

## Properties of jet engine combustion particles during the PartEmis experiment: Hygroscopicity at subsaturated conditions

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[1] Hygroscopic properties of combustion particles were measured online with a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) during PartEmis jet engine combustor experiments. The combustor was operated at old and modern cruise conditions with fuel sulfur contents (FSC) of 50, 410 and 1270  $\mu\text{g g}^{-1}$ , and hygroscopic growth factors (HGF) of particles with different dry diameters were investigated at relative humidities  $\text{RH} \leq 95\%$ . HGFs increased strongly with increasing FSC (HGF[95% RH, 50 nm, modern cruise] = 1.01 and 1.16 for low and high FSC, respectively), and decreased with increasing particle size at fixed FSC, whereas no significant difference was detected between old and modern cruise. HGFs agreed well with a two-parameter theoretical model which provided an estimate of the sulfuric acid content of dry particles, indicating a nearly linear dependence on FSC. *INDEX TERMS*: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry. *Citation*: Gysel, M., S. Nyeki, E. Weingartner, U. Baltensperger, H. Giebl, R. Hitzenberger, A. Petzold, and C. W. Wilson, Properties of jet engine combustion particles during the PartEmis experiment: Hygroscopicity at subsaturated conditions, *Geophys. Res. Lett.*, 30(11), 1566, doi:10.1029/2003GL016896, 2003.

### 1. Introduction

[2] Possible effects of aviation induced particle emissions in the upper troposphere and the lowermost stratosphere are alteration of natural cirrus clouds [Ström and Ohlsson, 1998] and initiation of formation of additional cirrus clouds [Boucher, 1999]. Hygroscopic properties of jet engine combustion particles have been previously investigated in airborne studies [Pitchford et al., 1991; Hagen et al., 1992]. These studies have shown that combustion particles originating from standard jet fuel are hygroscopic. Such hygroscopic behavior has been commonly attributed to sulfuric acid adsorbed on black carbon particles, which is known to increase water uptake below saturation [Wyslouzil et al., 1994].

[3] An extensive set of aerosol measurements were conducted on a jet engine combustor test-rig in order to measure the microphysical and chemical properties of combustion particles during the EU PartEmis project (Wilson et al., Measurement and prediction of emissions of aerosols and gaseous precursors from gas turbine engines (PartEmis): An experimental overview, submitted to *Aerosp. Sci. and Technol.*, 2003, hereinafter referred to as Wilson et al., submitted manuscript, 2003). A main focus was the influence of combustor operating conditions and fuel sulfur content (FSC) on particle properties. Microphysical properties and emission indices of combustion particles during the PartEmis test campaign in January to February 2001 are presented by A. Petzold et al. (Properties of jet engine combustor particles during the PartEmis experiment: Microphysics and chemistry, submitted to *Geophysical Research Letters*, 2003, hereinafter referred to as Petzold et al., submitted manuscript, 2003). The hygroscopic properties of the particles at subsaturated conditions are presented in this paper and linked to their behavior at supersaturated conditions in a companion paper (R. Hitzenberger et al., Properties of jet engine combustor particles during the PartEmis experiment: Hygroscopic growth at supersaturated conditions, submitted to *Geophysical Research Letters*, 2003, hereinafter referred to as Hitzenberger et al., submitted manuscript, 2003).

### 2. Methods

[4] The jet engine combustor was operated on a test-rig at QinetiQ, Farnborough, UK. Two different engine operation conditions (old and modern cruise conditions; inlet temperature  $T = 566$  and  $766$  K, respectively) and three different FSC levels (50, 410 and 1270  $\mu\text{g g}^{-1}$ ) were investigated. After exit from the combustor, the sample was immediately cooled down to  $\sim 150^\circ\text{C}$ , and then diluted by a factor of  $\sim 65$  with filtered air at about  $25^\circ\text{C}$ . More details of the experimental setup are given by Wilson et al. (submitted manuscript, 2003).

