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Processing of Soot by Controlled Sulphuric Acid and Water Condensation—Mass and Mobility Relationship

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1. INTRODUCTION

Soot aerosols are ubiquitous in the atmosphere and are of interest in studies related to adverse effects on human health and climate forcing. Fresh soot from numerous sources such as diesel (Kittelson 1998) and spark ignition engines (Kittelson et al. 2006), biomass emissions (Wierzbicka et al. 2005), laboratory scale burners (Maricq et al. 2003), and indoor sources (Pagels et al. 2009) has been characterized. However, processing of soot undergoing condensation of low vapor pressure oxidation reaction products, as occurs during ageing in the atmosphere, has received much less attention. An important property of soot is its structure—or morphology. The morphology of fresh soot contains information about particle formation processes. Furthermore, Mikhailov et al. (2006) have shown that the hygroscopic and optical properties of soot can change dramatically upon condensation of hygroscopic material. Atmospheric processing of soot considerably alters its ability to scatter light and form clouds (Zhang et al. 2007; Fan et al. 2008). A transformation from fresh hydrophobic to processed hygroscopic soot also influences adverse health effects as the deposition probability throughout the respiratory tract will be altered (Löndahl et al. 2008). Because all of these effects depend on morphology, it is important to understand how atmospheric processing affects morphology.

Fresh soot typically consists of agglomerated structures built up by a large number of primary particles. The morphology is often studied using Transmission Electron Microscopy (TEM), (Park et al. 2004a; Wentzel et al. 2003). A parameter describing the compactness of the population of agglomerates constituting the aerosol is the fractal dimension, \( D_f \). The relation between the radius of gyration, \( R_g \) (a suitable length scale of the agglomerate), and the number of primary particles, \( N \), is:

\[
N \propto R_g^{D_f} \tag{1}
\]

Based on this expression a number of investigators have theoretically studied the dependence of other particle properties including mass, light scattering and absorption, and mobility on the agglomerate fractal dimension. These analyses normally
involve simplifying assumptions about the size distribution of the primary particles (often assumed to be monodisperse), the angular distribution of the primaries relative to the center of mass (often assumed to be uniform), the extent to which “inner” primary particles are shielded from interactions with the carrier gas by other primary particles in the agglomerate, and the transport regime (free molecular, continuum, transition) (Schmidt-Ott et al. 1990; Chakrabarty et al. 2007; Lall and Friedlander 2006). Efforts have also been made to theoretically account for those dependencies (Naumann 2003). The fractal dimension for agglomerates, $D_f$, has been determined experimentally using TEM (e.g., Wentzel et al. 2003; Park et al. 2004a; Neer and Koylu 2006). Uncertainties in determining $D_f$ from TEM analysis include extracting 3D structural properties from measured 2D projected properties (Brasil et al. 1999; Park et al. 2004a).

Rather than basing our analyses on Equation (1), we developed the Differential Mobility Analyzer—Aerosol Particle Mass Analyzer (DMA–APM) (McMurry et al. 2002; Park et al. 2003) technique to characterize agglomerate properties. This approach involves direct, accurate measurements of the mobility diameter $d_m$ and mass $m$ of the same agglomerate particles over a range of mobility sizes. The following empirical expression is then used to determine the relationship between mass and mobility diameter:

$$ m \propto d_m^{D_{fm}} $$

where $D_{fm}$ is the mass fractal dimension, which is not necessarily equal to the fractal dimension defined by Equation (1). We have found that this power law expression typically provides an excellent fit to mass-mobility data for agglomerates produced by other primary particles in the agglomerate, and the transport regime (free molecular, continuum, transition) (Schmidt-Ott et al. 1990; Chakrabarty et al. 2007; Lall and Friedlander 2006). Efforts have also been made to theoretically account for those dependencies (Naumann 2003). The fractal dimension for agglomerates, $D_f$, has been determined experimentally using TEM (e.g., Wentzel et al. 2003; Park et al. 2004a; Neer and Koylu 2006). Uncertainties in determining $D_f$ from TEM analysis include extracting 3D structural properties from measured 2D projected properties (Brasil et al. 1999; Park et al. 2004a).

Values of $D_{fm}$, derived from the mass-mobility relationship, reflect true 3D interaction of the soot agglomerates with the surrounding gas, and accounts for the effects of shielding on mobility (drag), particle transport regime, variabilities in primary sizes, and asymmetries in spatial distributions of primaries about the center of mass. Measurements of mass and mobility diameter can also be used to determine the effective density, $\rho_{eff}$ (particle mass divided by the “effective volume” based on the mobility diameter), which we define as:

$$ \rho_{eff} = \frac{6m}{d_m^3\pi}. $$

Other techniques to determine $D_{fm}$ involve inferring the particle mass or effective density from aerodynamic diameter measurements at reduced pressures by applying a low pressure impactor or an aerosol mass spectrometer (DeCarlo et al. 2004; Park et al. 2008) downstream a DMA.

