is measured as followed:

$$\text{Hgf} = D_p^{90}/D_p^{10}$$

where D_p^{90} is the particle diameter at RH=90% and D_p^{10} is the particle diameter at RH=10%. The mean residence time of the aerosol in the pre-humidifier and in the subsequent line leading to DMA2 is about 6 s. In the DMA-CPC, the particles stay for another 6 s before being finally counted, leading to an overall conditioning time of about 12 s.

The Volatility "growth" factor (Vgf) can be derived from the Volatility scan. It is the relative size change of a particle due to thermal conditioning. For a given thermo-desorbing temperature T°, it is calculated as the ratio between the particle diameter at RH=10% ($D_p^{10,T°}$) and the dry particle diameter at RH=10% and ambient temperature ($D_p^{10,\text{Tamb}}$), thus:

$$\text{Vgf} = D_p^{10,T°}/D_p^{10,\text{Tamb}}$$

For a thermo-desorbing temperature ranging from ambient temperature to 300°C, the resulting residence time in the oven heating path (30 cm) is t_R=1 s.

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Logically, the Volatility-Hygroscopic growth factors (VHgf), that is the hygroscopic growth of a thermally processed particle is derived as:

$$\text{VHgf} = D_p^{90,T^\circ}/D_p^{10,T^\circ}$$

where D_p^{90,T° is the particle diameter at RH=90% and $T>T_{amb}$. The VHgf is therefore
5   calculated considering the "new" diameter resulting from thermo-desorption.

The modes are determined by fitting the distribution after an inversion procedure that accounts for the instrumental broadening of the modes caused by the finite width of the transfer functions of the DMAs and for the system transmission efficiency. For simplicity, it is often assumed that the growth factors within each group of particles
10   are normally distributed. The uncertainty on the VHgf measurements propagates from the uncertainty on the Hgf measurements. It was pointed out in recent H-TDMA intercomparison workshops, that most variability in Hgf measurements results from the RH control of DMA2. Because the VH-TDMA scans are performed under the same conditions of RH and because no RH drift in DMA2 has been detected, uncertainty
15   on the VHgf measurements are similar to that on the Hgf measurement, that is close to ±2.0% at 90%RH. (Villani et al., 2008). During the campaigns, regular calibrations were performed using synthetic ammonium sulphate particles. The error on the resulting VHgf/Hgf ratio calculation was evaluated to be less than 3.0%.

Laboratory studies confirmed that thermo-desorption is very efficient to remove species
20   condensed onto the particle surface as long as the prescribed volatilisation temperature of the thermo-desorbing unit exceeds the volatilisation temperature of material condensed onto the particle surface (Johnson et al., 2004; Villani et al., 2008). The heating temperature for the volatility and Volatility-Humidity scans is identical and set between 90°C and 110°C. This temperature is lower than that used in most V-TDMA
25   studies. This is because the goal of this study is to investigate the role of semi-volatile organic and inorganic that evaporates at these temperatures. Careful checks were performed to insure that re-condensation does not take place onto the particles during cooling. As confirmed by laboratory experiments, changes in Hgf between H-TDMA

and VH-TDMA scans can be attributed to the removal of condensed material from the particle surface back to the gas phase. Loss of material from the particle is controlled through comparison between DRY scan and V-TDMA scan. In most cases, conditioning leads to a reduction of the particle diameter of less than 5%, corresponding to a change in volume of less than 15%.

During field operations, 2 particle sizes were selected based on the aerosol size distribution. In most cases, one size was selected in the Aitken mode (20–30 nm) and another size in the accumulation mode (90–110 nm). The duration of the complete scan for each particle diameter is of the order of 15 min. For consistency, we only report, in this paper, results obtained for accumulation mode particles.