[5] The particle hygroscopic properties were measured at ambient conditions using a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) system, similar to the

instrument described by Weingartner *et al.* [2002]. Briefly, a monodisperse fraction of dry combustion aerosol was selected with a first DMA. This monodisperse aerosol was then humidified, and the resulting particle size distribution was measured by scanning the whole size range with a second DMA and Condensation Particle Counter. The HTDMA was kept at constant temperature ( $T \sim 25^\circ\text{C}$ ), and the RH was determined by measurement of the system temperature and sheath air dew point using dew point mirrors. At constant conditions the RH accuracy is  $\pm 1.2\%$  at 95% RH, but it may be reduced due to RH-changes during the growth factor measurement. The DMAs were operated with a closed-loop sheath air setup, which allows a growth factor accuracy of  $\pm 0.01$ . Hygroscopic growth factors (HGF)  $g_{exp}(RH) = D(RH)/D_0$  were measured in the range  $\sim 70$  to 95% RH for particles with dry ( $RH \leq 7\%$ ) diameters of  $D_0 = 30, 50$  and 100 nm.

### 3. Theoretical Model

[6] Two different models for the hygroscopic growth of combustion particles, Model A for spherical particles and Model B for agglomerates, are shown in Figures 1a–1b, respectively. Both models assume an insoluble soot core surrounded by a sulfuric acid coating under dry conditions. The water content of the sulfuric acid coating depends on RH. At equilibrium the particle diameter of the mixed particle can be described by a theoretical HGF  $g_{th}$  as follows [Pitchford and McMurry, 1994]:

$$g_{th}(RH) \equiv \frac{D(RH)}{D_e} = (1 + \varepsilon(g_{sol}^3(RH) - 1))^{1/3}, \quad (1)$$

where  $D$  and  $D_e$  are the humid and dry volume equivalent diameters, respectively,  $\varepsilon$  is the soluble volume fraction,  $g_{sol} = D_{sol}/D_{e,sol}$  is the theoretical HGF of a pure soluble particle. HGFs  $g_{sol}$  for sulfuric acid are calculated with Köhler theory as described by Gysel *et al.* [2002]. The Kelvin correction is included in the size dependence of  $g_{sol}$ , according to Pitchford and McMurry [1994]. Empirical values for the water activity and the surface tension of sulfuric acid at room temperature are reported by Tang [1996] and Chen [1994], respectively. Equation 1 describes  $g_{th}(RH)$  in terms of volume equivalent diameters for both Model A and Model B. Experimental results achieved with the H-TDMA are measured and presented in terms of mobility diameters. To compare theoretical ( $g_{th}$ ) with experimental HGFs ( $g_{exp}$ ), a mobility correction factor  $f$  is introduced:  $g_{exp} = f \cdot g_{th}$ . As mobility and

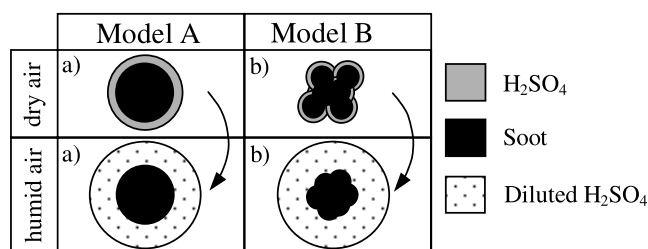


Figure 1. Theoretical models for hygroscopic growth.

