



Measurements of Nanoscale TiO₂ and Al₂O₃ in Industrial Workplace Environments – Methodology and Results

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ABSTRACT

The possible release of engineered nanomaterials was investigated based on a previously developed but now refined methodology. Data from altogether eight industrial work areas in production plants of nanostructured TiO₂ and Al₂O₃ particles were obtained and used to test the methodology and to derive a first assessment of possible exposure of workers. Particle size distributions were determined in work area environments with concurrent measurements at a comparison site. Data from the comparison site were used to estimate the particle background level in the work area and distinguish it from potentially released nanomaterial. The analysis is based on the comparison of time resolved data from the work area and the comparison site as well as data determined during periods with and without work activities in the work area. The data analysis method introduced delivers size-resolved information on the potential nanoparticle exposure of workers.

A significant release of particles in the size range 100–562 nm was observed in the work area of bagging aluminum oxide and is stemming from damaging or overfilling of bags, and the necessary activities during the cleaning of the work area. The maximum particle diameter of these particles was around 340 nm. At all other investigated locations no significant releases of particles in the size range 100–562 nm were determined. Also, no significant release of particles < 100 nm was observed in all work areas.

The average PM₁₀ exposure during the work activities varied from 48 to 1,330 µg/m³ in the different work areas. The maximum concentrations of aluminum were 118 µg/m³ and 58 µg/m³ for PM₁₀ and PM₁, respectively, during the bagging of Al₂O₃ in small bags. In comparison, the maximum concentrations of titanium were 550 µg/m³ and 434 µg/m³ for PM₁₀ and PM₁, respectively, during the bagging of TiO₂ and indicate a significant release of coarser particles.

Keywords: Nanoparticles; Exposure; TiO₂; Al₂O₃; Measurement strategy; Data analysis.

INTRODUCTION

The production and use of functional nanomaterials with new chemical and/or physical properties is one of the key technologies of the 21st century. Nanoparticles (particle with at least one dimension smaller than 100 nm, (EU, 2011) with novel properties are used in a wide range of applications. For example, the use of nanoparticles during the material production may influence material properties (surface properties, catalytic activity, etc.; Roco, 2005). Besides the unique properties of nanomaterials resulting in special applications, possible negative health effects are under discussion (Maynard *et al.*, 2006; Handy and Shaw, 2007). A possible risk from these materials for human beings or the environment may only arise if exposure exists to a potentially hazardous material (Krug and Klug, 2008).

There are various scenarios for human exposure to nanoparticles, but exposure scenarios during particle manufacturing and handling processes are among the most important as the concentrations may potentially be the highest. The measurement strategy and investigations on possible release of nanoparticles during production and handling of TiO₂ (mean primary particle size 21 nm) and Al₂O₃ (mean primary particle size 13 nm) presented here were developed to assess possible exposure to airborne nanoparticles and hence allow for a first risk estimate within the production areas. The received data are discussed in the section *Discussion and Conclusions* together with comparisons of literature data which are provided in a review of existing studies.

MEASUREMENT STRATEGY

Several assessment strategies have been developed for the determination of exposure to engineered nanoparticles at workplaces (e.g., Methner *et al.*, 2009; Brouwer *et al.*, 2012; Ramachandran *et al.*, 2012; Witschger *et al.*, 2012; nanoGEM, 2013). Two questions of priority are related to

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the purpose and the lower determination limit because they define the measurement devices necessary.

The first question is that of the purpose of measurement. It can be monitoring, screening or exposure assessment for subsequent risk assessment. The degree of details on particle characteristics needed increases in the order given before. Simple particle number or surface concentration measurements are usually sufficient for monitoring or screening purposes, i.e., to check whether or not particle concentrations in the workplace may be elevated. Detailed particle characterizations e.g., identifying the chemistry, differentiating agglomerates from primary particles, specific surface area concentration and particle reactivity are necessary for more thorough exposure assessments and subsequent linkage to possible health effects. These measurements are extensive but needed for health risk evaluation and future epidemiological studies.

The second basic question, the lower particle concentration detection limit, is important since it also determines the measurement devices and methods. Integral measurement devices such as particle counters (which display measurement values as particle size integrated and time resolved values) can only be used if high increase of the workplace particle concentrations over background particle concentrations e.g., by $> 100,000 \text{ \#/cm}^3$ are of interest and therefore process particles can easily be discriminated from background particles.

Background concentrations of particles, i.e., particles infiltrating from outside become important at lower concentration levels and hence have to be accounted for. Single particle analysis methods (like scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)) have to be used if the evaluation has to be very specific, i.e., detection limits down to a few particles are of interest. In this manuscript a measurement strategy is described which can be employed in the case when engineered nanoparticle concentrations on the order of several thousand per cm^3 are of interest.

To assess the potential of this strategy as well as possible exposure at workplaces producing similar nanoparticles but in different production pathways, particle number and mass concentrations, and chemical composition were determined in work areas with concurrent measurement at a second measurement (comparison) site. The second measurement site was always located near the work areas but far enough away that the work areas did not directly influence to the

second measurement sites.

The measurements were conducted at eight different work areas in two different production plants of nanostructured material. One main difference between plant 1 and 2 was the way of production of the nanomaterial. While TiO_2 particles in plant 1 were produced via the liquid phase, TiO_2 and Al_2O_3 were produced by combustion in plant 2. The measurements of the bagging of TiO_2 in 500 kg bags were done twice because of constructional changes in the work area of plant 2. The measurement plan included the measurements in nanomaterial process work areas with and without the process in operation as well as concurrent measurements at a comparison site. No measurements without the process in operation were conducted in the dryer and filtration areas of plant 1 and reactor areas of plant 2 since they include only continuous processes. The different work areas are summarized in Table 1 and briefly described in the following.

Milling and Bagging Area for 10 kg Bags (TiO_2 , Plant 1)

The milling and bagging area for small bags was a separate small room of about $5 \text{ m} \times 2.5 \text{ m} \times 2.5 \text{ m}$. Two measurements of at least 8 hours were conducted in this area, one without bagging activities and one during bagging of titanium dioxide. A filling system was used for bagging the milled titanium dioxide into plastic bags. The plastic bags were placed in cardboard boxes for stabilization. The filling system was handled manually with regard to the exchange of the plastic bags. The filled bags were stapled on a palette outside the bagging area. The palettes were covered with a foil and the foil was shrink-wrapped with hot air around nine cardboard boxes on one palette. Thereafter, a forklift took the palette to the storage depot. Two different forklifts were in use, one running on natural gas and the other on electricity.

Bagging Area for 10 kg Bags (Al_2O_3 , Plant 2)

The area for the Al_2O_3 bagging was a hall with several filling systems. The aluminum oxide particles were filled into paper bags using an automatic filling system. Only the placement of the paper bags was handled manually. After filling, the bags were stapled on a palette next to the filling system and transported out of the hall with a hand stacker. Two measurement periods of at least 8 hours were conducted in the bagging area, one without bagging activities and one during bagging of aluminum oxide.

Table 1. Investigated work areas.