Lower quality data are excluded from the row data with quality assurance routines. Scans showing one data point deviating more than 2% from the excess air default humidity, in flow rate deviating more than 2% from the default flow rate, or in inlet concentration deviating more than 20% from the average inlet concentration of the scan, did not pass the quality criteria. In a second step each hygroscopic growth distribution is fitted using a Gaussian fit algorithm and reduced to two parameters. One is the hygroscopic growth factor (GF) of each particle group found in the hygroscopic growth distribution. The second parameter is the number fraction (nf) of each particle group and is defined as the ratio of particles belonging to one hygroscopicity group and the number of particle of the entire hygroscopic growth distribution.

Particles are classified into 3 different classes according to their Hgf: "class I" (i.e. hydrophobic mode) with GF in the range 1.0–1.3 (±0.1), the "class II" (i.e. moderately-hygroscopic mode) with GF in the range 1.3–1.6 (±0.1) and the "class III" (i.e. hygroscopic mode) with GF in the range 1.6–2.3 (±0.1).

2.2 Description of sampling conditions

A series a field campaigns were performed at four locations in Europe during 2005, 2006 and 2007, representing different environments. Here, we shortly describe the four different sites used in this study:

Site #1: Puy de Dôme – From 19–26 October 2005 aerosol particles were sampled in the experimental station located at the summit of Puy de Dome (1465 m a.s.l.). Meteorological parameters including wind speed and direction, temperature, pressure, relative humidity, and radiation (global, UV and diffuse), gases (O_3, NO_x, SO_2, CO_2,

5 CO), black carbon (BC) and particle size distribution are monitored throughout the year. During the sampling period, access to the site was restricted to authorized persons, cars being stopped 5 km before the summit at 850 m a.s.l. At this time of year, the Puy de Dôme summit lies most of the time in the free troposphere.

Site #2: Clermont-Ferrand-Aubière – From 1–15 December 2005 aerosol particles

10 were sampled in the city of Aubiere Cedex, France. A field campaign were performed at the LaMP (Laboratoire de Meteorologie Physique), a few kilometers south-est of the Clermont-Ferrand city center, at the Cezeaux Campus (394 m a.s.l.). The choice of the site is justified by the fact that it shows both an urban character because of an intense circulation at peak hours of working days and a perish-urban character during

15 the night and the public holidays, being located at a few kilometers of the centre town of Clermont-Ferrand.

Site #3: Mace Head, Ireland – Located on the western coast of Ireland, the research station in Mace Head (88 km of Galway) offers an exposure to the Northern Atlantic Ocean, hence the possibility to study the background atmospheric composition in the

20 Northern Hemisphere during western wind sectors and continental emissions of Europe during eastern conditions sector. Hygroscopic properties of 85 nm particles were determined from 12 to 27 January 2006.

Site #4: Leipzig, Germany – The measurements were performed from 4 to 27 February 2007 at an urban measurement station in Leipzig, Germany. At this station we

25 obtained a dataset of three weeks characterizing the volatile and hygroscopic properties of urban atmospheric data (street canyon level). Thus, sources for primary and secondary aerosols are available, comprising sulfate, nitrate, and carbonaceous compounds.

At each site, we have sampled one or more air mass types during the duration of the campaign which lasted from one week (Puy de Dôme) to several weeks (Clermont-Ferrand, Leipzig and Mace head campaigns).

Table 1 summarizes the sampling sites location and characteristics of the air masses sampled during the campaign at each site.

3   Results from H-TDMA and VH-TDMA measurements

Averaged measurement of Hgf and VHgf (and their respective standard deviations) for the time periods corresponding to the air masses described in Table 1 are summarized in Table 2 for the different field campaigns.

In this paper, we will not investigate in detail the time evolution of the Hgf at the different locations but focus on the information provided by average values from each measuring period. As seen clearly from Table 2, the aerosol population for a given diameter is composed of several hygroscopic classes, an indication of externally mixed particles, regardless of the location. The relative fractions of particles in the different hygroscopic modes derived from the H-TDMA and VH-TDMA runs are indicated in Table 3.