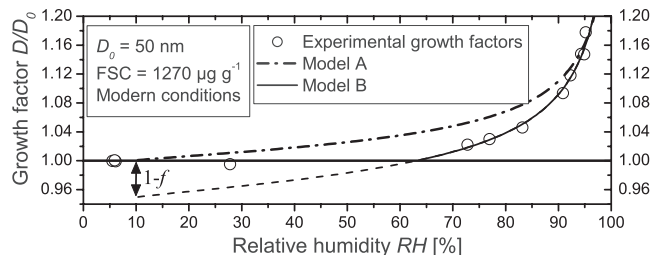


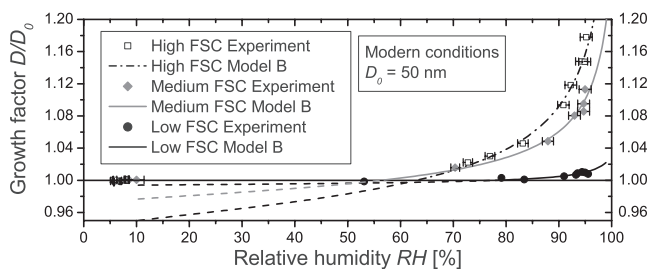
Figure 2. Experimental HGFs compared with two different models. Models A and B were fitted to experimental results at RH = 95% and RH = 70–95%, respectively.

volume equivalent diameters are equal for spherical particles, the mobility correction factor is  $f = 1$  for Model A. The sulfuric acid volume fraction  $\varepsilon_A$  was adjusted to fit the experimental HGF at 95% RH. Model B assumes that non-spherical dry particles are transformed into spheres at sufficiently high RH, as a result of water uptake by the soluble coating (reversible) and by restructuring of the insoluble core (irreversible). Therefore the ratio of mobility to volume equivalent diameter decreases with increasing RH until the particle is spherical and hence experimental (mobility) HGFs are smaller than the corresponding volume equivalent values. In order to model mobility growth factors in the high RH range the mobility correction factor  $f$  is used as a RH independent parameter  $f \leq 1$  in Model B. The two free parameters,  $f$  and  $\varepsilon_B$ , were varied to fit experimental HGFs in the range RH = 70–95%.

[7] Figure 2 shows a comparison between measured and theoretical HGFs for  $D_0 = 50$  nm particles at high FSC and modern conditions. Model A, which does not consider restructuring and shape effects, is not able to satisfactorily describe hygroscopic growth, while Model B agrees well with experimental results at high RH (see Figure 2). Comprehensive investigations of gas and particulate phase exhaust properties as well as modeling approaches indicated that sulfuric acid is mainly responsible for the observed hygroscopic growth, but the minor influences of water-soluble organics, coating-core interactions or mobility correction deficiencies cannot be fully excluded. Model B and experiment differ at low RH, since  $f$  is a constant fitted to high RH HGFs. The absolute difference at RH = 10% ( $1 - f = 5\%$  in this case) is equal to the sum of reversible shape and irreversible restructuring effects. Despite this small shortcoming, Model B is at present considered to be optimal, and hence only results using this model are presented below.

### 4. Results

[8] HGFs of  $D_0 = 50$  nm particles for different FSC levels are shown in Figure 3 for modern conditions. Results for old conditions were comparable and are hence not shown here. The combustion particles are not hygroscopic at low FSC with a HGF of only  $g_{exp}(95\%) = 1.01$ . This is less than the equivalent of one monolayer of water, which can be explained with water adsorption only. Accordingly, the estimated sulfuric acid volume fraction  $\varepsilon = 0.6\%$  is negli-

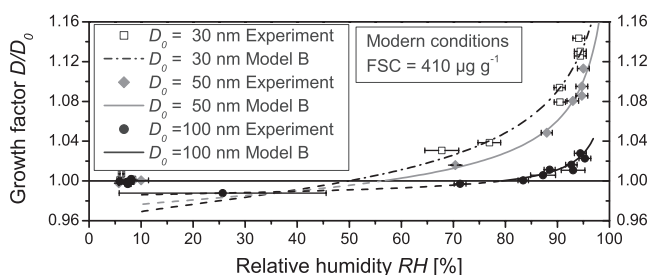


**Figure 3.** Experimental and theoretical HGFs at FSC = 50, 410, and 1270  $\mu\text{g g}^{-1}$ .

gible. At medium and high FSC, particles are distinctly more hygroscopic with HGFs of 1.10 and 1.16 at RH = 95%, respectively. Due to an identical experimental setup (except for FSC level) this increased water uptake can most likely be attributed to sulfuric acid, which forms during combustion, and adsorbs onto particles during cooling and dilution.