Plant	Material	Investigated work area
1	TiO_2 (wet chemical)	Milling and bagging for 10 kg bags
		Milling and bagging for 500 kg bags
		Dryer area
		Filtration area
2	Al_2O_3 (combustion)	Bagging for 10 kg bags
		Reactor area
	TiO_2 (combustion)	Bagging for 500 kg bags
		Bagging for 500 kg bags (after constructional changes)
		Reactor area

Bagging Areas for 500 kg Bags (TiO₂, Plants 1 and 2)

The measurements in the bagging areas for 500 kg bags were conducted during bagging of titanium dioxide and without bagging activities for periods of eight hours each. The titanium dioxide was filled into the bags using a filling system. A palette was placed under the filling system before bagging and the empty bag was manually connected and sealed to the filling system. A forklift (plant 1) or a hand stacker (plant 2) took the palette with the bag and placed it next to the filling system after the bag was filled. A product sample was taken from the bag for quality control. Later, the bag was sealed and together with a palette covered with foil. The foil was shrink-wrapped by a gas burner.

Dryer Area (TiO₂, Plant 1)

The dryer was in line above the filling system for 500 kg bags (prior measurement site). None of the activities in the drying area was expected to emit nanoparticles during normal conditions. The main normal activity on the same floor is in a control room (separate room). Hence only one measuring period was monitored in the dryer area over a time period of 8 hours.

Filtration Area (TiO₂, Plant 1)

The measurements in the filtration area were conducted for 8 hours. No other work or activities were ongoing in this area besides cleaning of the filter. Only one measurement period was investigated due to the mainly continuous character of the working process.

Reactor Areas (TiO₂, Al₂O₃, Plant 2)

The measurements in the reactor areas were conducted for periods of eight hours each. Because of the reduced pressure in the reactor none of the real work activities were expected to emit nanoparticles into the reactor areas. Only one 8 h measurement was carried out per reactor area.

MEASUREMENT METHODS

Measurement methods employed in this study can be separated into online (size resolved/integrated and time resolved with directly measured value display) and offline (size and time integrated) as well as methods determining physical and/or chemical methods (Table 2).

A Scanning Mobility Particle Sizer (SMPS Model 3936, DMA Model 3081, CPC Model 3010 or CPC Model 3786, TSI Inc.) classifies the aerosol particles according to their electrical mobility diameter and counts the classified

particles with a Condensation Particle Counter (CPC). The SMPS-System was setup to cover a size range of 14 nm to 750 nm electrical mobility diameter with a resolution of up to 64 channels per decade. A Fast Mobility Particle Sizer spectrometer (FMPS Model 3091, TSI Inc.) measures aerosol particles in a size range from 5.6 nm to 562 nm electrical mobility diameter with a resolution of 16 channels per decade (Tamm et al., 1998). Due to its design, the FMPS spectrometer is capable of making particle size distribution measurements with one-second time resolution. SMPS and FMPS have been shown to produce comparable results, with the largest deviations in upper particle size range (Asbach et al., 2009; Jeong and Evans, 2009; Kaminski et al., 2013). All online data were calculated to 5 minute averages for comparison reasons. Nevertheless, single measurement values and scans were checked for validity.

Two Low Volume Samplers (2.3 m³/h; LVS 3, Derenda) and one High Volume Sampler (30 m³/h, DHA 80, DIGITEL) were used as manual filtration samplers in this measurement campaigns to determine the mass concentration and chemical composition (here mainly aluminum and titanium) of two different size fractions (PM₁ and PM₁₀). Both filtration samplers are in accordance with EN12341 (1999) and the guidelines VDI 2463 Part 7 (1982) and Part 11 (1996). The LVS samplers were equipped with a single stage PM₁ and PM₁₀ inlet, respectively, and the HVS sampler was also equipped with a PM₁₀ inlet. The particles were collected on preheated quartz fiber filters (MN QF10, Macherey-Nagel, 47 mm for LVS and 150 mm diameter for HVS). Additionally, a Tapered Element Oscillating Microbalance (TEOM, Series 1400ab, Rupprecht and Patashnick Co., Inc.) was used as online PM₁₀ mass concentration (5 min time resolution) monitor running in the work area. The operation principle of the TEOM is based on the drawing air through a filter attached at the tip of a tapered glass tube. An electrical circuit places the tube into oscillation, and the resonant frequency of the tube is proportional to the square root of the mass of the tube-filter system, which increases with increasing filter loading (Patashnick and Rupprecht, 1991). The measurements of mass concentrations were for additional information because occupational exposure guidelines specify limit values for the maximum workplace concentrations which are usually based on mass concentrations.

Additional samples were collected on glassy carbon substrates with an electrostatic precipitator (ESP or Nanometer Aerosol Sampler (NAS Model 3089, TSI Inc.); Dixkens and Fissan, 1999) for consecutive chemical and

Table 2. Instrumentation employed.

Instrumentation	Size range	Property	Type of instrument	Online
SMPS	13.8–750 nm	Number size distribution,	Electrical mobility analysis	Yes
FMPS	5.6–562 nm	Number concentration		
NAS/ESP + SEM/EDX	< 10,000 nm	Single particle size + chemistry	Particle deposition and microscopy	No
TEOM	< 10,000 nm	PM mass concentration	Filtration sampler	Yes
LVS 3	< 1,000 nm	PM mass concentration	Filtration sampler	No
HVS DHA 80	< 10,000 nm			

morphological analysis. To enhance the sampling efficiency the NAS was equipped with a homemade unipolar charger.

The instruments were placed in the work areas as close as possible to the workers' activities, but in such a way that they did not hamper the workers. If possible, the sampling tube inlets of the measurement devices were placed in the height of the breezing zone of the workers.

DATA QUALITY

For plant 1 and 2 only one SMPS and one FMPS were available for the determination of particle number size distributions and number concentrations. For the repeated measurements in the bagging area for 500 kg bags of plant 2 two sets of SMPS were used to conduct the measurements. For the reason of using different instrument types and to exclude any alterations due to transport, the performance of the instruments were tested with ambient air side by side prior to and after each measurement campaign. The measured concentrations in the appropriate size ranges (SMPS/FMPS 13.8–562 nm and SMPS/SMPS 13.8–750 nm, respectively) with the time resolution of 5 min and the parameters describing the lognormal-like size distribution were compared:

- The geometric mean diameter was calculated with

$$GMD = \exp \left(\frac{\sum_i C_{n,i} \cdot \ln d_{p,i}}{C_N} \right)$$

- the geometric standard deviation were calculated with

$$\sigma_g = \exp \left(\frac{\sum_i C_{n,i} \cdot (\ln d_{p,i} - \ln GMD)^2}{C_N} \right)^{0.5}$$

- the number concentrations C_N (≤ 100 nm, > 100 nm, total) of the respective measurements were potted against each other to receive the coefficient of determination R^2 .

where $d_{p,i}$ stands for the particle diameter and $C_{n,i}$ for the number concentration in the i -th size class of d_p , and C_N is the size integrated concentration over the respective size range.

Table 3 summarizes the results of an 8 h comparison. The second set of rows in the first column (comparison measurements) indicates the comparison measurements before (1) an after (2) each measurement campaign. It is clearly seen that the comparability is given for the instruments used. The coefficients of determination R^2 are in the range of 0.88–0.98, and results for the geometric mean diameters GMD and geometric standard deviations σ_g are also very comparable.

