Supplemental Information

Particle size distributions and hygroscopic restructuring of ultrafine particles emitted during thermal spraying

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Figure S1. Schematic illustration or the facility investigated



Figure S2. Schematic illustration of the thermal spraying techniques, (a) APS and (b) HVOF and their potential particle emission mechanisms.



Figure S3. Major parts of the HTDMA system assembled for the characterization of UFPs hygroscopicity and mixing state.

Sampled particles were initially dried through a silica gel diffusion drier, brought to a charge equilibrium by passing through a soft X-ray aerosol neutralizer (TSI Model 3088) before entering the first DMA of the system (DMA-1). The quasi-monodisperse particles downstream DMA-1 are then exposed to elevated RH conditions by passing through a nafion membrane humidity exchanger (Permapure Model MD-700-06S-1), before their size distribution is measured by the second DMA (DMA-2) of the system that is coupled to a CPC (TSI 3010). Both DMAs employ closed loop sheath flows, while an additional humidification system, consisting of a second nafion humidifier (Permapure PD-50T-MPR) is added to the sheath flow of DMA-2 in order to maintain it at the same RH level with that of the sample flow. Two RH and temperature sensors (Rotronic HC02-05), together with a software closed loop control (National Instruments Labview 2014), are utilized for measuring and controlling the stability of the RHs in the system. The system was operated at a constant 87±2% RH, as this is above the deliquescence RH (i.e., RH above which a solid particle will form a droplet) of ammonium sulfate (i.e., one of the most abundant, hygroscopic, inorganic species in the atmosphere), while being low enough to

prevent accidental forming of supersaturated conditions in parts of the HTDMA. The performance of the HTDMA was tested prior the measuring campaign by using ammonium sulfate particles, which have known and well studied hygroscopic properties (i.e., well defined deliquescence RH, and hygroscopic growth factors at different RH).

Deriving hygroscopic factor from the HTDMA.

In the HTDMA the first DMA (DMA-1) operates at a steady voltage during each sample, thus constantly classifying particles having a quasi monodisperse electrical mobility (Z), while the voltage of DMA-2 is scanned, allowing the classification of particles having different electrical mobilities, which are then detected by the CPC. In general, the electrical mobility Z of the particles that are classified in a cylindrical DMA (i.e., like the ones used in the HTDMA) is related with its geometrical features and operating conditions (Baron and Willeke, 2001) as:

$$Z = \frac{(Q_{\rm sh} + Q_{\rm e}) \ln \frac{R_2}{R_1}}{4\pi V L}.$$
 (S1)

Here, R_1 , R_2 are respectively the inner and outer radii of the DMA, *L* is characteristic classification length, Q_{sh} the sheath flow rate, Q_e the excess flow rate and *V* the applied potential in its inner electrode.

In the case of spherical particles, Z is related to particle diameter (d) using Hinds (1999):

$$Z = \frac{neCc}{3\pi\mu d},\tag{S2}$$

where *n* is the number of elementary charges, *e* the electron charge (1.6e-19 Cb), μ the air viscosity (1.81e-5 Pa S, at 20 °C) and *Cc* the Cunningham slip correction factor.

The Cunningham slip correction factor, *Cc*, can be calculated via the empirical formula (Allen and Raabe, 1985) as:

$$Cc(Kn) = 1 + Kn \left[a + b \exp\left(-\frac{c}{Kn}\right) \right].$$
(S3)

Here *Kn* is the Knudsen number, which is the ratio of the gas mean free path (λ) to the radius of the spherical particle (*r*), while *a*= 1.257, *b*=0.4, *c*=1.1, are fitted parameters (Davies, 1945). Note that the *Kn* number, calculated as *Kn* = 2 λ /*d*, where λ is the gas mean free path and *d* the diameter of particles, is used for defining the behavior of a particle while moving inside its surrounding gas molecules (i.e., its flow regime). For example, a particle much bigger than the gas mean free path (i.e., *Kn*<<1) will be subjected to a number of gas molecules collisions while

a particle, much smaller than the gas mean free path (i.e., *Kn*>>1) will be subjected to significantly lower collisions by the surrounding gas molecules (i.e., resulting in a reduction in its drag).