[9] The effect of varying dry diameter  $D_0$  at a constant FSC is next considered in Figure 4, which illustrates hygroscopic properties of particles with different  $D_0$  at medium FSC and modern conditions. The HGFs of particles with dry diameters  $D_0 = 30, 50,$  and  $100$  nm measured at RH = 95% are 1.14, 1.10 and 1.03, respectively. Distinctly increasing HGFs with decreasing dry particle size were observed for all conditions, despite the Kelvin effect which counteracts this tendency. This size dependent hygroscopic behavior is attributed to a higher sulfuric acid volume fraction on smaller particles (see  $\varepsilon_B$  in Table 1). The observed size dependence of the sulfuric acid fraction at a fixed FSC originates from the relatively larger mass accommodation of smaller particles by condensation of gaseous sulfuric acid. Again, results were similar for old conditions, i.e. differences between old and modern condition were distinctly smaller than the influences of FSC and of particle dry diameter  $D_0$ .

[10] The width of the monodisperse aerosol size distribution at high RH compared to the original width at low RH provides information about the aerosol mixing state. The standard deviation  $\sigma$  increased from 1.048 without humidification to 1.063 at 95% RH ( $D_0 = 50$  nm, high FSC), which corresponds to a small range in growth factors from 1.141 to 1.173 (median 1.157). Hence particles were internally mixed with nearly identical hygroscopic properties. The internal mixture was also confirmed by volatility



**Figure 4.** Experimental and theoretical HGFs at medium FSC of particles with different dry diameters.

**Table 1.** Summary of Experimental Results and Model Parameters of the Hygroscopic Properties of Combustion Particles

Condition	FSC	$D_0$	HGF at 95% RH	$\varepsilon_B$	$f$	$S_{crit}$
	$\mu\text{g g}^{-1}$	nm	–	vol. %	–	%
Old	50	30	1.01	1.2	0.98	4.5
Old	50	50	1.01	0.7	0.99	2.8
Old	50	100	1.00	0.1	1.00	1.7
Modern	50	30	1.02	1.6	0.99	4.2
Modern	50	50	1.01	0.6	0.99	2.9
Modern	50	100	1.00	0.2	1.00	1.6
Old	410	30	1.11	10.0	0.94	2.5
Old	410	50	1.06	3.4	0.97	1.8
Old	410	100	1.02	0.7	0.99	1.2
Modern	410	30	1.14	8.8	0.97	2.5
Modern	410	50	1.10	5.0	0.98	1.5
Modern	410	100	1.03	1.2	0.99	1.0
Old	1270	30	1.28	25.0	0.93	1.7
Old	1270	50	1.19	13.0	0.93	1.1
Old	1270	100	1.06	2.7	0.98	0.7
Modern	1270	30	1.23	21.0	0.93	1.9
Modern	1270	50	1.16	9.5	0.95	1.2
Modern	1270	100	1.07	3.0	0.97	0.7

The accuracy of experimental growth factors is limited by counting statistics, and it is better than  $\pm 0.01$ . The sample variability is of the order of  $\pm 0.02$  and  $\pm 0.03$  at medium and high FSC, respectively.

measurements (Petzold et al., submitted manuscript, 2003) for particles larger than  $D_0 = 30$  nm.