DATA INTERPRETATION

It is important to be able to differentiate background particles from those being emitted by the process and more specifically to detect emitted engineered nanoparticles, free, as agglomerates or embedded in the material matrix. Kuhlbusch *et al.* (2011) identified four basically different approaches for background distinction: time series or spatial approach, an approach based on comparative studies with and without nanomaterial, and detailed (size resolved) chemical and/or morphological analysis. In this study a combined approach of time series and spatial analysis was used. Time series analysis basically assumes that the concentration at the work area determined during no work activity is the background concentration and any increased concentrations during the work activity can be attributed to the working process. The spatial analysis assumes that a background measurement location is representative for the background at the work area of interest. Any difference between the determined background and work area concentrations can be linked to the work activity and the nanomaterial investigated (Kuhlbusch *et al.*, 2011). Furthermore the data interpretation was conducted similar to that used in Kuhlbusch *et al.* (2004). Therefore, besides the measurement

Table 3. Summary of the side-by-side measurements with ambient air outside of the work areas of the plants. GMD and σ_g are calculated mean values with normal standard deviation and R^2 is the coefficient of determination of the compared number concentrations for the respective measurement times. In the column *Comparison measurements*, 1 stands for comparison before and 2 for comparison after a measurement campaign.

Comparison measurements			GMD [nm]	σ_g	R ²		
					≤ 100 nm	> 100 nm	total
Plant 1	1	SMPS	39.28 ± 7.43	2.04 ± 0.16	0.94	0.88	0.94
		FMPS	38.49 ± 8.08	2.06 ± 0.27			
	2	SMPS	48.29 ± 3.67	2.05 ± 0.10	0.98	0.97	0.98
		FMPS	41.15 ± 2.69	1.94 ± 0.08			
Plant 2	1	SMPS	72.95 ± 6.55	2.04 ± 0.06	0.92	0.89	0.93
		FMPS	77.68 ± 7.70	2.07 ± 0.08			
	2	SMPS	84.24 ± 8.25	1.96 ± 0.06	0.92	0.93	0.95
		FMPS	80.61 ± 7.86	1.96 ± 0.09			
	1	SMPS 1	36.51 ± 4.89	1.94 ± 0.13	0.98	0.98	0.98
		SMPS 2	34.93 ± 5.25	1.92 ± 0.12			
	2	SMPS 1	48.82 ± 6.53	2.08 ± 0.11	0.97	0.95	0.97
		SMPS 2	44.42 ± 7.07	2.08 ± 0.11			

location at the work area (WA) a second measurement location was necessary which enabled the calculation of the background particle concentration in the work area during the work activities. This second location, here always called the background measurement location (BML), which can be indoors or outdoors, had to be far enough away from the possible emission source in the workplace in order to not be affected by it. All other conditions at the BML should ideally be identical with those at the actual work area. It is assumed that measurements at the background measurement location mirror the surrounding of the work area to be investigated and that ‘no work activity’ particle concentrations (size distributions) at work areas can be calculated from those at the background measurement location (see Fig. 1). The background measurement location therefore has to be representative for the surrounding. Certain events close to the background measurement location, e.g., welding operation or lorry exhaust in the vicinity, influence the size distribution and those periods therefore have to be neglected for data interpretation. Those events can be clearly identified from the time series and the size distributions. Here, three BML were selected. The BML of the TiO₂ bagging for 10 kg bags in plant 1 was indoors (distance 5–10 m from WA) because the bagging area was a separate closed room in the hall. The other two BML were outdoors in the vicinity of the WA with distances

between 20–100 m. During the measurements the weather conditions, especially the wind direction were logged as were other activities (working activities, traffic, etc.) near the BML.

Data of the SMPS and FMPS were processed to achieve comparable size class resolution (16 channels per decade) and overlapping particle size ranges (13.8–562 nm). The following ratios were calculated to derive information on possible submicrometer particle release:

$$R_{\text{without WA activity}} = \frac{WA_{\text{without WA activity}}}{BML_{\text{without WA activity}}} \quad (1)$$

$$R_{\text{with WA activity}} = \frac{WA_{\text{with WA activity}}}{BML_{\text{with WA activity}}} \quad (2)$$

WA_{without WA activity}: Particle number concentration at work area without work activity.

BML_{without WA activity}: Particle number concentration at background measurement location without work activity at the work area.

WA_{with WA activity}: Particle number concentration at work area with work activity.

BML_{with WA activity}: Particle number concentration at background measurement location with work activity at the work area.

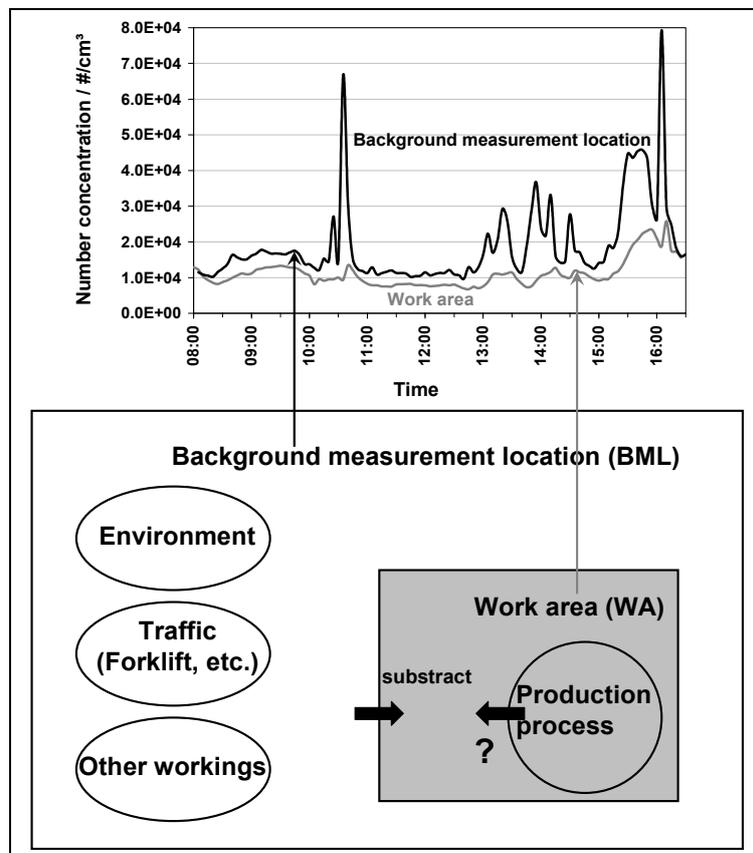


Fig. 1. Particle transport into the work area: The influence of ambient particles (here from background measurement location) on work area measurements is shown by the nearly parallel concentration changes in ambient and work area particle concentrations (Work area without work activity).