Mass fractal dimensions of fresh diesel soot, $D_{fm}$, are typically in the range of 2.2–2.4 (Park et al. 2003; Maricq and Ning 2004), indicating relatively open structures ($D_{fm}$ is 3.0 for spherical particles). Effective densities are in the range of 0.2–1.1 g/cm$^3$, typically decreasing with size, significantly lower than the inherent material density of soot, which was found to be 1.27–1.78 g/cm$^3$, increasing with size (Park et al. 2003, 2004b). Higher $D_{fm}$ values (up to 2.9), indicating more compact particles, have been attributed to condensation of organics and H$_2$SO$_4$ during sampling dilution (Skllas et al. 1998). Olfort et al. (2007) studied diesel emissions after an oxidative catalytic converter. At higher load, the H$_2$SO$_4$ fraction in the particles was higher and $D_{fm}$ was 2.76 compared to 2.44 at lower load.

DMA–Aerosol Mass Spectrometer (DMA–AMS) studies of soot generated using a lab burner with propane fuel showed that at an equivalence ratio above 4, $D_{fm}$ abruptly increased from around 1.7 to 2.95. This was associated with an increase in organic carbon from condensation (Slowik et al. 2004). Schneider et al. (2006) used the DMA–AMS technique to study particles from biomass emissions. For dry beech fuel they found $D_{fm} = 2.1$, while for several humid fuels they found $D_{fm}$ close to 3.0. Geller et al. (2006) used the DMA–APM technique to show that $D_{fm}$ was about 2.4–2.5 nearby two freeways, while at several other ambient locations, where particles were expected to be more processed, $D_{fm}$ was 2.8–3.0 indicating compact particles. These studies together demonstrate a link between $D_{fm}$ and $\rho_{eff}$ and after treatment/processing.

A topic where previous results are conflicting is whether restructuring of the soot core into a more compact form contributes to the transformation from agglomerates to compact particles. Diesel soot particles exposed to supersaturated RH in up to three cycles within an Environmental Scanning Electron Microscope showed only limited restructuring (Huang et al. 1994). No evidence for restructuring was found for ambient aggregates when passed through a cycle of supersaturated water before sampling (Kim et al. 2001) onto TEM grids. On the other hand, Mikhailov et al. (2006) coated laboratory generated micrometer sized soot aerosol with glutaric acid, a water soluble organic component of atmospheric relevance. Using TEM analysis they found that the coating process leads to compaction of the agglomerates to an extent that depends on the mass fraction of condensed material. Furthermore, exposing coated soot to saturated water vapor led to additional compaction.

Several authors have shown decreases in mobility size using Tandem DMA measurements of airborne soot particles upon exposure to subsaturated and supersaturated liquids such as water vapor (e.g., Weingartner et al. 1997; Rissler et al. 2005) organic solvents (Kutt and Schmidt-Ott 1992), and Scanning Mobility Particle Sizer (SMPS) measurements of reaction products from terpene oxidation condensing on soot (Saathoff et al. 2003). However, shifts in mobility diameter may be caused by alterations in both particle mass and morphology and it is often not possible to separate these effects using mobility measurements alone.

Slowik et al. (2007) used the DMA–AMS and TDMA techniques to measure changes in mobility diameter and vacuum
aerodynamic diameter of laboratory-generated ethylene soot upon condensation of either oleic acid or anthracene. A thermal denuder was used to evaporate condensed material. Using a model which involves assessing the particle mass and dynamic shape factor from measured properties (DeCarlo et al. 2004) they found that as the mass increased due to condensation onto the soot, the mobility diameter remained constant, while the dynamic shape factor decreased. As the dynamic shape factor reached a value close to 1, the mobility diameter started to increase. Only for oleic acid and soot generated at the lowest equivalence ratio did they observe moderate restructuring of the soot core upon a condensation–evaporation cycle.

It has been suggested that the restructuring of aggregates upon condensation is caused by the surface tension forces the condensed liquid exerts on the aggregate core (Kutz and Schmidt-Ott 1992). Condensation may be enhanced in small angle cavities between primary particles by the inverse Kelvin effect (Weingartner et al. 1997). Sulphuric acid and water have significantly higher surface tensions than those of the organic compounds studied by Slowik et al. (2007). Sulphuric acid and water are together with organics and nitrates common components in the ageing of soot through condensation in the atmosphere.

In the present study, soot processing has been investigated using controlled condensation of sulphuric acid and water vapor onto laboratory generated flame soot. We performed direct measurements of the change in mobility diameter and mass upon processing, using the TDMA and DMA-APM techniques, respectively. We used the mass-mobility relationship to calculate the effective density, fractal dimension and dynamic shape factor of soot undergoing processing of atmospheric relevance. From measurements involving a heater downstream of the condensation chamber we could quantify the extent of restructuring of the soot core upon a condensation-evaporation cycle. Other experiments involved a two-step condensation process, where first hygroscopic material in the form of sulphuric acid was condensed onto the soot at low RH, and then water was added by increasing the RH, before measurement at low RH. This allowed us to study the influence of a hydrophilic coating on soot restructuring during a high RH cycle. By conducting experiments using both spherical PolyStyrene Latex (PSL) and agglomerated soot particles we investigated the influence of morphology on the mass transfer through condensation. The on-line measurements were complemented with TEM measurements of fresh and processed soot. The well-characterized fresh and processed soot described in this paper has been used in studies presented in separate publications for detailed analysis on the effect of processing on hygroscopic growth (Khalizov et al. 2009) and optical properties (Zhang et al. 2008).