## 5. Discussion

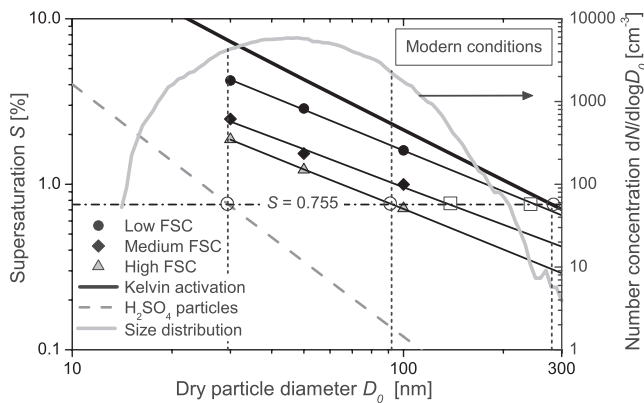
[11] The results of all different combustor operating conditions, FSC levels, and particle dry sizes are summarized in Table 1. HGFs are given as interpolated (by Model B) experimental values at RH = 95%. The parameters  $\varepsilon_B$  and  $f$  are the corresponding model parameters for Model B.

[12] Experimental HGFs and estimated sulfuric acid volume fractions  $\varepsilon_B$  show that hygroscopic particle properties are comparable at old and modern conditions, whereas the FSC level and particle dry size have a strong influence on the particle hygroscopicity.  $\varepsilon_B$  depends nearly linearly on the FSC for a fixed particle size. The trend of increasing  $\varepsilon_B$  with decreasing particle size is supported by volatility measurements at 120°C. In earlier studies, water soluble volume fractions of combustion particles investigated during airborne experiments were estimated to be  $\sim 10\%$  ( $D_0 = 34\text{--}49$  nm) [Hagen et al., 1992], and  $\sim 16\%$  ( $D_0 = 90\text{--}110$  nm) [Pitchford et al., 1991]. This does not necessarily indicate an opposite trend with particle size compared to our data, since FSC levels were not reported.

[13] Estimated shape and restructuring effects  $(1 - f)$  increase with increasing HGFs for a fixed particle size, indicating that restructuring occurs only at sufficiently high water uptake. This behavior was corroborated by additional experiments where particles were re-dried, as well as in studies of diesel engine particles [Weingartner et al., 1997]. Mobility corrections were larger for smaller particles, which is atypical for combustion particles. This can partially be attributed to the larger growth of smaller particles at a fixed FSC, but model deficiencies could somewhat compromise mobility correction estimates.

[14] Estimates of critical supersaturation  $S_{crit}[\%] \equiv RH[\%] - 100\%$  for droplet activation were obtained from theoretical growth curves (Model B) according to the classical definition of Köhler theory. Increasing hygroscop-





**Figure 5.** Critical supersaturation for droplet activation as a function of dry particle size.

icity with increasing FSC measured under subsaturated conditions results in lower values predicted for  $S_{crit}$ . Due to the Kelvin effect  $S_{crit}$  is larger for smaller particles, despite the higher water-soluble fraction of small particles.

[15] Hygroscopic properties under subsaturated conditions were also used to estimate cloud condensation nuclei (CCN) concentrations by combining extrapolated  $S_{crit}$  values with particle number size distributions measured by a SMPS system (see Petzold et al., submitted manuscript, 2003), as illustrated in Figure 5. Estimated  $S_{crit}$  values at a constant FSC are interpolated with so called critical lines. The critical lines for insoluble but wettable (Kelvin activation) and for pure sulfuric acid particles are also given. The number size distribution (right axis) is given as an example for one high FSC test point. CCN concentrations were also directly measured (Hitzenberger et al., submitted manuscript, 2003) at a supersaturation of  $S_{CCN} = 0.755\%$  at this test point, indicated by the horizontal dash-dotted line. The intersections (○) of this line with the critical lines for Kelvin activation ( $D_{crit} = 280$  nm), sulfuric acid ( $D_{crit} = 30$  nm), and partially soluble high FSC level combustion particles ( $D_{crit} = 92$  nm) mark the corresponding critical activation diameters  $D_{crit}$ . Integration of the number size distribution above these critical diameters then provides the estimated CCN concentrations for this specific high FSC test point under the assumption of Kelvin activation, sulfuric acid, and partially soluble combustion particles, respectively. Square symbols in Figure 5 mark the critical diameters at  $S_{CCN} = 0.755\%$  for low ( $D_{crit} = 246$  nm) and medium FSC ( $D_{crit} = 138$  nm) combustion particles. Estimated activation diameters agree with activation diameters obtained from measured CCN concentrations and number size distributions within  $\pm 16\%$  at low and medium FSC and within  $\pm 36\%$  at high FSC for both cruise conditions (see Hitzenberger et al. (submitted manuscript, 2003) for detailed comparison), which is fair agreement when considering the above assumptions.

