Nanoparticle release from nanocomposites due to mechanical treatment at two stages of the life-cycle

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Abstract. Currently, an increase of published studies regarding nano-object release into the air can be observed. In the absence of a harmonized methodology only a few studies provide quantitative data for further use. In this study, an appropriate methodology was adopted and partly enhanced for the characterization of the nanoparticle release from coatings and composites containing nanoscaled pigments. Systematic analyses at two stages of the life-cycle (non-weathered/arterially weathered) were performed for three simulated treatment processes – sanding, dynamic friction and wind erosion. Results show that the sample material, the sample composition, the sample condition (e.g. weathering state) and the type of mechanical treatment have a strong effect on the particle release. SEM, TEM and EDX analyses revealed that none of the released particles were free nanoscaled pigments.

1. Introduction

The ability and the quantity of nanoparticle release into air from engineered nano-composites due to mechanical treatment can be determined systematically by exposure studies in laboratory for estimating potential risk to health, safety and environment [1]. Currently, no harmonized methodology for nanoparticle release investigations in laboratory exists, whereby the comparability and transferability of most of such studies is very limited. This is firstly due to the huge variety of possible release scenarios and the multitude of materials and secondly results from limitations of the measurement technology and from physical constrains of aerosols. Figure 1 illustrates the complexity of the experimental design for analyses of particle release into the air, which is necessary for the determination of qualitative and quantitative data regarding an exposure assessment.

Save for a few exceptions [e.g. 2, 3], most laboratory studies [e.g. 4-8] regarding the release of engineered nano-objects into the air from nano-composites due to mechanical treatment processes have shown, that engineered nano-objects are firmly embedded in released wear/swarf particles [1]. The exceptions can maybe explained by artifacts from sample preparation and/or conditioning (e.g. incomplete wetting, incomplete or no surface modification, state of dispersion). In general, we believe that a release of isolated nano-objects from well-prepared nanocomposites requires a prior chemical or thermal degradation of the matrix material.

External impacts like sunlight, moisture or temperature fluctuations may promote the degradation of the matrix material and eventually expose embedded nanoparticle additives or nanoscaled pigments.

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In turn, this is probably associated with a higher release risk as shown in [9] for the transition of TiO2 from facades into the aquatic environment.

2. Materials and Methods

2.1. Sample selection, conditioning and characterization

Nanoparticle release was analyzed for a total of 22 different sample systems based on two different matrix-materials (11 acrylate coatings, 11 polypropylene composites). The matrices were filled with 10 different pigments, which varied in particle size, morphology and material. Apart from two (TD, CT), all pigments have dimensions in the nanoscale. In addition, a pigment-free coating (AL) and a pigment-free composite (PP) were examined. The coatings were applied on aluminum-substrates by a defined squeegee procedure, while the PP-composites fabrication was accomplished by injection molding.

\[ \text{Table 1. Sample description: Identification key of the sample systems, employed pigments, their intensity weighted harmonic mean size (} \xi_{\text{PCS}} \text{), polydispersity index (PI) and BET surface area.} \]

| sample ID | CIGPN\(^{a}\) pigment material | pigment content [wt.-%] | \( \xi_{\text{PCS}} \) [nm] | PI\(^{b}\) | BET surface area \([m^2/g]\) |
|-----------|-----------------------------|--------------------------|-------------------|--------|----------------------|
| coating | composite | coating | composite | coating | composite | coating | composite | coating | composite | coating | composite |
| AL-CB | PP-CB | black 7 | carbon black | 2.0 | 1.0 | 110 | 0.13 | 320 | 120 |
| AL-PC | PP-PC | green 7 | phthalocyanine green | 1.0 | 0.2\(^{d}\) | 212 | 0.28 | 47 | 37 |
| AL-TD | PP-TD | white 6 | titania | 10.0 | 0.2\(^{d}\) | 311 | 0.13 | n.a. | n.a. |
| AL-TT | PP-TT | white 6 | titania, transparent | 0.7 | 1.0 | 153 | 0.26 | 110 | 160 |
| AL-BS | PP-BS | white 21 | barium sulfate | 5.0 | 1.0 | 303 | 0.13 | 30 | 30 |
| AL-TE | PP-TE | red 101 | iron oxide, transparent | 1.9 | 0.2\(^{d}\) | 85 | 0.25 | 85 | n.a. |
| AL-RP | PP-RP | red 122 | quinacridon | 2.8 | 0.2\(^{d}\) | 227 | 0.27 | 78 | 78 |
| AL-AO | PP-AO | white 24 | aluminum oxide | 7.2 | 1.0 | 202 | 0.16 | 100 | 100 |
| AL\(^{c}\) | PP | - | - | - | - | 98 | 0.06 | - | - |
| AL-CT | PP-CT | brown 24 | chrom.-antimony-titan. | 15.0 | 1.0 | 829 | 0.25 | 2 | 2 |
| AL-KB | PP-KB | blue 28 | cobalt blue | 10.0 | 1.0 | 597 | 0.29 | 9 | n.a. |