2. EXPERIMENTAL SECTION

A schematic of the experimental set-up is shown in Figure 1. The main components are the soot generation system, DMA1 for selecting particles with given mobility size, an “aerosol

![FIG. 1. Experimental set-up to study the effect of soot processing on the mass-mobility relationship. In the TDMA (DMA-DMA) mode the effect on the mobility size upon processing was studied. In the DMA-APM mode the effect of processing on particle mass was studied. The different configurations used for soot processing are given in Table 1.](image-url)
conditioner," which simulates processing similar to that which may occur in the atmosphere, and either a second DMA to measure the altered mobility size or the APM to measure the mass of fresh and processed soot. The soot generation and processing procedures, the TDMA set-up and TEM analysis are described in more detail by Khalizov et al. (2009).

2.1. Aerosol Generation and Sampling

Briefly, a Santoro burner (Santoro et al. 1983) operating on propane fuel at an equivalence ratio of 0.5 was used to generate soot, using a laminar diffusion flame. Particles were sampled using a pinhole diluter. Spherical Polystyrene Latex (PSL) particles (Duke Scientific Inc., USA) of sizes 50, 79, 152, and 240 nm were suspended in deionized water (17 MΩ) and then nebulized with an atomizer (Model 3076, TSI Inc.). Particles from both sources were passed through two silica gel diffusion driers and a bipolar charger (210Po, 400 µCi) prior to entering DMA1.

2.2. Processing and Conditioning of Soot

The main components of the aerosol conditioner were a H2SO4 condensation chamber, a Nafion humidifier, a Nafion drier, and a heater (Orsini et al. 1999) to remove condensed volatile material. Several different aerosol conditioning configurations were used and are summarized in Table 1. The condensation chamber (Zhang and Zhang 2005) consists of a 500 mm long, 30 mm inner diameter horizontal Pyrex tube, filled to about 50% with sulphuric acid–water solution, 86% (low) and 96% (high) H2SO4 by weight. The residence time in the chamber was about 12 s. The temperature in the coating chamber was 26 ± 1°C. The flow rate through the chamber was equal to the aerosol flow rate in DMA1, 1.15 lpm. To stabilize the aerosol against evaporation downstream the condensation chamber, 0.05 lpm of N2 saturated with water vapor was added at the outlet of the coating chamber to increase the RH to 5% (Khalizov et al. 2009). The concentration of H2SO4 in the coating chamber was measured using Ion Drift–Chemical Ionization Mass Spectrometry (ID–CIMS) (Fortner et al. 2004, Zhang et al. 2004) to be 1.4·10^10 cm^-3 and 2.5·10^9 cm^-3 for the 96% (high) and 86% (low) H2SO4 solutions, respectively. The heater was operated at 200°C. Previous measurements (Sakurai et al. 2005) show that H2SO4 is completely vaporized at 200°C using the same heater design. When used at the reduced concentrations downstream of a DMA, recondensation of volatilized material on particles at the heater outlet is negligible (Sakurai et al. 2003).

2.3. DMA–APM Measurements

Briefly, the APM (Ehara et al. 1996) consists of two 250 mm tall cylindrical electrodes that rotate at the same angular speed. The inner radius of the outer cylinder is 63 mm, and the outer radius of the inner cylinder is 60 mm. Charged particles are introduced axially into the annular gap between the electrodes and rotate at the same speed as the electrodes as they travel downward through the gap. A positive voltage was applied to the inner electrode while the outer electrode was grounded, which generated a radial electric field. Particles in the gap experienced an outward centrifugal force and an inward electrostatic force since the particles from DMA1 were negatively charged. When these forces were balanced, particles penetrated through the gap without impacting on the electrodes and were detected by the CPC (model 3760, TSI Inc.). The mass of particles that pass

<table>
<thead>
<tr>
<th>Measurement series</th>
<th>Aerosol</th>
<th>H2SO4 concentration</th>
<th>Humidifier (RH%)</th>
<th>Nafion dryer</th>
<th>Heater</th>
<th>DMA2, APM (RH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Calibration</td>
<td>PSL</td>
<td>bp</td>
<td>bp</td>
<td>bp</td>
<td>bp</td>
<td>5%</td>
</tr>
<tr>
<td>B. Coated</td>
<td>PSL</td>
<td>low, high</td>
<td>bp</td>
<td>bp</td>
<td>bp</td>
<td>5%</td>
</tr>
<tr>
<td>C. Fresh</td>
<td>Soot</td>
<td>bp</td>
<td>bp</td>
<td>bp</td>
<td>bp</td>
<td>5%</td>
</tr>
<tr>
<td>D. Coated</td>
<td>Soot</td>
<td>low, high</td>
<td>bp</td>
<td>bp</td>
<td>bp</td>
<td>5%</td>
</tr>
<tr>
<td>E. Coated + High RH cycle</td>
<td>Soot</td>
<td>low, high</td>
<td>90%</td>
<td>Yes</td>
<td>bp</td>
<td>5%&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>F. Coated + Heated</td>
<td>Soot</td>
<td>low, high</td>
<td>bp</td>
<td>bp</td>
<td>200°C</td>
<td>5%</td>
</tr>
<tr>
<td>G. Coated + High RH cycle + Heated</td>
<td>Soot</td>
<td>high</td>
<td>90%</td>
<td>Yes</td>
<td>200°C</td>
<td>5%&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>H. High RH cycle</td>
<td>Soot</td>
<td>bp</td>
<td>90%</td>
<td>Yes</td>
<td>bp</td>
<td>5%&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>I. Coated + Elevated RH</td>
<td>Soot</td>
<td>low, high</td>
<td>20–90%</td>
<td>bp</td>
<td>bp</td>
<td>20–90%&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Only TDMA experiments, mass estimated from series D.
<sup>b</sup>Only TDMA experiments, mass estimated from series F.
<sup>c</sup>Only TDMA experiments.
<sup>d</sup>Limited number of APM measurements up to 80% RH and only for high H2SO4 concentration.
through the APM is determined by the rotational speed and voltage. It should be noted that mass classification by the APM is independent of particle size and shape. This is in contrast to size classification by the DMA, which separates particles according to their electrical mobility, a property that depends on particle size and shape. The APM flow rate was 1.2 lpm.