The hydrophobic particles, likely composed of freshly formed organic material, are ubiquitous to all sites except for background sites during clean conditions: marine conditions at Mace Head for which only class II and class III particles are detected (Sellegri et al., 2008) and at Puy de Dôme under South-West flow. The fraction of hydrophobic particles is the highest of all fractions in urban or sub-urban areas as observed in previous studies (Berg et al., 2000). The slightly lower fraction of hydrophobic particles (0.47) is surprising for the Leipzig conditions and may indicate the presence of a significant fraction of particles originating from regional-scale transport. At Mace head during continental air masses conditions, the night time aerosols had different hygroscopic properties than during daytime. The nigh time aerosol comprised a majority of hydrophobic particles, with a proportion close to urban areas. This feature can be

attributed to the frequent use of peat burning for domestic heating in the Conemara region.

The moderately hygroscopic particles are ubiquitous, and it was found in all experiments except at Puy de Dôme for a short period. This class of particles is likely composed of an internal mixing of more and less oxidized organic material and inorganic salts and presumably issued from aged aerosol.

Finally, a more hygroscopic fraction is detected at Puy de Dôme and Mace Head, corresponding to the presence of a mixture of sea salt with organic or inorganic compounds (1.82 HGF is lower than expected from pure sea salt, and higher than expected from ammonium sulphate or any atmospheric organic). More details concerning the variability of Hgf during the campaigns are given in Sellegri et al. (2008).

Volatility Hygroscopic Growth Factors have been measured during the campaigns, simultaneous to Hgfs. As seen from Table 2, thermal processing at 100°C leads to a 5 nm change in particle diameter for original particles of 100 nm. First, we can see that VHgf and Hgf are usually of the same order of magnitude. However, even considering the uncertainty on the Hgf (or VHgf) measurements, the ratio between VHgf and Hgf is sometime significant and can result in either significantly >1 (thermo-desorbed particles grow more than the original one) or significantly <1 (thermo-desorbed particle grow less that the original one).

The relative changes of Hgf, derived from Table 2, and number fraction derived from Table 3 in each hygroscopic mode are reported Fig. 1, together with the uncertainty expected from our measurement (as a dashed box).

As seen from Fig. 1, the relative difference between VHgf and Hgf can be as high as +8% and as low as –10%. But most importantly, Fig. 1 outlines interesting features regarding the changes implied by the thermodesorption process.

– The hydrophobic particles (class I, small symbols in Fig. 1) experience little changes in hygroscopicity on average, neither in term of mean GF (Table 2) nor in term of number fraction of particles found in this mode (Table 3). The highest positive change is observed at Puy de Dome, period 1, which number fraction increased

after thermodesorption (+25% but class III disappeared). The highest negative change is observed at Mace Head, period 3, which −12% in number fraction after thermodesorption.

– The thermal processing of moderately hygroscopic particles (class II, medium symbols in Fig. 1) usually leads to increased Hgf as in the case of Puy de Dôme, period 1 (+5%) but also occasionally decreased Hgf as in the case of Mace Head, period 1 (−5%). However, the most striking point concerning this class of particles is a clear change of number fraction after thermodesorption. In the case of the Puy de Dôme (periods 1 and 2), the more hygroscopic particles (class III) are found back in the moderately hygroscopic mode (class II) hence a change from the range 1.83–1.86 to the range 1.43–1.51.

– The Hgf of the more hygroscopic particles (class III, big symbols in Fig. 1) are either decreased (Puy de Dôme, period 3, −9%) or slightly increased (Mace Head, period 1) with increased number fraction after thermal processing. In the case of Mace Head, the increase of Hgf and number fraction after thermodesorption could be attributed to the volatilization of organic compounds internally mixed with sea salt in the accumulation mode (Sellegri et al., 2008). As mentioned above, the most pronounced impact of thermodesorption on the hygroscopic mode is found for the periods 1 and 2 of the Puy de Dôme campaign, during which the class III particles disappeared to the benefit of the class II particles. The theoretical explanations for such a change will be explored next section.