\(^{a}\) CIGPN . . . color index generic pigment name

\(^{b}\) data valid for the coating-pigments, obtained by DLS (HPPS5002, Malvern Inst. GmbH, Herrenberg, Germany)

\(^{c}\) reference systems: polyacrylate dispersion (AL) for coatings and polypropylene (PP) for composites

\(^{d}\) white balance with 0.8 wt.-% TiO2
For each sample system, ten individual subsamples were produced. Four of them were conditioned by artificial weathering in a weathering device (Model Xenotest Beta LM, Atlas Material Testing Technology GmbH, Linsengericht, Germany) by filtered xenon-arc radiation according to ISO 11341:2004 to simulate a natural weather impact for a time span between 2 and 5 years. The AL-coatings were weathered in two phases. In the first phase the samples have experienced an alternating illumination (bright and dark cycle’s à 120 min) for 1000 h, while the second phase lasted for 1500 h and consisted of repeated dry (102 min illumination) and wet phases (18 min irrigation). The PP-composites were weathered for 1000 h similar to the second phase of the coatings. Surface conditions of the samples were analyzed before, during and after the artificial weathering procedure by specular gloss measurements in accordance with DIN EN ISO 2813:1999 (see figure 2), color difference measurements in accordance with DIN 6174:2007 and scanning electron microscopy (SEM) analyses.

2.2. Experimental details

2.2.1. Sample treatment. The prepared samples were exposed to sanding, dynamic friction and wind erosion, which were simulated by an extended version of the experimental apparatus described in [4]. Within the apparatus the samples were supplied by a translation sample carrier beneath the acting tools, which were encapsulated for sampling of all released particles as close as possible to the particle source. The used treatment process parameters are given in table 2.

The parameters of the sanding procedure for the AL-coatings were adopted from [4] except for the abrasive paper graining. Finer abrasive paper was used to achieve a cutting depth < 5 µm, thus to

Table 2. Process parameters of the simulated treatment processes.

| process parameter          | sanding process coatings | dynamic friction coatings | wind erosion coatings |
|----------------------------|--------------------------|--------------------------|----------------------|
| stressed area [cm²]        | 10.4                     | 12.7                     | 1.6                  |
| sample speed [mm min⁻¹]    | 5.0                      | 5.0                      | 5.0                  |
| maximum face velocity [m s⁻¹] | 4.9                      | 1.5                      | 3.0                  |
| normal force [N]           | 0.5                      | 13                       | -                    |
| contact pressure [kPa]     | 84                       | 84                       | -                    |
| abrasive paper graining    | P1200                    | P240                     | -                    |
| rotational velocity [m s⁻¹] | 1.83                     | 0.73                     | -                    |
| cutting velocity ratio [-]  | 366                      | 146                      | -                    |
| power [W]                  | 1.3                      | 0.5                      | < 0.078 < 0.103      |

1 in the case of sanding and dynamic friction parallel velocity between the lower part of the sampling hood and the sample surface, in the case of wind erosion parallel velocity between nozzle inlet and sample surface.
2 cutting power for sanding, friction power for dynamic friction
ensure that sanding occurs within the weathered region of the weathered samples. Preliminary investigations have shown that the sanding parameters used for the AL-coatings led to a thermal particle generation in the case of the PP-composites, which was indicated by high number concentrations and average particle sizes below 30 nm. Accordingly, the sanding parameters for the PP-composites were adjusted as shown in table 2. Since the PP-composites showed larger weathering depths as the AL-coatings, the cutting depths remained within the weathered region.