Assuming particles of spherical shape, carrying one elementary charge, equations S1 to S3 are used for inverting the HTDMA measurements and for calculating the geometric mean electrical mobility diameters of particles selected by DMA-1 and measured by DMA-2 and the CPC, thus deriving their hygroscopic factor.

Calculating particle hygroscopic factor on different than 87% RH.

The water affinity of soluble particulate matter can be represented by the single hygroscopic parameter κ (Petters and Kreidenweis, 2007), which can be also used for calculating its water uptake characteristics at various RHs. The value of κ can be calculated from the measured (i.e., by the HTDMA) hygroscopic factor (Kreidenweis et al., 2008):

$$\kappa_{HTDMA} = \frac{\left(g(87\%)^3 - 1\right)}{a_W/(1 - a_W)} , \qquad (S4)$$

where g(87%) is the measured hygroscopic factor (i.e., at 87% RH in our measurements) and a_w is the water activity of the solution droplet, which can be calculated by:

$$\boldsymbol{a}_{\mathsf{W}} \approx \frac{\mathrm{RH}}{100} \left(exp\left(\frac{4\sigma_{s/\alpha} \ M_{\mathsf{W}}}{RT\rho_{\mathsf{W}}d_{m}(\mathrm{RH})}\right) \right)^{-1}.$$
(S5)

Here $\sigma_{s/a}$ and M_w are the surface tension and molecular weight of pure water (0.072 J m⁻² and 18⁻³ kg/mol, respectively), *R* is the universal gas constant, *T* is the absolute temperature, ρ_w is the density of water and d_m is the diameter of the particles at 87% RH.

The single hygroscopic parameter κ (i.e., calculated using the Eqs. S4 and S5) can be used for predicting the hygroscopic factor of the same particles at 99% RH (i.e., similar to that inside the human respiratory system) as follows:

$$g(99\%) = \left(1 + \kappa_{\mathrm{HTDMA}}\left(\frac{a_{w}}{1 - a_{w}}\right)\right)^{1/3}.$$
(S6)

In Eq. S6, the water activity of the solution droplet (a_w) is calculated iteratively for 99% RH using Eq. S5.



Figure S4. HTDMA measurements of particles having dry mobility diameters of 30- (**a**) and 90- (**b**) nm, sampled from during the non-working hours on 15-16 Nov. 2017. The size of the symbols (i.e., the size of the circles) is proportional to the number fraction of each hygroscopic mode. Particles which exhibited hygroscopic factor below 1.15 (hydrophobic/less hygroscopic; HP) are denoted with different symbols (i.e. open circles), than the more hygroscopic ones (i.e., hygroscopic factor > 1.15; HS).



Figure S5. Number concentrations of particles classified by the NanoScan-SMPS as having midpoint electrical mobility diameters of 27.4 and 86.6 nm, measured during the non-working hours between 16 and 17 Nov. 2017. These size bins were selected due to their proximity to dry electrical mobility diameters selected by the HTDMA (i.e., 30 and 90 nm, respectively).



Figure S6. HTDMA measurements of particles having dry mobility diameters of 30 nm (**a**) and 90 nm (**b**), sampled from within spraying booth #1 (APS). The size of the circles is proportional to the number fraction of each hygroscopic mode. Particles having hygroscopic factors below 1.15 (hydrophobic/less hygroscopic; HP) are denoted with open circles, while closed circles denote particles with hygroscopic factors above 1.15 (hygroscopic). Vertical lines, added for clarification reasons, denote externally mixed samples, while the shaded areas mark time intervals during activity periods.



Figure S7. HTDMA measurements of particles having dry mobility diameters of 30- (**a**, **c**) and 90- (**b**, **d**) nm, sampled from within booth #3 (HVOF) on 16 and 17 Nov. 2017. The size of the symbols (i.e., the size of the circles) is proportional to the number fraction of each hygroscopic mode. Particles which exhibited hygroscopic factor below 1.15 (hydrophobic/less hygroscopic; HP) are denoted with different symbols (i.e. open circles), than the more hygroscopic ones (i.e., hygroscopic factor > 1.15; HS). Vertical lines, added for clarification reasons, denote externally mixed samples, while the shaded areas mark time intervals during activity periods and the period when the HTDMA was sampling from the storage area, outside booth #3, while it was active.





Figure S8. EDX analysis from the respective TEM samples of emitted UFP from (a) APS and (b) HVOF

b)

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