Particles of a given mobility size were selected using DMA1 and the mass of these particles was then determined using the APM. Experiments were first conducted for spherical PSL particles with known size and material density to calibrate the DMA–APM system, as described by McMurry et al. (2002). After this, measurements were made for fresh soot. The effect of conditioning (Table 1) on particle mobility and mass was then studied for these same aerosols. The masses of fresh ($m_{\text{fresh}}$) and processed soot ($m_{\text{proc.}}$) particles were always measured in adjacent runs to minimize effects of small variations in the soot properties on the determined mass growth factor ($G_{\text{fm}}$, Equation [4]).

$$G_{\text{fm}} = \frac{m_{\text{proc.}}}{m_{\text{fresh}}}$$  \[4\]

The APM was operated in the stepping mode. An APM voltage was set and after a sufficient waiting time the concentration was determined using the CPC. The APM was also operated at RH up to 80%. Measurements employing NaCl aerosol were used to determine the actual RH inside the APM before and after each soot session at 80% RH (Khalizov et al. 2009).

The mass of particles of a given mobility size from the DMA–APM measurements were fitted using a data inversion routine described by Emery (2005). This methodology involves convoluting the individual transfer functions of the DMA and APM to obtain the DMA–APM transfer function using a gradient search routine that minimizes an $\chi^2$ function of three parameters. The specific mass, mass dispersion, and number concentration of particles entering the APM are varied to minimize the difference between predicted system response and the experimental N ($N_{\text{APM}}$) relationship. The altered mobility diameter of processed soot obtained from the TDMA data was used as input in the case of processed soot. DMA–APM measurements of fresh and processed soot were corrected for slight offsets using the PSL calibration. In all cases a single peak could be fitted indicating that both the fresh and processed soot were internally well mixed. The effective density and mass fractal dimension was calculated from the mobility diameter and fitted mass using Equations (2) and (3).

### 2.4. TDMA and Size Distribution Measurements

The TDMA set-up was based on the design of Gasparini et al. (2004), consisting of two long column TSI DMAs (LONG DMA, TSI Inc.) operating at a sheath flow rate of 6.5 lpm $N_2$. TDMA measurements were performed in the size range 30–360 nm. Measurements bypassing the processing unit (for both soot and PSL particles) were used to correct for the slight offset between DMA1 and DMA2. DMA1 was also used as a Scanning Mobility Particle Sizer to determine the mobility size distribution of the diluted fresh soot. At least one SMPS scan was taken before each TDMA series of 5–6 DMA1 sizes. Typically, the Number Geometric Mean Diameter was 130 nm with a Geometric Standard Deviation of 1.8. Hygroscopic growth measurements (using the TDMA and the DMA–APM methods) of the coated soot are reported separately (Khalizov et al. 2009).

### 2.5. TEM Collection and Analysis

Samples for Transmission Electron Microscopy were collected onto TEM grids using an 8 stage Low Pressure Impactor (LPI) (Hering et al. 1979). We collected particles which were first mobility classified in DMA1 upstream and downstream the processing unit. The aerodynamic diameter was calculated using the effective densities determined with the DMA–APM method. This information was used to identify the stage with the appropriate aerodynamic cut-off diameter. A transmission electron microscope (model 2010, JEOL Ltd.) was operated with an accelerating voltage of 100 kV and a magnification of 5,000–50,000 to obtain images of the particles deposited. Copper TEM grids coated with carbon (200 mesh, Ted Pella Inc.) were used.

### 3. RESULTS AND DISCUSSION

#### 3.1. Mass–Mobility Relationship

The fraction of material volatile at 200°C, for example organic carbon, was low for the propane soot used in this study. In experiments where DMA-selected fresh soot particles were either first passed through the heater or passed directly to the APM, the mass ratio of heated to fresh soot was 0.99 ± 0.04 (Figure 2). The size dependent mass growth factors (Equation [4]) when coating fresh soot and PSL using the high sulphuric acid concentration ($1.4 \times 10^{10}$ cm$^{-3}$) are also shown in Figure 2. For soot the mass growth factor is between 2.0 and 2.8, which corresponds to a mass fraction of 50–64% H$_2$SO$_4$–H$_2$O mixture of the coated particle mass. Note that mass growth factors for PSL are typically lower than for soot and show stronger size dependence. When the soot was first passed over the H$_2$SO$_4$ solution and then through the heater, the mass ratio of processed to fresh soot was 1.01 ± 0.04. This illustrates that H$_2$SO$_4$ condensing onto the soot can be removed efficiently using the heater and negligible chemical interaction takes place in agreement with previous findings (Zhang and Zhang 2005).