Wind erosion was simulated by a stainless steel suction nozzle with an inner diameter of 2 mm, while surface stressing by dynamic friction was realized by a flat-lying and circular elastic polyurethane body (diameter of 14 mm) with a depth of roughness of Rz = 7.4 µm (mean roughness index Ra = 1.3 µm, total height of roughness Rt = 13.1 µm).

2.2.2. Measuring, sampling and conditioning instruments. The instruments employed for sampling, conditioning and characterization are listed in table 3. Detailed information on the operation principles can be gathered from the cited references. Target measurands for the (nano)-particle release characterization are the particle number concentration (PNC), the number weighted particle size distribution (PSD) and the material composition of the released particles. Both, PNC and PSD, can be detected by means of conventional aerosol measurement techniques, while the determination of the material composition requires additional analyses. Thus, electrostatic precipitated aerosol particles were subsequently analysed by scanning electron microscopy (SEM, Model Gemini 982, Karl Zeiss AG, Jena, Germany), transmission electron microscopy (TEM, Model Tecnai 20, FEI Company, Hillsboro, USA) and energy dispersive X-ray spectroscopy (EDX). The used dilution units DDS 560 and DIL 556 realised well-defined (non-classifying) dilution of aerosols.

Table 3. Operated measuring, sampling and conditioning instruments for the aerosol characterization.

| Instrument                      | Model; manufacturer                  | metric; equivalent diameter | size range; aerosol flow rate; | reference |
|---------------------------------|--------------------------------------|-----------------------------|---------------------------------|-----------|
| Condensation Particle Counter (CPC) | Model 3022A; TSI Inc., Shoreview, USA | PNC                         | 6 nm - <10 µm; 1 s; 0.3 L min⁻¹ | [10]      |
| Diffusion Filter Battery (DB) + CPC | Model 3022A; TSI Inc., Shoreview, USA | PNC                         | >100 nm; 1 s; 0.3 L min⁻¹       | [11]      |
| Engine Exhaust Particle Sizer (EEPS) | Model 3090; TSI Inc., Shoreview, USA | PNC, PSD; electrical mobility diameter | 5.6 nm – 560 nm; 10.0 L min⁻¹ | [12]      |
| Aerodynamic Particle Sizer (APS) | Model 3321; TSI Inc., Shoreview, USA | PNC, PSD; aerodynamic particle diameter | 0.5 µm – 20 µm; 5.0 L min⁻¹ | [13]      |
| Electrical Aerosol Detector (EAD) | Model 3070A; TSI Inc., Shoreview, USA | aerosol length              | sampling; 100 s; 0.3 L min⁻¹ | [14]      |
| Electrostatic Precipitator (ESP) | Prototype of Model 3089; TSI Inc., Shoreview, USA | sampling                    | >5 µm; >100 s; 0.3 L min⁻¹ | [15]      |
| Dynamic Dilution System (DDS) | DDS 560; Topas GmbH, Dresden, Germany | dilution 1:10                | -; 0.6 L min⁻¹; 5.0 L min⁻¹ |           |
| Dilution Unit (DIL) | DIL 556; Topas GmbH, Dresden, Germany | dilution 1:10                | -; 0.6 L min⁻¹; 5.0 L min⁻¹ |           |
| Mass Flowmeter (MFM) | Model 41221; TSI Inc., Shoreview, USA | flow rate                   | -; -; -; -; -; - |           |

⁴ adjusted time resolution
⁵ adjusted aerosol flow rate
2.2.3. Experimental setups. Depending on the applied stress and the associated PNC two different experimental setups (see figures 3 and 4) were installed for the (nano)-particle release characterization. Both experimental setups were operated in a laminar flow bench (Model LF-VM-K0615; Steag Laminarflow Prozesstechnik GmbH, Pliezhausen, Germany) to achieve a nearly particle free environment with PNC < 0.01 cm\(^{-3}\). Each experimental setup can be divided in three main sections, i.e. aerosol generation, aerosol conditioning and aerosol characterization.

Figure 3. Schematic diagram of the experimental setup used for the (nano)-particle release characterization from coatings and composites due to wind erosion and dynamic friction.

Previous investigations [e.g. 4, 5] have shown that sanding lead to a considerable release of particles. Thus the experimental setup shown in figure 4 consisted of two dilution stages (adjustable predilution for the complete aerosol flow and device specific dilution) with known dilution factors to avoid changes in the PSD (e.g. by coagulation) and to enable best measurement conditions (e.g. single particle count mode of the CPC).