As mentioned previously, any change >+3% or <−3% is significant under our operating procedures. It is clear from Fig. 1 that, with this extended data set, we have shown that gentle thermo-desorption of particles can have a significant effect on particle growth. It is likely that the semi-volatile compounds have different hygroscopic properties than the more refractory particle core. Removal of this volatile fraction therefore would lead to significant change in Hgf and number fraction, either positive or negative. We can conclude that thermal processing can, in some cases, significantly affect

hygroscopic growth of accumulation mode particles. However, additional tests are necessary to check whether a 5% volatilized mass can explain the measured GF changes simply by modifying the aerosol soluble (hydrophilic) mass fraction, or if the volatilized mass had higher effects of the particle hygroscopic growth.

4   Model calculations of removal of an aerosol component on hygroscopic growth

We have used a numerical model of hygroscopic growth based on the Kohler theory to test the effect of removal of condensed species by thermo-desorption on hygroscopic growth. The model describes the interaction between water vapor and aerosol particles by combining the Kelvin curvature effect and Raoult's law (Kohler, 1936). This theory, with some improvements, is widely in use when describing the water uptake of particles. Because we do not have access to the extensive chemical composition of each of the aerosol particles studied in this work, we will study limit cases of mixtures of a highly hygroscopic compound (sulphuric acid) with a hydrophobic organic (fulvic acid).

Tests are performed with a 2-component particle composed of a fully hygroscopic compound (sulphuric acid) with a fully hydrophobic compound (fulvic acid). In that case, the inorganic particle fraction is considered hygroscopically active, while the organic fraction is assumed to be inactive and does not interact either with the water condensed onto the particles nor the surrounding water vapour. We have chosen fulvic acid as a proxy for the organic fraction because thermodynamic data is largely lacking for the majority of relevant organic species (Saxena and Hildemann, 1996) in particular for the relevant organic species which might be of importance for the hygroscopic behaviour. Water activity (a_w), surface tension (σ) and density (ρ) for the fulvic-sulphuric Acids composition tests are calculated by a physic-chemical model (Topping et al., 2005). The particles are considered to be originally composed of 40% Fulvic acid and 60% Sulphuric acid (by mass).

In a first sensitivity test, we have considered that 1/3 of the sulphuric acid mass is lost during thermo-desorption, resulting in a thermally processed particle composed of equal mass of both fulvic and sulphuric acids (i.e. composition 50:50). This leads to a diameter reduction of 7% of the original particle diameter (93 nm as respect to 100 nm) and of 20% of the particle volume. Results of this sensitivity test are shown in Fig. 2a.

We can obviously perform the opposite test to increase the particle Hgf. The original particle is this time originally composed of 40% sulphuric acid and 60% fulvic acid. Preferential desorption of 1/3 fulvic acid during the thermal processing leads to a particle composed of equal quantities of fulvic and sulphuric acids and to an increase in hygroscopic growth (Fig. 2b).

For a diameter reduction of 7% as respect to the original diameter (20% by volume), the new Hgf is 1.7 at 90% RH as respect to the original value of 1.66. Note that this change in Hgf is again, independent of particle size.

Not surprisingly, this test confirms that the ratio between soluble and insoluble material in a particle highly influences the hygroscopic growth (Kulmala et al., 1996; Swietlicki et al., 1999). As expected, the thermally processed particle can be either less or more hygroscopic than the original particle, depending on the Hgf of the component removed. However, we can see that, in both cases, the growth factor change at 90% RH is about 2%: in order to produce significant changes in the Hgf, a thermo-desorption process should remove a fraction of the particle leading to more than a 5% change in size, which is not observed (see Table 2). For pure AS particles, noticeable effects of thermo-desorption are detected only after a diameter decrease of the particle of more than 40% of its original value.