The shifts in mobility size are given in Figure 3. In most cases the mobility diameter of soot decreased upon processing, which demonstrates that the soot morphology was altered to a more compact shape (the electrical mobility increases and the drag decreases). This tendency is more pronounced for agglomerates with larger initial mobility size. Only for coated particles of the smallest size (30 nm) did the mobility diameter increase. This is the only case when the effect of increased mass dominates...
FIG. 2. Mass growth factors, \( G_{fm} \), of soot and PSL particles measured with the APM. The particles were coated at the high \( \text{H}_2\text{SO}_4 \) concentration (\( 1.4 \times 10^{10} \text{ cm}^{-3} \)) with a residence time of 12 s. Also shown are results for fresh and coated soot particles which passed through a heater at 200°C to remove volatile constituents.

FIG. 3. Ratio of processed to fresh mobility size, \( \frac{d_{B,\text{proc}}}{d_{B,\text{fresh}}} \), for soot and PSL particles, measured with the TDMA technique. Particles were coated at the high \( \text{H}_2\text{SO}_4 \) concentration (\( 1.4 \times 10^{10} \text{ cm}^{-3} \)) with a residence time of 12 s. Soot particles which passed through a high RH cycle were dried to \( \sim 5\% \) RH before classification. Also shown are coated soot particles which passed a heater at 200°C to remove condensed material.

FIG. 4. Effective density, \( \rho_{eff} \), of fresh and processed soot particles calculated from the mass (DMA-APM) and mobility (DMA-DMA) measurements. Particles were coated at the high \( \text{H}_2\text{SO}_4 \) concentration (\( 1.4 \times 10^{10} \text{ cm}^{-3} \)) with a residence time of 12 s. Particles exposed to a high RH cycle were dried to \( \sim 5\% \) RH before classification or further processing. Also shown are coated soot particles which passed through a heater at 200°C.
collapsed to spheres after processing have identical inherent material density and effective density.

To estimate the inherent material density of coated soot (Equation [5]), the mass fractions of soot, \( f_{\text{soot}} \), and \( \text{H}_2\text{SO}_4 - \text{H}_2\text{O} \) mixture, \( f_{\text{H}_2\text{SO}_4 - \text{H}_2\text{O}} \), were first determined from the APM measurements. The density of the \( \text{H}_2\text{SO}_4 - \text{H}_2\text{O} \) mixture, \( \rho_{\text{H}_2\text{SO}_4 - \text{H}_2\text{O}} \), was calculated according to Lide (2006) using the composition of \( \text{H}_2\text{SO}_4 \) at 5\% RH from water activity data for the \( \text{H}_2\text{SO}_4 - \text{H}_2\text{O} \) system (Perry and Green 1997). We assumed no interaction with the soot core and neglected the Kelvin correction. The inherent material density of fresh soot, \( \rho_{\text{soot}} \), was assumed to be 1.77 g/cm\(^3\) (Park et al. 2004b).

\[
\rho_{\text{true, mixed}} = \frac{1}{f_{\text{H}_2\text{SO}_4 - \text{H}_2\text{O}}} \rho_{\text{H}_2\text{SO}_4 - \text{H}_2\text{O}} + f_{\text{soot}} \rho_{\text{soot}} \tag{5}
\]

Heating the coated soot particles decreases the effective density (Figure 4), however, to values significantly higher than for fresh soot. Since the mass of particles first coated and then heated is similar to fresh soot (Figure 2), the increased effective density is in this case caused entirely by restructuring of the soot cores to a more compact form. However, note that the fractal dimension of coated and coated + heated soot is similar. Both the heated series converge to \( \rho_{\text{eff}} \) close to 1 g/cm\(^3\) for the smallest sizes. The reduced \( \rho_{\text{eff}} \) compared to the soot bulk density is likely caused by the internal voids of compacted soot. Taking a material density for soot of 1.77 g/cm\(^3\) would lead to an effective density of 1.33 g/cm\(^3\) for the maximum packing density (0.74 for the face center cubic structure) of the soot primary particles. The lower values we obtain may reflect non-complete restructuring of coated + heated soot. Another explanation is that a non-uniform primary particle size increases the total void fraction.

Representative TEM images of DMA-selected particles are shown in Figure 5. The image on the left shows fresh, unprocessed soot, while other images show soot coated with sulphuric acid (center) and soot that was coated with sulphuric acid and subsequently heated (right). The fresh soot shows a highly irregular structure as expected from the low fractal dimension and effective density. The coated soot shows that considerable compaction has taken place. The smaller droplets between the particles are likely sulphuric acid, which comes off from the soot during impaction. In areas on the substrate with large distances between soot agglomerates, it was evident that each agglomerate was surrounded by a cloud of such satellite droplets. For collected soot particles where sulphuric acid was first condensed and then evaporated, it could be seen that considerable compaction of the particles had occurred.

The effective densities and fractal dimension of the fresh propane soot from the Santoro burner operated at the studied equivalence ratio are lower than the values typically found for diesel engine exhaust. Diesel soot typically consists of up to 50\% volatile material (Sakurai et al. 2003), which may lead to an increased \( \rho_{\text{eff}} \) and \( D_{\text{fm}} \). Further, the primary particle size of the propane soot was around 15 nm, which is smaller than for diesel soot (typically 20–35 nm, Park et al. 2004a). However, in urban environments particles with effective densities lower than those typically found for diesel emissions have been identified (Geller et al. 2006; Park et al. 2008).