## 6. Conclusions

[16] This study showed that water uptake by combustion particles under subsaturated conditions is generally inde-

pendent of combustor operating conditions evaluated, but increases significantly with increasing FSC level, which is attributed to an increasing amount of sulfuric acid adsorbed on the particles. This results in a reduction of the critical diameter for droplet activation at supersaturated conditions, confirmed by a comparison with measured CCN concentrations. Particulate aircraft emissions acting as CCN or ice nuclei might modify natural cirrus clouds or induce additional cirrus cloud formation. This potential impact is expected to increase with increasing FSC level. On the other hand, the influence of FSC level on contrail formation has been shown to be small [Schumann et al., 2002], although the observed trends of slightly increased threshold temperature and increased ice particle number concentration agree with a reduction of critical supersaturation for CCN activation as deduced from the results in this study.

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## References

- Boucher, O., Air traffic may increase cirrus cloudiness, *Nature*, 397, 30–31, 1999.
- Chen, J.-P., Theory of deliquescence and modified Köhler curves, *J. Atmos. Sci.*, 51, 3505–3516, 1994.
- Gysel, M., E. Weingartner, and U. Baltensperger, Hygroscopicity of aerosol particles at low temperatures. 2. Theoretical and experimental hygroscopic properties of laboratory generated aerosols, *Environ. Sci. Technol.*, 36, 63–68, 2002.
- Hagen, D. E., M. B. Trueblood, and P. D. Whitefield, A field sampling of jet exhaust aerosols, *Particulate Sci. Technol.*, 10, 53–63, 1992.
- Pitchford, M. L., and P. H. McMurry, Relationship between measured water vapor growth and chemistry of atmospheric aerosol for Grand Canyon, Arizona, in winter 1990, *Atmos. Environ.*, 28, 827–839, 1994.
- Pitchford, M., J. G. Hudson, and J. Hallet, Size and critical supersaturation for condensation of jet engine exhaust particles, *J. Geophys. Res.*, 96, 20,787–20,793, 1991.
- Schumann, U., F. Arnold, R. Busen, J. Curtius, B. Kärcher, A. Kiendler, A. Petzold, H. Schlager, F. Schröder, and K. H. Wohlfrom, Influence of fuel sulfur on the composition of aircraft exhaust plumes: The experiments SULFUR 1–7, *J. Geophys. Res.*, 107(D15), 4247, doi:10.1029/2001JD000813, 2002.
- Ström, J., and S. Ohlsson, In situ measurements of enhanced crystal number densities in cirrus clouds caused by aircraft exhaust, *J. Geophys. Res.*, 103, 11,355–11,361, 1998.
- Tang, I. N., Chemical and size effects of hygroscopic aerosols on light scattering coefficients, *J. Geophys. Res.*, 101, 19,245–19,250, 1996.
- Weingartner, E., et al., Hygroscopic properties of carbon and diesel soot particles, *Atmos. Environ.*, 31, 2311–2327, 1997.
- Weingartner, E., M. Gysel, and U. Baltensperger, 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.
- Wyslouzil, B. E., K. L. Carleton, D. M. Sonnenfroh, W. T. Rawlins, and S. Arnold, Observation of hydration of single, modified carbon aerosols, *Geophys. Res. Lett.*, 21, 2107–2110, 1994.

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