In conclusion, we can see that a change in Hgf of about 2 % (both positive and negative) can be obtained by a 5% change in particle size. Obviously, because the numerical simulations are performed with a mixture of completely hydrophobic and completely hygroscopic compounds, this numerical simulation has to be considered as the maximum change of Hgf due to the Raoult effect. These calculations show that the significant changes which were observed in the natural aerosols after thermodesorp-

tion can not be explained by the resulting modification of the hydrophilic fraction unless the aerosol is composed of substances with higher surfactant properties. We believe that, in addition to the Raoult effect due to preferential desorption of the semi-volatile components of the particles, additional effects, most probably linked to condensation kinetics or surface tension is witnessed by our results. Other hypotheses, such as changes in the chemical structure of particles (i.e. polymerization) induced by heating cannot be excluded at this point, but appear less straightforward to account for the important changes. Our results would show that some volatile compounds, although present at low concentrations, would drastically influence the hygroscopic growth of particles in the way that can not be predicted by the Kohler theory at equilibrium. Kinetic effects, in the form of the accommodation coefficient, are also playing a role in instruments such as HTDMA because of the limited residence time the particles have in the humidified module. In the case of the Puy de Dôme particles, the volatilization of a highly hygroscopic volatile compound results in a drastic change of hygroscopicity. As shown by laboratory experiments (Villani et al., 2008), the VH-TDMA is, in fact, capable of efficiently removing the totality of a freshly condensed hydrophobic material without altering the Hgf of the inner core material. In Villani et al. (2008), it is shown that if the fresh hydrophobic organic coating is thick enough, the final hygroscopic growth behaviour will be the one of the coating only. The behaviour of particles in a humid environment is therefore dependent upon both the bulk chemical composition and the composition of the particle surface layer. Here we show that, in the natural environment, even a small mass fraction of volatile compounds may drastically modify the global particle hygroscopic growth behaviour. Observation of time series of hygroscopic changes due to volatilization shows that changes are taking place over a limited amount of time (a few hours). The averages presented here are hence lower limits of changes which can be punctually very high. This behaviour may indicate that hygroscopic growth dependency to semi-volatile species is a transient phase in the lifetime of accumulation mode particles.

For the specific cases studied in this work, we can formulate the following hypotheses:

– Disappearance of the more hygroscopic mode of Free Tropospheric aerosol at PDD is likely linked to volatilization of HNO_3 present on the particle surface. Chemical analyses of particles sampled simultaneously at PDD with both ambient and heated inlets indicate a clear loss of NO_3^- after thermo-desorption at 70°C (not presented here). Presence of HNO_3 on the particle surface, even at low concentration, is likely to increase hygroscopic growth (Kulmala et al., 1998). After removal of HNO_3, the more hygroscopic particles have HGF similar to the moderately hygroscopic particles. Discrepancies with modelling results may be linked to the fact that the model does not account for the presence of HNO_3 onto the particle surface but just as a contribution to the particle soluble fraction.

– Increase in Hgf after thermo-desorption of the moderately hygroscopic particles at Cezeaux/Clermont-Ferrand, and for hygroscopic particles at Mace Head may be resulting from volatilization of hydrophobic organic substances from the particle surface. As opposed to the HNO_3 effect, presence of hydrophobic substances onto the particle surface may lead to stronger effects on hygroscopic growth as respect to similar amounts mixed in the particle composition. The surface effect is not accounted for in the model. Investigation of the chemical nature of the thermo-desorbed material would be of great interest to understand.

– The successive detection of particles sensitive to thermo-desorption and particles not sensitive to thermo-desorption at the same site may indicate that hygroscopic growth dependency to semi-volatile species is a transient phase in the lifetime of accumulation mode particles.