Another set of experiments involved coating soot at the lower concentration of \( \text{H}_2\text{SO}_4 \) in the gas phase (2.5 \( \times \) 10\(^9\) cm\(^{-3}\)). The mass growth factors (\( G_{\text{fm}} = m_{\text{proc}} / m_{\text{fresh}} \)) were in this case lower for both soot and PSL (Figure 6). The coated soot particles consisted of 24\% (50 nm) to 18\% (240 nm) condensed species (by mass), while the coated PSL particles consisted of from 18\% (50 nm) to 4\% (240 nm) condensed species. The size

\[
\text{FIG. 5. TEM images of fresh and processed soot particles sampled using a low pressure impactor. Left: Fresh soot, mobility diameter, } d_{B, \text{fresh}} = 240 \text{ nm. Middle: Coated soot (sulphuric acid concentration 1.4 \( \times \) 10\(^9\) cm\(^{-3}\), exposure time 12 s), } d_{B, \text{fresh}} = 240 \text{ nm, } d_{\text{B, proc.}} = 158 \text{ nm. Right: Coated and heated (200\°C) soot, } d_{B, \text{fresh}} = 152 \text{ nm, } d_{\text{B, proc.}} = 102 \text{ nm.}
\]

\[
\text{FIG. 6. Mass growth factor, } G_{\text{fm}} = m_{\text{proc}} / m_{\text{fresh}} \text{ (top) and absolute mass uptake, } \Delta \text{m. } m_{\text{proc}} - m_{\text{fresh}} \text{ (bottom) for soot and PSL particles upon sulphuric acid coating, plotted versus average mobility diameter (arithmetic mean of fresh and processed diameter). The APM was used to measure mass alterations of DMA-selected soot and PSL particles when coated at the low } \text{H}_2\text{SO}_4 \text{ concentration (2.5 \( \times \) 10\(^9\) cm\(^{-3}\)) with a residence time of 12 s.}
\]
dependency of $G_{fm}$ for soot and PSL was similar to that observed at the high H$_2$SO$_4$ concentration. Note that even though the mass growth factor is significantly higher for soot than for PSL, the absolute mass uptake ($\Delta m = m_{\text{proc.}} - m_{\text{fresh}}$) is within 20% for PSL and soot particles of the same mobility diameter. The difference in $G_{fm}$ arises from the higher mass and effective density of fresh PSL particles ($\rho_{\text{eff}} = 1.05 \text{ g/cm}^3$) compared to fresh soot particles ($\rho_{\text{eff}} = 0.11-0.55 \text{ g/cm}^3$) of the same mobility size. Our findings are in agreement with Rogak et al. (1991) who studied the attachment of radioactive lead clusters to TiO$_2$ agglomerates and to spherical particles using an instrument called the Epiphaniometer. They found differences in mass transfer of the lead clusters to be less than 15% between spheres and agglomerates of the same mobility size.

A limiting case for mass transfer via condensation is that for transparent agglomerates (Lall and Friedlander 2006), when each primary particle is fully visible to the condensing molecules. Given no restructuring and a primary particle size that is independent of agglomerate size would then imply that $G_{fm}$ is independent of agglomerate size. The other limiting case is that of spheres. According to mass transfer models using the transition regime correction, $G_{fm}$ then decreases strongly with size. The propane soot particles show an intermediate behavior and are likely not fully transparent initially, restructuring will lead to additional shielding.

Mobility sizes of coated soot decreased upon exposure to low concentration H$_2$SO$_4$, but to a smaller extent compared to the high sulphuric acid concentration (Figure 7). Note that the influence of the high RH cycle was substantial in this case. However, exposing fresh soot to a high RH cycle had a negligible effect on the mobility size, indicating that a hydrophilic coating is needed for restructuring to occur. This is in contrast to measurements on spark-discharge soot reported by Weingartner et al. (1997), where strong restructuring of fresh soot took place already at moderate RH levels. Effective densities and mass fractal dimensions for results shown in Figures 6 and 7 are presented in Figure 8. The mass fractal dimension showed only small variations for fresh (2.15), coated (2.10), and coated + heated (2.20) soot. A pronounced increase in effective density and $D_{fm}$ was found after high RH cycling of coated soot ($D_{fm} = 2.41$). Olert et al. (2007) studied diesel soot emitted from a light duty vehicle equipped with an oxidation catalyst; they used a similar DMA–APM technique (involving a modified APM). As the engine load was increased from 5 to 40%, the effective density increased and the fractal dimension increased from 2.22 to 2.76. This was associated with an increased sulphate concentration in particles as the load increased.

Note that DMA–APM measurements are made on gasborne particles at ambient pressure. Previous approaches to determine the effects of processing on the fractal dimension using electron microscopy techniques may have been influenced by restructuring during sampling and handling of the substrate, the bonding between primary particles and the substrate, and evaporation of volatile compounds.