Figure 4. Schematic diagram of the experimental setup used for the (nano)-particle release characterization from coatings and composites due to sanding.

2.2.4. Experimental procedure. Each sample was treated 5 times (2 × sanding, 2 × dynamic friction, 1 × wind erosion) at different local positions. Hence, a total of 8-12 analyses for sanding and dynamic friction and 4-6 analyses in the case of wind erosion were performed for each condition of a sample system.
To monitor the whole release process (including startup and shutdown), the total measurement time of one sanding test was 100 s and in the cases of dynamic friction and wind erosion 90 s. Within this time, measurement instruments were successively switched on for data recording. The actual treatment process was started after all instruments were running for \( \geq 10 \) s (lead time for zero background characterization) and lasted for 16 s. Subsequent the aerosol analyses were continued for \( \geq 30 \) s (lag time for collecting all released particles).

### 2.3. Data evaluation

In order to draw meaningful conclusions about the (nano)-particle release, it is necessary to distinguish between the process concentration (PNC based on the simulated treatment and the suction flow rate at the particle source), the measuring concentration (PNC after aerosol conditioning or far away from the source) and the true concentration. In the literature, it is common to show the measured process concentration (PNC based on the simulated treatment and the suction flow rate at the particle source), the measuring concentration (PNC after aerosol conditioning or far away from the source) and the true concentration. But without additional sampling parameters the data can be severely misinterpreted by underestimation.

A reasonable approach is the determination of absolute release numbers from the measurement data and their relation to suitable process parameters (e.g. surface area or sample mass) to enable a consistent emission characterization, which is the basis for the estimation of particle-immersion into the working space or atmosphere. This approach was already used for the data evaluation in [4, 6, 16] and is now an inherent part of ISO/TS 12025:2012.

The released number of particles \( n(x,\Delta t) \) in a time interval \( t_1 - t_2 \) of a size fraction \( x_i - x_j \) can be determined for a closed experimental system by equation (1), where \( Q_{\text{tot}} \) is the total volumetric air flow rate and \( f \) the used total dilution ratio.

\[
n(x,\Delta t) = Q_{\text{tot}} \cdot f \cdot \int_{t_1}^{t_2} \int_{x_i}^{x_j} q_0(\xi, \tau) c_{n,\text{tot}}(\tau) d\xi d\tau
\]

The measured PNC in each size class \( c_{n}(\xi, \tau) \) are available as discrete data. Numerical integration without additional steps gives equation (2), which was used in this study and in previous works [4, 16] for the data evaluation.

\[
n_k(\Delta t) \approx Q_{\text{tot}} \cdot f \cdot \Delta t \cdot \sum_{i:a}^{b} \left( \sum_{k:x\leq}^{d} c_{n,k,i} \right)
\]

In equation (2) \( \Delta t \) is the time between to measurement points. The running index \( k \) refers to the size class, while \( i \) is the running index of the time course.

Table 4 shows the fractional release numbers that are used in this study. Note that fractional release numbers can be in principle established for each size channel (high statistical uncertainty) or over the whole PSD (low information content) for each operated instrument.

The fractional release numbers can be used for comparison within one treatment procedure and are independent from the adjusted aerosol conditioning. In order to compare different treatment processes, the process characteristic fractional numbers of released particles have to be related to a suitable parameter of the process. This study dealt with surface treatment of coatings and composites, thus the corresponding stressed areas (see table 2) of the simulated treatment processes were used.

Assuming ideal mixing without particle coagulation or particle losses a simple way to convert the

| release fraction | device | annotation |
|-----------------|--------|------------|
| \( x \leq 100 \) nm | EEPS or CPC-CPC+DB* | number of released nanoparticles (5.6 nm \( \leq x \leq 100 \) nm) |
| \( x < 10 \) \( \mu m \) | CPC | total particle release (6 nm \( \leq x < 10 \) \( \mu m \)), most robust results |
| \( x \geq 1 \) \( \mu m \) | APS | number of released particles in the micrometre size (1 \( \mu m \) \( \leq x \leq 20 \) \( \mu m \)) |

* based on non-ideal separation and particle deposition, the DB-principle can lead to an overestimation of \( n(x \leq 100 \) nm)
resulting fractional release numbers in a model concentration is the relation to an appropriate air column volume [4], as performed for this study. The usage of dispersion models is also conceivable.