The ratio calculation for the time period without activity in the work area is of particular importance since this period allows for the estimation of the background contribution to the work area. The ratios $R_{with\ WA\ activity}$ and $R_{without\ WA\ activity}$ should be equal assuming there is no particle release caused by the work or production process. This assumption allows for the calculation of background particle concentrations in the work area, originating from infiltration from outside or from other places and other activities near the work area. Here, the infiltrating particle concentrations were measured at the background measurement sites (BML) near the work areas. Hence a theoretical background concentration in the work area (*theo. BG_{WA}*), the estimated concentration in the work area during work activity due to background particles, can be calculated as follows:

$$theo. BG_{WA} = \frac{WA_{without\ WA\ activity}}{BML_{without\ WA\ activity}} \cdot BML_{with\ WA\ activity} \quad (3)$$

The infiltration ratios may furthermore be significantly influenced by weather conditions, especially wind direction and precipitation if the background measurement location is outdoors.

The particle concentration of potential particle release is calculated by calculating the difference of the measured effective particle concentration at the work area and the theoretical background concentration.

$$\begin{aligned} Release &= WA_{with\ WA\ activity} - theo. BG_{WA} \\ &= WA_{with\ WA\ activity} - \frac{WA_{without\ WA\ activity}}{BML_{without\ WA\ activity}} \cdot BML_{with\ WA\ activity} \end{aligned} \quad (4)$$

The equations given above were also applied to the various size classes of the measured number size distributions to account for size dependent particle transport processes and to assess size dependent particle release at work areas. This approach is similar to the description in the Consent Report (2011), Pitzko *et al.* (2013), and nanoGEM (2013). If the particle concentration is increased over the background concentration, it has to be evaluated whether this increase is statistically significant. According to the suggestion of nanoGEM (2013), the work area particle concentration is regarded as significantly increased over background concentration if the mean particle concentration in the work area is greater than the background concentration plus three times the geometric standard deviation of the theoretical background concentration.

$$Release_{significant} > 3 \cdot \sigma_g \text{ theoretical Background Work area} \quad (5)$$

This means if the ratio

$$\frac{Release\ particle\ concentration}{3 \cdot \sigma_g \text{ theoretical Background Work area}} > 1 \quad (6)$$

the released particle can be considered as significantly increased over the background concentration.

It has to be noted that the ratios obtained for the appropriate bagging work areas without activities were used for the calculations in the cases of analyzing continuous processes in the dryer area, filtration area, and reactor areas. Thus, only a rough estimation can be made for the dryer, filtration, and reactor areas because measurements without work area activity in continuous working processes are not possible. Furthermore it should be noted that all these investigations were carried out in work areas without forced ventilation. In work areas with an active ventilation system, it may be more representative to monitor the air from the ventilation system.

Additionally data derived from the NAS samples by SEM/EDX analysis were used for the verification of the results obtained by the online measurements and data analysis as well as for the identification of the possible source.

MEASUREMENT RESULTS

Number Size Distribution

The following figures show exemplarily the data interpretation for the measuring point bagging area for 10 kg bags (TiO₂, plant 1). The online measured data were processed according to Eqs. (1)–(5).

Fig. 2(a) shows the average particle size distributions in the TiO₂ bagging area for 10 kg bags in plant 1 without work activity (in the working area location “before”, grey line) and at the background measurement location (black line) for a time period of 8.25 h. In addition, the ratio work area/background measurement location is given in Fig. 2 (dotted black line). The ratio is larger than unity for particles > 320 nm, indicating a possible particle source inside the bagging area even though no work is ongoing. This may be due to activities at other locations of the bagging enclosure in the hall.

Fig. 2(b) shows the same as the left diagram but with the work activity in the TiO₂ bagging work area for 10 kg bags. The data in Figs. 2(a) and 2(b) were obtained on two consecutive days. Size distributions measured in the background show that the local conditions did not vary significantly between the two days.

Fig. 3(a) shows the theoretical background size distribution (estimated background distribution calculated according to Eq. (3)) and the actually measured size distribution in the work area for the bagging of TiO₂ during work activity. The measured particle curve is generally above the theoretical background curve. The area between the two size distributions integrated across the (nano) particle size range is a measure for particle release. Nevertheless, with these measurements, it cannot be distinguished whether these particles originate directly from the bagging or an auxiliary process, e.g., from a pump or a forklift. If possible, measurements without work activity should hence be carried out with all relevant non-product particle related processes active. This is, however, often not possible and could not be pursued in this study.

The ratio shown in Fig. 3(a) (dotted line) is generally

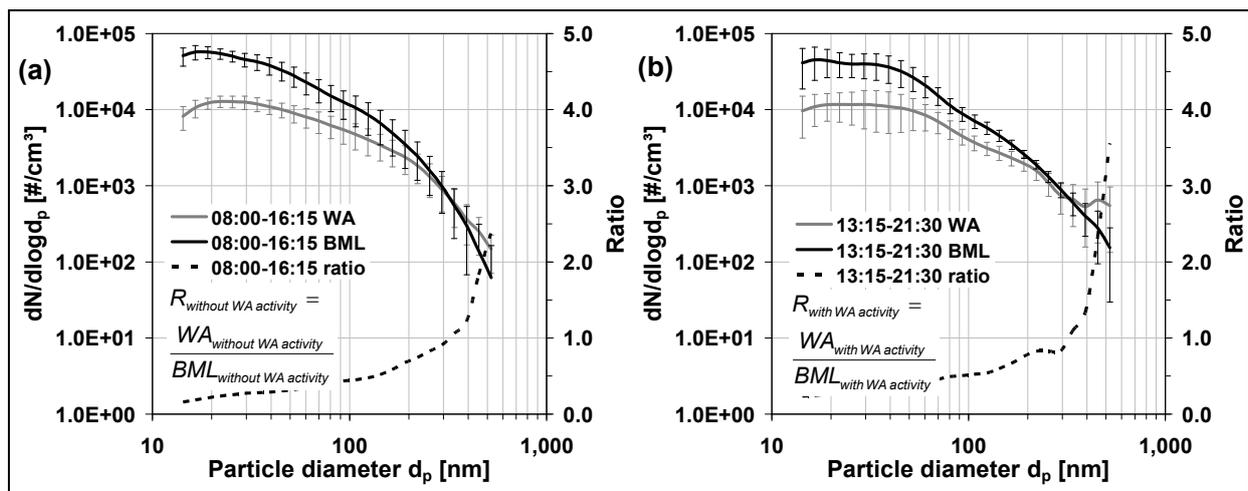


Fig. 2. Average particle size distribution without (a) and with work activity (b) in the TiO₂ bagging work area (WA) for 10 kg bags (grey line) and at the background measurement location (BML, black line) with normal standard deviation. The dotted black lines indicate the mean size distribution ratios WA/BML.