5 Conclusions

We have shown in our study that, under some air mass conditions, gentle thermal processing of aerosol particles can lead to significant changes of the hygroscopic growth factor. These changes are either positive (thermally processed particles are more hygroscopic than the original ones) or negative (thermally processed particles are less hygroscopic than the original ones). These changes are, in some cases, drastic. Under specific air mass conditions, the Hgf of 100 nm hydrophobic particles can be increased by 6% on average at Mace Head and Clermont-Ferrand Cézeaux. On other occasions, thermal processing of moderately hygroscopic particles leads to decreased Hgf as in the case of Clermont-Ferrand Cézeaux (−8%). At Puy de Dôme, and, to a lesser extent, at Leipzig, thermo-desorption of very hygroscopic particles leads to the suppression the more hygroscopic mode. On shorter time scale, gentle thermodesorption leads to difference between VHgf and Hgf can be as high as +16% and as low as −14%.

Using numerical modelling of hygroscopic growth, we have shown that neither the Kelvin effect nor the Raoult effect alone can explain our findings. We have simulated hygroscopic growth for internally mixed particles composed of fulvic and sulphuric acids, one totally hydrophobic and the other totally soluble. Because numerical modelling considers a mixture of totally soluble and totally hydrophobic substances, results of the simulation provide maximum estimates for the Raoult's effect. The change in Hgf cannot theoretically exceed 2% when a particle is not allowed to loose more than 5% of its original diameter.

We therefore believe that additional effects are taking place in addition to the Raoult effect, due to desorption of semi-volatile compounds. Alternative hypotheses, such as changes in the chemical structure of particles (i.e. polymerization) induced by heating cannot be excluded at this point, but appear less straightforward to account for both positive and negative changes.

Because this effect is not observed at all time, we formulate the hypothesis that hygroscopic growth dependency to semi-volatile species condensed onto the particle surface is a transient phase in the lifetime of accumulation mode particles. This transient phase explains the increase in Hgf observed between freshly formed particles (Hgf close to 1) and more mature oxidized particles (Hgf close to 1.5). During the transient phase, condensable material can be removed from the particle surface only shortly after initial condensation. Photochemical and/or chemical evolution of the particle leads to stronger chemical bindings and less sensitivity of Hgf to gentle thermal treatment.

Our results imply that, in the natural environment, the chemical properties of the particle semi-volatile material influence the hygroscopic growth in specific conditions. Because the link between hygroscopic growth and CCN activity is not linear, it is, however, difficult at this point to predict this effect on CCN activation from our measurements.

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Table 1. Air mass type categorized with NOAA HYSPLIT MODEL back trajectories analysis calculated on three days for the four sampling sites.

Site	Period	Dates	Dry size	Air mass type/origin
#1 – Puy de Dome, France	1	22–24 October 2005	100 nm	Marine Air Mass/West
	2	25 October 2005	100 nm	Continental Air Mass/South-West (Spain)
	3	26 October 2005	100 nm	Continental Air Mass/South-West (Spain)
#2 – Clermont-Fd, France	1	1–4 December 2005	100 nm	Continental Air Mass/South-West (Spain)
	2	5–9 December 2005	100 nm	Marine Air Mass/North-West
	3	10–16 December 2005	100 nm	Continental Air Mass/North-Est (Germany)
#3 – Mace Head, Ireland	1	16–22 January 2006	85 nm	Marine Air Mass/West
	2	21–23 January 2006 (day)	85 nm	Continental Air Mass/South-Est (France)
	3	21–23 January 2006 (night)	85 nm	Continental Air Mass/South-Est (France)
#4 – Leipzig, Germany	1	4–27 February 2007	100 nm	Continental Air Mass

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Table 2. Averaged measurement of Hgf and VHgf (with standard deviation) corresponding to air masses described in Table 1 and different field campaigns. HGF are sorted into 3 hygroscopic classes: Class 1 – hydrophobic particles (Hgf<1.3), Class 2 – moderately hygroscopic particles (1.3<Hgf<1.6) and Class 3, more hygroscopic particles (Hgf<1.6). VHgf are sorted in a similar manner; (X=disappeared).