3. Results
Figure 5 shows the determined numbers of released nanoparticles for the AL-coatings (left) and the PP-composites (right).

![Graphs showing nanoparticle release numbers](image)

**Figure 5.** Experimental determined nanoparticle release numbers of the simulated treatment processes (sanding and wind erosion); error bars = extrema; dotted lines and values in brackets = process concentration at particle source.

3.1. Impact of pigmentation
The comparison between the non-pigmented samples with the pigmented ones for both the non-weathered and the artificial weathering state (figures 5 and 6) lead to the conclusion that the pigmentation has a non-negligible impact on the particle release. For example, the total particle release \(x < 10 \mu m\) due to sanding of the non-weathered coatings tends to increase with growing pigment size \(x_{PCS}\) (table 1), but it should be noted that for the examined samples the pigment size positively correlates with solid content (see table 1), too.

Extensive SEM-analyses of the contact materials and electrostatically precipitated aerosol particles showed no indication for free nanoscaled pigments. Independently performed TEM- and EDX-Analyses have shown firmly embedded pigments. Pigments with dimension significantly larger than the nanoscale (TD, CT, KB) were recovered during SEM-analyses on the contact materials (abradants for dynamic friction and sanding) that can maybe explained by shearing off due to their large contact surface.
3.2. Impact of artificial weathering

3.2.1. Sanding. Results in the case of sanding have shown more often than not a significant increase in the total particle release (x < 10 µm) for coatings after they had been artificially weathered, whereas the reverse effect was observed for PP-composites. The artificial weathering of the coatings led also to a significant increase in the nanoparticle release (x ≤ 100 nm). No significant differences in the nanoparticle release (x ≤ 100 nm) were detected for the PP-composites. Both, coatings and composites, have shown a significant weathering-induced increase in the release of micron particles (x ≥ 1 µm).

3.2.2. Dynamic friction. The artificial weathering led in the case of dynamic friction to a significant increase in the release x ≥ 1 µm for the AL-coatings and the PP-composites. The release fractions x < 10 µm and x ≤ 100 nm showed only for the coatings the tendency to increase, whereas no significant differences were determined for the PP-composites.

3.2.3. Wind erosion. Wind erosion led in the majority of cases to a significant increase in the particle release x < 10 µm, x ≤ 100 nm and x ≥ 1 µm for the artificially weathered PP-composites in comparison to the non-weathered counterparts. No significant differences in each release fraction resulted from wind erosion of the coatings.

Figure 6. Cross-process comparison of the AL-coatings and PP-composites by the area specific number of released particles < 10 µm; error bars = extrema.
3.3. Comparison of the treatment processes and data transferability

Figure 6 shows for example the resulting data for $x < 10 \mu m$ for the non-weathered (a, b) and weathered (c, d) samples.

In the case of the analysed coatings (non-weathered and artificially weathered), the most particles were released by sanding followed by wind erosion. The lowest numbers of released particles were observed for dynamic friction. The non-weathered PP-composites showed a similar behaviour, although no significant difference between wind erosion and dynamic friction could be observed. However, wind erosion of the weathered PP-composites led in most cases to higher particle release numbers than the other simulated processes.

Model concentrations of $x < 10 \mu m$ for selected air columns are given in table 5. For the purpose of comparison, measured urban PNC ($x \leq 0.8 \mu m$) in a street canyon ranged from $2.5 \cdot 10^3 \text{ cm}^{-3}$ - $5.5 \cdot 10^4 \text{ cm}^{-3}$ in the night and on weekend and up to $1.5 \cdot 10^5 \text{ cm}^{-3}$ during traffic rush hour on weekdays [17]. Comparable concentrations yielded only the simulated sanding processes. Natural flow velocities in the magnitude as simulated in this study accompany with significantly higher air volumes and thus would result in negligible low concentrations.