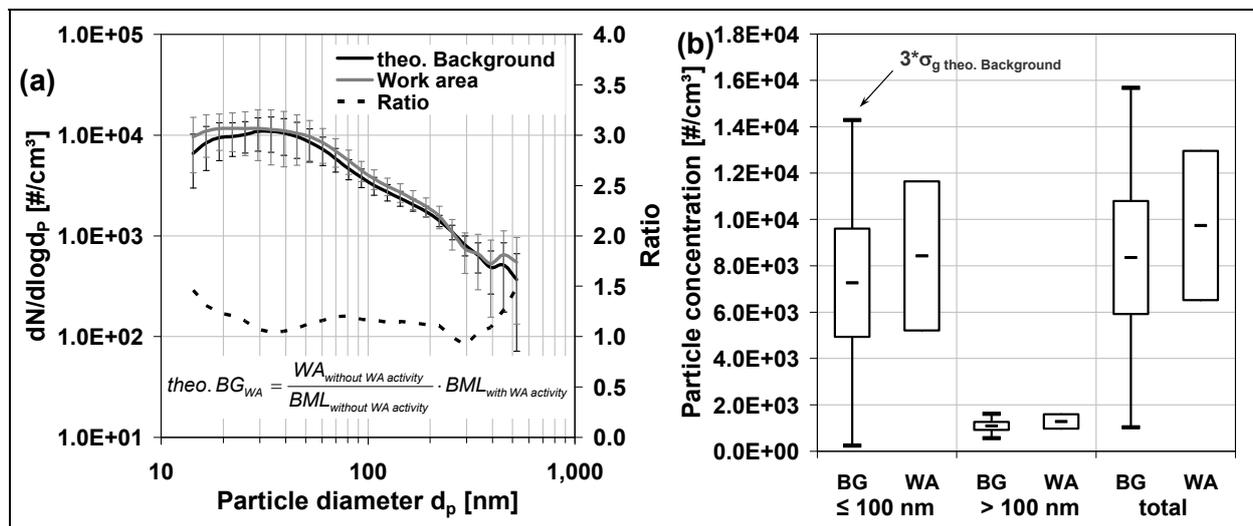


Fig. 3. (a) Calculated average background (black line) and actually average measured (grey line) size distributions with normal standard deviations during bagging activities in the TiO₂ bagging area for 10 kg bags in plant 1. (b) Box plots of size integrated particle concentrations for the background (BG) and the work area (WA) with mean value and normal standard deviations in the TiO₂ bagging area during bagging. The whiskers mark the significance level of $3 \times \sigma_{g, theo. Background}$

larger than one over the entire measured particle size range, excluding the particle size range from 270–320 nm, indicating a release of particles. But the release cannot be viewed as significant for plant 1. Fig. 3(b) shows the actually measured average size integrated particle concentrations for the particles ≤ 100 nm, > 100 nm, and the total size range of 13.8–562 nm in the work area as box plots with mean value and normal standard deviation. Additionally, the significance level of average $\pm 3 \times \sigma_{g, theo. Background}$ is marked as the whiskers. The average particle number concentrations in the work area were $8,423 \pm 3,218$ #/cm³ for particles ≤ 100 nm and $1,282 \pm 312$ #/cm³ for particles > 100 nm, respectively. An average particle release for particles ≤ 100 nm of $1,158 \pm 1,258$ #/cm³ and for particles > 100 nm of 195 ± 333 #/cm³ was calculated during the

bagging in the bagging area. The theoretical background was $7,266 \pm 2,341$ #/cm³ for particles ≤ 100 nm and $1,087 \pm 175$ #/cm³ for particles > 100 nm, respectively. Here, it is clearly seen that the particle releases are always lower than three times the standard deviation of the theoretical background. The values of $3 \times \sigma_{g, theo. Background}$ are $7,022$ #/cm³ for ≤ 100 nm and 526 #/cm³ for > 100 nm, and therefore the particle releases can be considered as not significant.

An overview of all measurement results obtained for all work areas are given in Fig. 4 and in Table 4. In Fig. 4 for all locations the average theoretical background concentrations and the average measured values are shown for the stated time period (working period) which is given in column 2 of Table 4. The significance limit according Eq. (5) is also

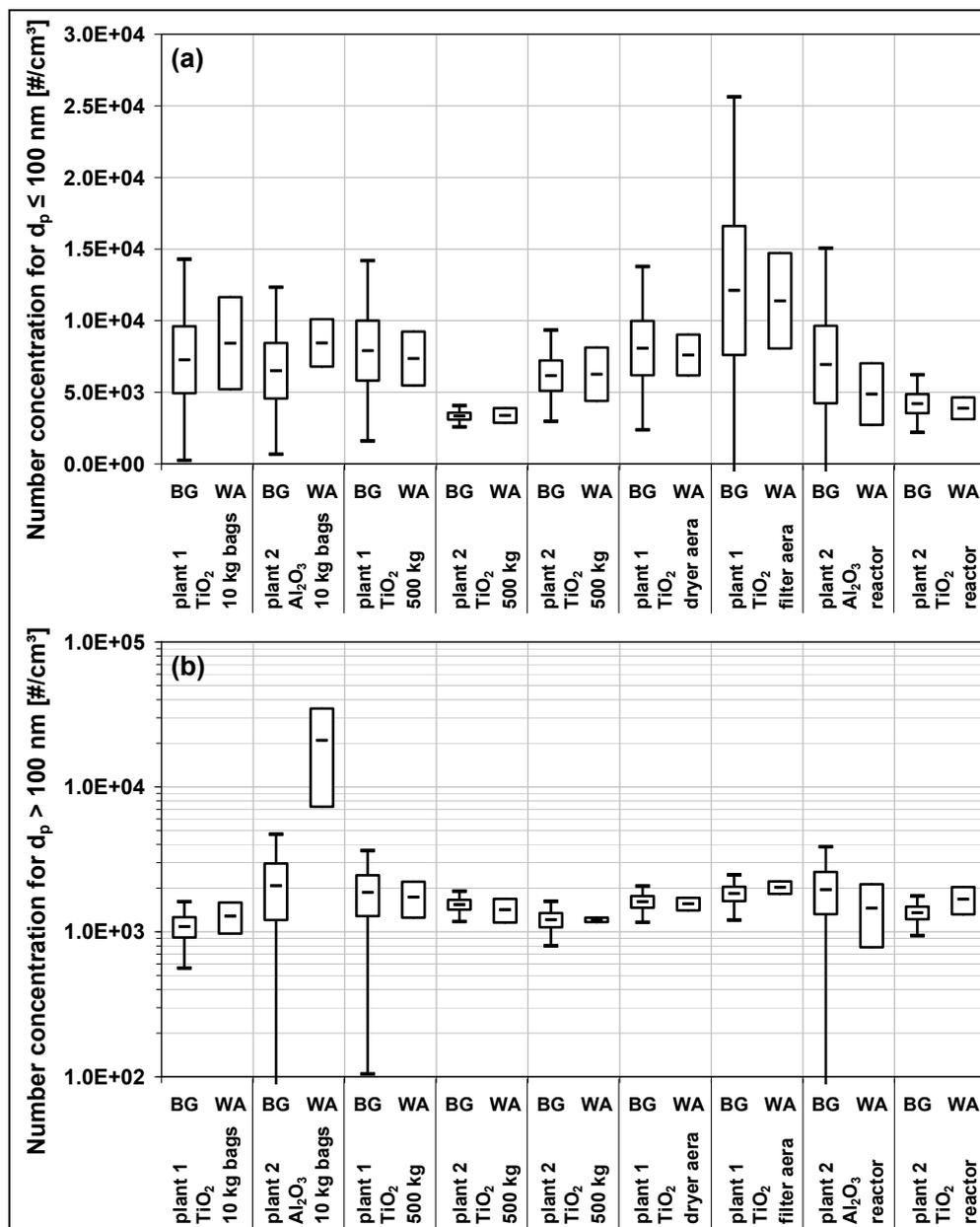


Fig. 4. Summary of the measurement results in the different work areas for particles ≤ 100 nm (a) and > 100 nm (b); Box plots with mean value and normal standard deviation, the whiskers mark the significance level of $3 \times \sigma_{g \text{ theo. Background}}$