Kutz and Schmidt-Ott (1992) studied restructuring of butane flame soot when exposed to three different vapors at subsaturation (n-Hexane, 2-Propanol and Water) using the TDMA technique. Significant restructuring was found for n-Hexane and 2-Propanol, but for water (RH = 95%) the shift in mobility size was <1%. They hypothesized that for restructuring to occur at subsaturation, the contact angle ($\theta$) between the particle surface and the condensing liquid needs to be <90° (e.g., water and a
hydrophilic particle surface). Once a sufficient amount of liquid has condensed, the surface tension in the liquid will tend to bring the primary particles into a closer configuration to minimize the surface of the liquid phase (Glasstetter et al. 1991). Our results also support this hypothesis by noting that the sulphuric acid-coated (θ can be assumed <90°), but not the fresh hydrophobic soot (θ can be assumed >90°) show considerable restructuring upon a high RH cycle. However, we have observed that when particles are exposed to supersaturated water vapor, even hydrophobic soot (e.g., from the Santoro burner) restructures when a sufficient amount of water condenses onto the particle.

3.2. Relationship Between Condensed Mass Fraction and Morphology

Comparing the results for the two different H₂SO₄ concentrations it is clear that the morphology of soot depends strongly on the mass or volume fraction of condensed material. To further investigate this dependence, we used mass and mobility diameter data taken at the two previously described sulphuric acid concentrations but at several different relative humidities (5–90%) in DMA2 and the APM. Mass data were only recorded up to 80% RH and for the lower H₂SO₄ concentration only at 5% RH. The particle mass at other relative humidities was estimated according to the water activity model using the measured mass fraction of condensed H₂SO₄–H₂O mixture at 5% RH. In Figure 9 the ratio of processed to fresh mobility diameter (Gfd) is plotted versus the ratio of processed to original particle mass (Gfm). The initial mobility diameter is 152 nm and the initial mass of fresh soot, m_fresh, is 0.42 fg. The mobility diameter decreases as more liquid mass is added up to a mass ratio of about 2.5. For comparison the volume equivalent diameter, d_ve, was calculated according to Equation (6), where ρ_true denotes the inherent material density (Equation [5]).

\[ d_{ve} = \left( \frac{6m}{\pi \rho_{true}} \right)^{1/3} \]  \[ 6 \]

For mass ratios larger than about 2.5, the experimental data are reasonably close to the calculated volume equivalent diameter, indicating a nearly complete transformation from agglomerates to spheres. Note that in this case only water is added to the particles as the mass ratio increases for each H₂SO₄ concentration. If no restructuring of the soot core occurred (no initial decrease of the mobility diameter), a significantly higher mass ratio would be required for the full transformation to spheres.

3.3. Dynamic Shape Factor

The mobility diameter depends on both volume (mass) and morphology. A property solely determined by the particle morphology is the dynamic shape factor, χ. The dynamic shape factor is 1.0 for spheres. It is a measure of the increased drag an irregular particle experiences compared to its volume equivalent sphere moving at the same speed. The higher the value of χ, the larger the difference between the volume equivalent diameter and the mobility diameter. χ is given by Equation (7)

\[ \chi = \frac{d_{proc}}{d_{ve}} \]

FIG. 9. Relationship between processed mobility diameter, \( d_{B,proc} \), and mass, \( m_{proc} \), of soot particles with initial mobility diameter, \( d_{B,fresh} = 152 \) nm and particle mass, \( m_{fresh} = 0.42 \) fg. First the particles were coated at either of the two H₂SO₄ concentrations, then the altered mass and mobility size were measured at a controlled RH between 5 and 90%. In cases when only TDMA (mobility) data was available, the additional water mass for increased RH was calculated using the water activity model, starting from the measured mass of coated particles at 5% RH. The points in each series where the water activity model was used, correspond to RH = 20, 50, 80, 85, and 90% for increasing masses. The volume equivalent diameter, \( d_{ve} \), was calculated using measured H₂SO₄ concentrations and modelled water uptake.

FIG. 10. Dynamic shape factors, \( \chi \), of fresh and processed soot particles calculated from the mass (DMA-APM) and mobility (DMA-DMA) measurements and the estimated bulk density. Coatings were produced upon exposure of soot to the high concentration of H₂SO₄ (1.4·10¹⁰ cm⁻³).
reduced upon coating with H$_2$SO$_4$ (at the higher H$_2$SO$_4$ concentration) and is further reduced upon an additional high RH cycle. For the smallest sizes a value of 1 is approached, indicating fully collapsed spherical particles. When the condensed material is evaporated in the heater, $\chi$ decreases to a value of around 1.4–1.5. The reason for $\chi$ being substantially larger than 1 in this case is presumably due to the internal voids of the collapsed agglomerated soot.

Dynamic shape factors for fresh propane soot in our study are typically higher than those previously found for diesel soot (Park et al. 2004a). Slowik et al. (2007) reported that for the lowest sulphuric acid concentration in this study, dynamic shape factors of fresh soot increased with mobility diameter and decreased with increasing burner equivalence ratio.

3.4. Influence of Multiple Charging on Obtained Results

For spheres, multiply charged particles can typically be cleanly separated in the APM, provided that the APM operating conditions are chosen to optimize the mass resolution. However, it was observed that due to the strongly size dependent effective density of the low fractal dimension soot in this study, the predicted peak voltages of the specific masses of singly and multiply charged particles show a significant overlap, which makes it more difficult to separate multiply charged particles. We estimate that the fraction of multiply charged particles selected with DMA1 varied between 11–28% for the mobility diameters selected in this study.