Site	Dry Size (nm)	Period	Averaged Hgf classes			T_{vol} (°C)	Averaged VHgf classes			Vgf
			I class	II class	III class		I class	II class	III class	
Puy de Dôme	100	1	1.07±0.06	1.37±0.08	1.83±0.09	70°	1.15±0.06	1.43±0.11	X	0.94
		2	1.09±0.09	-	1.86±0.08		1.11±0.07	1.51±0.09	X	0.97
		3	-	1.45±0.07	1.89±0.08		-	1.48±0.07	1.71±0.08	
Clermont-Ferrand	100	2	1.04±0.04	1.38±0.10	-	70°	1.06±0.04	1.39±0.08	-	0.95
		3	1.08±0.06	1.41±0.12	-		1.12±0.07	1.34±0.07	-	0.92
Mace Head	85	1	-	1.40±0.18	1.82±0.16	90°	-	1.33±0.19	1.86±0.17	0.95
		2	1.03	1.51	-		1.06	1.56	-	0.89
		3	1.05	1.48	-		1.02	1.48	-	
Leipzig	100	1	1.0±0.02	1.44±0.07	-	110°	1.03±0.01	1.48±0.06	-	0.95

Table 3. Averaged relative number fractions derived from the H-TDMA and VH-TDMA measurements corresponding to air masses described in Table 1, hygroscopic classes of Table 2 for the different field campaigns; (X=disappeared).