marked (whiskers of the box plots). One value is directly peculiar in the diagram of Fig. 4(b): During the bagging of 10 kg bags in the Al_2O_3 bagging area in plant 2 a significantly increased value for the release of particles > 100 nm was determined. The bagging work activity in this work area was often interrupted because of bag over fillings or bag damages. During the interruptions the work area had to be cleaned with suction devices (vacuum cleaner). An analysis of the size distributions of the released particles showed that the maximum particle diameter of these particles was around 340 nm. The highest total concentration in the size range 13.8–562 nm was approximately $48,200 \text{ \#/cm}^3$ and during the breaks the total concentrations decreased to around $10,100 \text{ \#/cm}^3$.

For all other locations no significant releases of particles

≤ 100 nm or > 100 nm in diameter were observed. Besides the released particle concentration Table 4 also lists the ratio according Eq. (6). This ratio indicates a significant release of particles during the work activity in the work area if the value is greater than one. Only in the Al_2O_3 bagging area for 10 kg bags in plant 2 this ratio is greater than one with a value of 7.2 for particles > 100 nm and shows clearly a release of particles. The ratio for particles > 100 nm in the TiO_2 reactor area of plant 2 is increased with a value of 0.8 but according to Eq. (6) the particle release is regarded as not significant.

Additionally conducted SEM/EDX analyses of the NAS samples confirm this finding of the released particles in the Al_2O_3 work area. Al-containing particles < 400 nm in diameter were detected on the samples which were taken

Table 4. Calculated particle releases for TiO₂ and Al₂O₃ work areas during work activities. Ratios (released particle concentration/ $3 \times \sigma_{g \text{ theo. Background}}$) greater than one indicates the significant release of particles during the work activity in the work area.

	Time	Released particle concentration [#/cm ³]		Ratio $\frac{\text{released particle conc.}}{3 \cdot \sigma_{g \text{ theo. Background}}}$	
		≤ 100 nm	> 100 nm	≤ 100 nm	> 100 nm
		Plant 1 TiO ₂ 10 kg bags	13.15–21.30	1,158 ± 1,258	195 ± 333
Plant 2 Al ₂ O ₃ 10 kg bags	09.35–17.35	1,939 ± 2,460	18,903 ± 13,594	0.33	7.17
Plant 1 TiO ₂ 500 kg bags	16.00–00.00	–551 ± 2,155	–136 ± 223	–0.09	–0.08
Plant 2 TiO ₂ 500 kg bags	22.00–06.00	51 ± 410	–119 ± 296	0.07	–0.33
	23.55–04.30	158 ± 1,758	0 ± 143	0.05	0.00
Plant 1 TiO ₂ Dryer area	11.00–19.00	–479 ± 1,934	–53 ± 246	–0.08	–0.12
Plant 1 TiO ₂ Filtration area	06.30–14.30	–724 ± 4,679	187 ± 287	–0.05	0.30
Plant 2 Al ₂ O ₃ Reactor area	08.00–15.30	–2,066 ± 3,074	–499 ± 638	–0.25	–0.26
Plant 2 TiO ₂ Reactor area	10.30–18.45	–330 ± 482	322 ± 283	–0.16	0.78

Table 5. Total mass concentration results (no mass concentration measurements in plant 2 during the repeated measurements of bagging TiO₂ in 500 kg bags) and parts of the analysis data of the filters: PM₁₀ and PM₁ mass concentrations of Al and Ti in the work areas.

	WA Activity	Time	WA PM ₁₀ [μg/m ³]	WA PM ₁₀ / BML PM ₁₀	WA PM ₁ /PM ₁₀	WA Al [μg/m ³]		WA Ti [μg/m ³]	
						PM ₁₀	PM ₁	PM ₁₀	PM ₁
Plant 1 TiO ₂ 10 kg bags	without	08.00–16.15	142	0.95	0.38	6	0.8	21	3
	with	13.15–21.30	1,331	7.46	0.75	74	53	550	434
Plant 2 Al ₂ O ₃ 10 kg bags	without	21.45–02.15	138	2.76	0.77	20	7	0.7	< 0.2
	with	09.35–17.35	339	7.19	0.62	118	58	2.4	0.8
Plant 1 TiO ₂ 500 kg bags	without	16.00–00.00	47	3.22	0.43	1.4	0.1	14	4
	with	07.30–15.40	48	1.12	0.59	< 0.2	< 0.2	6	0.4
Plant 2 TiO ₂ 500 kg bags	without	17.15–01.15	223	5.75	0.79	8	3	< 0.3	< 0.3
	with	22.00–06.00	247	5.76	0.65	24	11	40	18
Plant 1 TiO ₂ Dryer area		11.00–19.00	54	1.70	0.40	1.2	< 0.1	11	2
Plant 1 TiO ₂ Filtration area		06.30–14.30	65	1.14	0.44	1.7	0.3	16	5
Plant 2 Al ₂ O ₃ Reactor area		08.00–15.30	124	2.88	0.95	29	22	1.3	0.2
Plant 2 TiO ₂ Reactor area		10.30–18.45	142	3.12	0.83	1.3	0.2	19	3

in the Al₂O₃ work area. With this method no Ti-containing particles in the size range up to approximately 500 nm were detected on the samples from the TiO₂ work areas. It has to be noted that this method of particle sampling on substrates is rather indicative than quantitative.

Mass Concentration

Table 5 summarizes the mass concentration measurement results from the different facilities. The values indicate partially elevated mass concentration as expected in these work areas during work activity. The PM₁/PM₁₀ ratios determined at the work areas are generally comparable to those expected for ambient air samples (Gomiscek et al., 2004). The increased ratio observed in the reactor areas of plant 2 indicates the release of submicrometer particles. Since no elevated number concentration were determined for particles < 562 nm it can be assumed that the additional PM₁ mass stems from particles > 562 nm in diameter.

DISCUSSION AND CONCLUSIONS

The measurement strategy and data analysis method introduced in this paper was applied to various work areas in 2 different plants. The methodology introduced allows the calculation of size dependent values towards nanoscale particles at actual workplaces. This is of importance since the uptake probability of nanoparticles by inhalation is size dependent (e.g., ICRP, 1994) and may range from around 30–40% for particles around 200 nm diameter to more than 80% for particles < 30 nm diameter.