Table 5. Model concentrations for $x < 10 \mu m$ based on the simulated processes; estimation based on the maxima values of the measured data.

| process     | example                          | air column height [cm] | model PNC for $x < 10 \mu m$ |
|-------------|----------------------------------|------------------------|------------------------------|
|             |                                  |                        | non-weathered [cm$^3$] | weathered [cm$^3$] | non-weathered [cm$^3$] | weathered [cm$^3$] |
| sanding     | processing of semi-finished parts; re-preparation of surfaces | 10                     | $\leq 3.3 \cdot 10^7$ | $\leq 2.3 \cdot 10^7$ | $\leq 2.5 \cdot 10^7$ | $\leq 1.8 \cdot 10^7$ |
|             |                                  | 50                     | $\leq 6.7 \cdot 10^7$ | $\leq 4.7 \cdot 10^7$ | $\leq 4.9 \cdot 10^7$ | $\leq 3.6 \cdot 10^7$ |
|             |                                  | 200                    | $\leq 1.7 \cdot 10^8$ | $\leq 1.2 \cdot 10^8$ | $\leq 1.2 \cdot 10^8$ | $\leq 8.9 \cdot 10^7$ |
| dynamic friction | handling of objects (e.g. toys, pencils, …) | 10                     | $\leq 3.9 \cdot 10^7$ | $\leq 1.5 \cdot 10^7$ | $\leq 6.0 \cdot 10^7$ | $\leq 1.5 \cdot 10^7$ |
|             |                                  | 50                     | $\leq 7.7 \cdot 10^7$ | $\leq 3.0 \cdot 10^7$ | $\leq 1.2 \cdot 10^7$ | $\leq 2.9 \cdot 10^7$ |
|             |                                  | 200                    | $\leq 1.9 \cdot 10^8$ | $\leq 7.6 \cdot 10^8$ | $\leq 3.0 \cdot 10^8$ | $\leq 7.3 \cdot 10^7$ |
| wind erosion | facades erosion; moved vehicles  | 10                     | $\leq 7.4 \cdot 10^7$ | $\leq 4.0 \cdot 10^7$ | $\leq 1.9 \cdot 10^7$ | $\leq 5.7 \cdot 10^7$ |
|             |                                  | 50                     | $\leq 1.5 \cdot 10^7$ | $\leq 8.1 \cdot 10^7$ | $\leq 3.7 \cdot 10^7$ | $\leq 1.1 \cdot 10^8$ |
|             |                                  | 200                    | $\leq 3.7 \cdot 10^8$ | $\leq 2.0 \cdot 10^8$ | $\leq 9.3 \cdot 10^8$ | $\leq 2.9 \cdot 10^8$ |

4. Summary and conclusions

A recently published analysis method [4] was used and partly enhanced for the qualitative and quantitative characterization of the (nano)particle release from AL-coatings and PP-composites. Systematic analyses were performed for artificially weathered samples based on three simulated treatment processes – sanding, dynamic friction and wind erosion.

Immediate results of the methodology are total and size-fractionated number concentrations and number weighted particle size distributions. With attention to the process conditions, these data were converted in process- and fractional numbers of released particles for the size ranges $x \leq 100 \text{ nm}$, $x < 10 \mu m$ and $x \geq 1 \mu m$. Combined with sufficient reproducibility, the evaluation allows comparison of non-pigmented reference samples with pigmented ones and also of non-weathered samples with weathered ones.

4.1. Nanoparticle release results

Investigations have shown that the sample material, the sample composition, the sample condition (e.g. weathering state) and the type of mechanical treatment have a strong effect on the particle release. For example artificial weathered coatings showed in the case of sanding a higher (nano)-particle release as the non-weathered samples. In contrast, the artificially weathering of PP-composites led to a reduced release.

Despite occasional high numbers of released (nano)-particles, no free nano-pigments were observed during independently performed SEM- and TEM-analyses of electrostatic precipitated aerosol
particles. SEM-analyses of used abradants for sanding and dynamic friction showed the presence of pigment particles with dimensions significantly larger than the nanoscale for both the non-weathered and weathered samples.

4.2. Methodology
Particle concentration, particle size and particle material are the three main measurands which are necessary for exposure assessment. Despite the increasing amount of published studies, there is still a need for a harmonized methodology of investigations on the (nano)-particle release into the air, especially in the field of experimental implementation and data evaluation. Most published studies have only a qualitative character, while exposure assessment requires additional quantitative data to enable cross-process comparison and data transferability.

As demonstrated in this study by analysis of millions of particles, particle size and number concentration can be determined statistically reliable with commercial aerosol measurement instruments. In contrast, the representativeness of the particle nature identification by SEM and TEM image analysis is limited by the small number of analyzed particles.

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