We made a rough assessment of the impact of multiple charges on the obtained masses by calculating ratios of expected specific masses of multiply charged particles to those of singly charged particles. From these we estimated the potential overestimation of the fitted mass due to multiple charges. For fresh soot this overestimation varied between 3–11% for the mobility diameters selected in DMA1. For coated soot the corresponding number was 1–9%. For sizes below 100 nm specific masses of singly and doubly charged particles are separated by less than 25%. For coated soot, the increase in mass transfer rate was assumed to be the same for spherical and agglomerated particles of the same mobility size (Figure 6 in this work and Rogak et al. 1991). Using the effective density of sulphuric acid, it is expected that the inherent material density, the fractal dimension approaches 3 and the dynamic shape factor approaches 1. If the condensate is hygroscopic, a high RH cycle even below 100% can significantly progress the compaction.

3.5. Atmospheric Implications and Summary

The atmospheric implication of our findings is that fresh hydrophobic soot will remain agglomerated when exposed to high RH cycles at subsaturation or upon condensation of small amounts of low-volatile reaction products from, for example, oxidation reactions. However, as more material condenses, a gradual compaction of agglomerates takes place, which leads to full compaction at a mass growth ratio of 2–3 using the data from our study. At that point the effective density approaches the inherent material density, the fractal dimension approaches 3 and the dynamic shape factor approaches 1. If the condensate is hygroscopic, a high RH cycle even below 100% can significantly progress the compaction.

We estimated the time required for a 100 nm soot particle to increase its mass 2.5 times under typical atmospheric conditions, assuming a moderate condensational growth rate of 2 nm/h for 100 nm spherical particles (Kulmala et al. 2004) and a bulk density of the condensing species of 1.3 g/cm$^3$. The mass transfer rate was assumed to be the same for spherical and agglomerated particles of the same mobility size (Figure 6 in this work and Rogak et al. 1991). The effective density of soot from our study, this leads to a residence time of about 5 hours to increase the mass by a factor of 2.5.

After 1 h the originally 100 nm soot particles would consist of about 20% condensed material by mass. As shown for the lower sulphuric acid concentration in this study, the changes in $Dfm$ and $\rho_{eff}$ are then only moderate. This agrees with the observations from measurements near freeways by Geller et al. (2006), where low fractal dimensions were found.

However, in some environments significantly higher growth rates have been observed (Kulmala et al. 2004) and the transformation from agglomerates to compact particles will progress faster. Assuming a growth rate of 10 nm/h, a mass ratio of 2.5 is reached for the soot after about 1 h. Our results also have important implications for radiative forcing associated with soot aerosols in the atmosphere, since the optical and hygroscopic properties (Zhang et al. 2008; Khalizov et al. 2009) of soot depend on the ratio of liquid to solid mass in the particles as well.

$$\chi = \frac{d_B}{d_{ve}} \cdot \frac{C_{ve}}{C_B}$$

where $C_B$ and $C_{ve}$ denote the Cunningham correction factor calculated at the volume equivalent diameter ($d_{ve}$) and the mobility diameter ($d_B$), respectively.

We found that the dynamic shape factor typically increases with increasing mobility diameter (Figure 10), $\chi$ is substantially reduced upon coating with H$_2$SO$_4$ (at the higher H$_2$SO$_4$ concentration) and is further reduced upon an additional high RH cycle. For the smallest sizes a value of 1 is approached, indicating fully collapsed spherical particles. When the condensed material is evaporated in the heater, $\chi$ increases to a value of around 1.4–1.5. The reason for $\chi$ being substantially larger than 1 in this case is presumably due to the internal voids of the collapsed agglomerated soot.

Dynamic shape factors for fresh propane soot in our study are typically higher than those previously found for diesel soot (Park et al. 2004a). Slowik et al. (2007) reported that for the lowest sulphuric acid concentration in this study, $\chi$ was equal to 2.8 (at $d_B = 225$ nm) for fresh flame soot and decreased towards 1 as oleic acid was condensed onto the particles, similar to our findings for sulphuric acid. Slowik et al. (2007) showed that dynamic shape factors of fresh soot increased with mobility diameter and decreased with increasing burner equivalence ratio.

($\text{Hinds 1999}$)
as on their morphology. Zhang et al. (2008) for example studied the optical properties of the fresh and coated soot described in the present paper. For soot coated at the high sulphuric acid concentration, they found that the scattering efficiency increased by up to 10 times and the absorption cross section increased by a factor of 1.5 at 80% RH, compared to fresh soot.

Finally, it should be pointed out that the mass–mobility relationship from our study may not be directly applicable to other combinations of condensing liquids and soot sources. For example, organic liquids condensing onto diesel soot may behave differently than sulphuric acid. Organic components of atmospheric relevance typically have lower surface tension and water affinity than sulphuric acid (Zhang et al. 2004), and may therefore be less efficient in restructuring the soot core. Slowik et al. (2007), for example, found that oleic acid did not induce restructuring of laboratory generated soot except at the lowest burner equivalence ratio used in their study, while no restructuring was found upon condensation of anthracene. If restructuring is inefficient, the transformation from agglomerates to droplets in the atmosphere can then be significantly prolonged. It is expected that for given soot source it is the volume growth ratio together with the surface tension rather than the mass ratios measured here that determines restructuring efficiency. Other factors that may influence restructuring are the primary particle size (Slowik et al. 2007), the condensation of volatile material during dilution of exhaust emissions (Olfert et al. 2007), and the magnitude of the bonding forces between the primary particles of the agglomerates.

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