Particle Number Concentrations

Overall 8 different work areas were investigated during this study. In none of the cases emission on the significant level of $3 \times \sigma_g$ of background particles for particles < 100 nm and only in one case for particles > 100 nm were detected. The size distribution measurements showed that in all cases

70–87% of the particle number concentration was attributable to particles ≤ 100 nm with the exception of Al_2O_3 bagging in 10 kg bags where only 29% of the particles were ≤ 100 nm. In the latter case, the highest total particle concentration in the size range 13.8–562 nm was approximately 48,000 $\#/ \text{cm}^3$ during work activities, decreasing to around 10,000 $\#/ \text{cm}^3$ during the breaks. The bagging process was often interrupted because of bag overfilling or bag damages. Also a significant release of particles > 100 nm (size range 100–562 nm) was observed. A time series plot (here not shown) of the released particles vs. the working time showed that the main particle release occurred as described after bag damages and during the necessary cleaning after bagging stops. The average particle concentration for particles > 100 nm was $20,985 \pm 13,707 \#/ \text{cm}^3$. During the breaks (e.g., lunchtime) the particle concentrations decreased to nearly 5,000 $\#/ \text{cm}^3$. The modal value of the released particle distribution was at 340 nm. The determined modal value agrees with that observed at carbon black work areas (Kuhlbusch *et al.*, 2004; Kuhlbusch and Fissan, 2006) where increased particle number concentrations during handling of the powders showed modal values > 400 nm diameter. The released particles were in a similar size range to this study but no significant release of particles < 100 nm was detected. Furthermore, Koivisto *et al.* (2012a) found during the automated packing of TiO_2 in small bags elevated particle concentrations only when the packing closure was opened for pressurized air cleaning and other activities. Bagging into large bags increased especially the concentration of particles > 500 nm in diameter. Other studies also show that only agglomerates of nanoparticles with diameters > 400 nm are released during handling, e.g., dustiness measurements conducted with nanomaterials (Kuhlbusch *et al.*, 2009, Stahlmecke *et al.*, 2009).

In this study the highest sub-100 nm ratio (released particle concentration/ $3 \times \sigma_{g \text{ theo. Background}}$) were also determined in the Al_2O_3 bagging area for 10 kg bags in plant 2 with a ratio of up to 0.33. This means that particle number concentrations were just within the interval of the normal background standard deviation during the work activity. The ratio for particles > 100 nm in the TiO_2 bagging area for 10 kg bags is 0.37 and hence also just on the $1 \times \sigma_g$ significance level of the background concentration. In all other cases total particle number concentrations for particles ≤ 100 nm were in the range or lower than the calculated background concentrations. Hence, no significant particle emission for particles ≤ 100 nm diameter were determined.

The results for the TiO_2 reactor area in plant 2 show for the particles > 100 nm a ratio (released particle concentration/ $3 \times \sigma_{g \text{ theo. Background}}$) up to 0.78. This means that the mean particle number concentrations were 2.3 times higher than the normal background standard deviation during the measurements. This value is indeed considered as not significant, but the mass concentration ratio $\text{PM}_1/\text{PM}_{10}$ of > 0.8 indicates and confirms the elevated particle value. On the other hand, it should be noted that the TiO_2 reactor was working in reduced pressure such that a leakage would normally not have the potential for emitting nanoparticles into the reactor area. The TiO_2 reactor area was very close to

Al_2O_3 bagging area. The work areas were indeed separate closed rooms, the reactor area was on a higher floor. But carryovers through open doors cannot be excluded. It is assumed that detected elevated particle concentrations stem from the Al_2O_3 bagging area especially since significant release was in the bagging area detected, but cannot be clearly proved by SEM/EDX.

In summary it can be said that ratios (released particle concentration/ $3 \times \sigma_{g \text{ theo. Background}}$) greater than 1 clearly show a particle release and measures against the release must be taken. This was only the case on one occasion in this study. If the ratios are in the range 0.33–1, additional investigations should be carried out to clarify whether further preventive measures must be taken.

Particle Mass Concentration

The PM_{10} mass concentrations determined in the work areas during work activities were always elevated compared to those determined concurrently at the comparison site. This was likely caused by re-suspension and is commonly observed during activities in indoor environments. The average PM_{10} exposure during the work activities varied from 48 to 1,330 $\mu\text{g}/\text{m}^3$ in the different work areas. The maximum concentration of aluminum was 118 $\mu\text{g}/\text{m}^3$ and 58 $\mu\text{g}/\text{m}^3$ for PM_{10} and PM_1 , respectively, during the bagging of Al_2O_3 in 10 kg bags in plant 2. The maximum concentration of titanium was 550 $\mu\text{g}/\text{m}^3$ and 434 $\mu\text{g}/\text{m}^3$ for PM_{10} and PM_1 , respectively, during the bagging of TiO_2 in 10 kg bags in plant 1. With the assumption that the above mentioned nanoscale number based criteria are applicable for the microscale PM_{10} mass concentrations, the calculation (released mass concentration/ $3 \times \sigma_{g \text{ theo. Background}}$) results in a ratio of 4.43 in the case of bagging of TiO_2 in 10 kg bags. This indicates a significant release in the micron size range. In this context it is interesting to note that in the case of bagging/milling of TiO_2 with overall PM_1 concentrations on average of 1,000 $\mu\text{g}/\text{m}^3$ no significantly elevated particle number concentrations below 562 nm diameter were observed (the ratio (released particle concentration/ $3 \times \sigma_{g \text{ theo. Background}}$) was 0.37). The assumption is that the increased PM_1 concentrations stem from the particles > 562 nm. Particle measurement devices which cover the particle size range > 500 nm would be very helpful to verify this assumption. For further measurement campaigns it is therefore advisable to employ also APS or OPC. The SEM/EDX analysis shows that no large amounts of coarser particles were detected in this size range. It is possible that few larger particles (agglomerates) increase the mass concentrations, since with the SEM, only a limited number of images were analyzed and thereby SEM images represent only a very small fraction of the sample. It has to be noted that this method of particle sampling on substrates is rather indicative than quantitative. Koivisto *et al.* (2012a) found in different packing areas of TiO_2 that the worker exposures varied from 225 to 700 $\mu\text{g}/\text{m}^3$ with over 90% of the particles smaller than 100 nm which were mainly soot and particles from process chemicals. Forklifts also re-suspended settled dust from floors which consists mainly of TiO_2 particles (Koivisto *et al.*, 2012a). Lee *et al.* (2011)

carried out a study in which workers handled nano-TiO₂ at workplaces was the detected gravimetric concentration of TiO₂ in the range from 100 to 4,990 µg/m³ and the particle number concentrations in the size range of 15–710 nm ranged from 11,400 to 45,900 #/cm³ during the reaction. This concentration decreased to 14,000 #/cm³ when the reaction was stopped (Lee *et al.*, 2011).

Measurement Strategy

The approach presented here certainly has advantages and disadvantages. For this approach two sets of measurement devices for measuring size segregated particle concentrations are needed. Furthermore the strategy requires considerably long measurement times, sometimes over several days. On the other hand, a main advantage is that the background distinction over a full shift period can be achieved. Through the contemplation of the processes without and with work activities in the work areas the different processes and release options can be considered.