Site	Period	Averaged H number fraction			Averaged VH number fraction		
		I class	II class	III class	I class	II class	III class
Puy de Dome	1	0.12	0.62	0.26	0.15	0.85	X
	2	0.80	–	0.20	0.81	0.18	X
	3	–	0.57	0.43	–	0.6	0.4
Clermont-Fd	2	0.68	0.32	–	0.72	0.28	–
	3	0.61	0.39	–	0.59	0.41	–
Mace Head	1	–	0.42	0.58	–	0.35	0.65
	2	0.14	0.86	–	0.14	0.86	–
	3	0.66	0.34	–	0.58	0.42	–
Leipzig	1	0.47	0.53	–	0.51	0.49	–
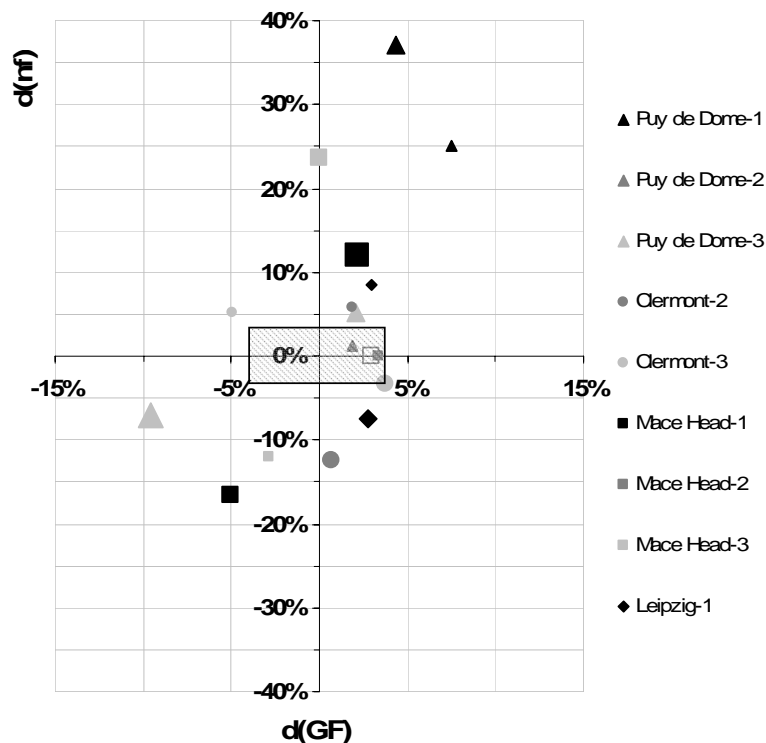
Fig. 1. Number fraction relative difference, d(nf), as a function of VHgf and Hgf relative difference, d(GF) for the different hygroscopic classes corresponding to air masses and for each field campaign described in Table 1.
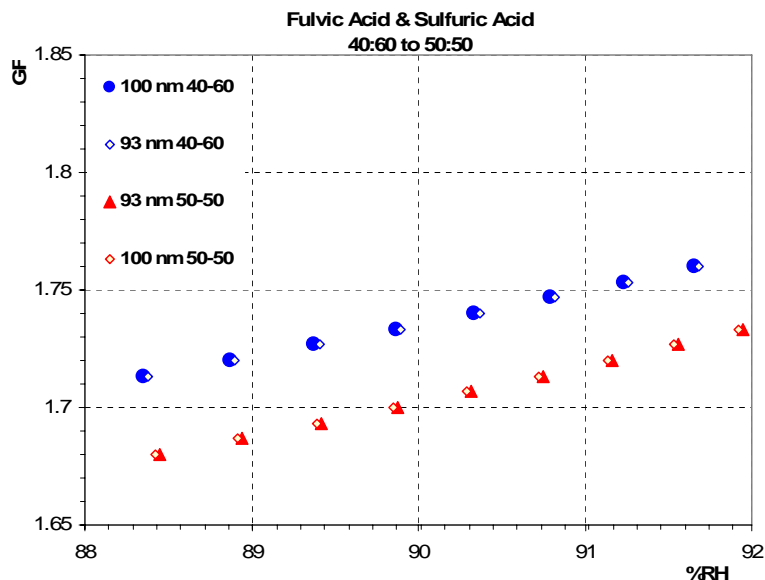
Fig. 2a. Modeled hygroscopic particle growth with initial composition of 40:60 (mass ratio) fulvic acid-sulphuric acid and preferential desorption of sulphuric Acid.
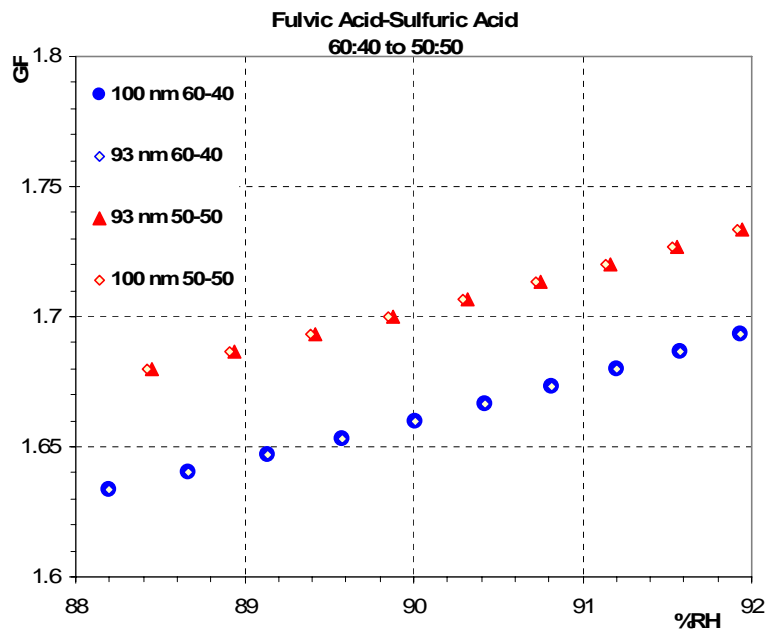
Fig. 2b. Modeled hygroscopic particle growth with initial composition of 60:40 (mass ratio) fulvic acid-sulphuric acid and preferential desorption of fulvic Acid.