Some published articles (e.g., Consent Report, 2011, nanoGEM, 2013, Plitzko *et al.*, 2013) also presented an approach to detect potential particle release by the use of only one set of measurement devices. Koivisto *et al.* (2012b) differentiated the process particles in a TiO₂ work area near the reactor from the background particles by means of measurements before and after the nanoparticle activity. The adopted background concentration during the NP collection were calculated from the previously and subsequently performed measurements. They found that the particle concentration in terms of TiO₂ NP collection was within the normal standard deviation interval of the calculated background concentration. The disadvantage of this approach is the assumption, of course, that the background concentration during the use of nanoparticle is the same as without nanoparticles and possible temporal changes in the background cannot be considered.

Generally, data on airborne nanoparticle exposure or exposure related measurements are still not very common (Wake *et al.*, 2002; Kuhlbusch *et al.*, 2004; Maynard *et al.*, 2004; Kuhlbusch and Fissan, 2006; Fujitani *et al.*, 2008; Tsai *et al.*, 2008; Yeganeh *et al.*, 2008; Brouwer *et al.*, 2009; Liao *et al.*, 2009; Curwin and Bertke, 2011; Lee *et al.*, 2011; Ling *et al.*, 2011; Zang *et al.*, 2011, Dylla and Hassan, 2012; Koivisto *et al.*, 2012a, b) and do not always clearly differentiate ambient from engineered particles.

In most cases it was seen that no primary particles but only greater agglomerates of nanoparticles are released. Only in one of the cases cited above (Yeganeh *et al.*, 2008) significant increases of sub-100 nm particle number concentrations during the handling of carbonaceous nanomaterials as well as during cleaning procedures were reported.

Overall, it is concluded from this study as well as the literature that generally only very few particles in the nanoparticle size range (< 100 nm diameter) are released during normal handling and processing. But it is also evident that for specific procedures and/or nanoscale materials release of these particles into the airborne phase may occur (Kuhlbusch *et al.*, 2004; Yeganeh *et al.*, 2008). Hence,

systematic approaches towards better identifying the processes and materials are needed to enable risk assessments. This approach may be based on the measurement strategy and data analysis methodology presented here.

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REFERENCES

- Asbach, C., Kaminski, H., Fissan, H., Monz, C., Dahmann, D., Mülhopt, S., Paur, H.R., Kiesling, H.J., Herrmann, F., Voetz, M. and Kuhlbusch, T.A.J. (2009). Comparison of Four Mobility Particle Sizers with Different Time Resolution for Stationary Exposure Measurements. *J. Nanopart. Res.* 11: 1593–1609.
- Brouwer, D., van Duuren-Stuurman, B., Berges, M., Jankowska, M., Bard, D. and Mark, D. (2009). From Workplace Air Measurement Results Toward Estimates of Exposure? Development of a Strategy to Assess Exposure to Manufactured Nano-Objects. *J. Nanopart. Res.* 11: 1867–1881.
- Brouwer, D., Berges, M., Virji, M.A., Fransman, W., Bello, D., Hodson, L., Gabriel, S. and Tielemans, E. (2012). Harmonization of Measurement Strategies for Exposure to Manufactured Nano-Objects; Report of a Workshop. *Ann. Occup. Hyg.* 56: 1–9
- Consent Report (2011). Tiered Approach to an Exposure Measurement and Assessment of Nanoscale Aerosols Released from Engineered Nanomaterials in Workplace Operations, IUTA, BAuA, BGRCl, IFA and VCI, Germany.
- Curwin, B. and Bertke, S. (2011). Exposure Characterization of Metal Oxide Nanoparticles in the Workplace. *J. Occup. Environ. Hyg.* 8: 580–587.
- DIN EN 12341 (1999). Ermittlung der PM₁₀-Fraktion von Schwebstaub, Referenzmethode und Feldprüfverfahren zum Nachweis der Gleichwertigkeit von Messverfahren und Referenzmessmethoden.
- Dixkens J. and Fissan, H. (1999). Development of an Electrostatic Precipitator for Off-Line Particle Analysis. *Aerosol Sci. Technol.* 30: 438–453.
- Donaldson, K., Li, X.Y., MacNee, W. (1998). Ultrafine (Nanometre) Particle Mediated Lung Injury. *J. Aerosol Sci.* 29: 553–560.
- Dylla, H. and Hassan, M.M. (2012). Characterization of Nanoparticles Released during Construction of Photocatalytic Pavements Using Engineered Nanoparticles. *J. Nanopart. Res.* 14: 825.
- EU (2011). Commission Recommendation of 18 October 2011 on the Definition of Nanomaterial, 2011/696/EU, Official Journal of the European Union.

- EU-OSHA (2009). Workplace Exposure to Nanoparticles. Literature Review. *European Agency for Safety and Health at Work*.
- Fujitani, Y., Kobayashi, T., Arashidani, K., Kunugita, N. and Suemura, K. (2008). Measurement of the Physical Properties of Aerosols in a Fullerene Factory for Inhalation Exposure Assessment, *J. Occup. Environ. Hyg.* 5: 380–389.
- Gomišček B., Hauck, H., Stopper, S. and Preining, O. (2004). Spatial and Temporal Variations of PM₁, PM_{2.5}, PM₁₀ and Particle Number Concentration during the AUPHEP-Project. *Atmos. Environ.* 38: 3917–3934.
- Handy, R.D. and Shaw, B.J. (2007). Toxic Effects of Nanoparticles and Nanomaterials: Implications for Public Health, Risk Assessment and the Public Perception of Nanotechnology. *Health Risk Soc.* 9: 25–144.
- ICRP (1994). International Commission on Radiological Protection: Human Respiratory Tract Model for Radiological Protection, ICRP Publication 66, Elsevier, Tarrytown, NY.
- Jeong, C.H. and Evans, G.J. (2009). Inter-Comparison of a Fast Mobility Particle Sizer and a Scanning Mobility Particle Sizer Incorporating an Ultrafine Water-Based Condensation Particle Counter. *Aerosol Sci. Technol.* 43: 364–373.
- Kaminski, H., Kuhlbusch, T.A.J., Rath, S., Götz, U., Sprenger, M., Wels, D., Polloczek, J., Bachmann, V., Dziurawitz, N., Kiesling, H.J., Schwiegelshohn, A., Monz, C., Dahmann, D., Asbach, C. (2013). Comparability of Mobility Particle Sizers and Diffusion Chargers. *J. Aerosol Sci.* 57: 156–178.
- Koivisto, A.J., Lyyränen, J. Auvinen, A., Vanhala, E., Hämeri, K., Tuomi, T. and Jokiniemi J. (2012a). Industrial Worker Exposure to Airborne Particles during the Packing of Pigment and Nanoscale Titanium Dioxide. *Inhalation Toxicol.* 24: 839–849.
- Koivisto, A.J., Aromaa, M., Mäkelä, J., Pasanen, P., Hussein, T. and Hämeri, K. (2012b). Concept to Estimate Regional Inhalation Dose of Industrially Synthesized Nanoparticles. *ACS Nano* 6: 1195–1203, doi: 10.1021/nn203857p.
- Krug, H.F. and Klug, P. (2008). Impact of Nanotechnological Developments on the Environment. In *Nanotechnology: Environmental Aspects, Vol. 2*, Krug, H.F. (Ed.), Wiley-VCH, Weinheim, ISBN-10: 3-527-31735-X, 291–306.
- Kuhlbusch, T.A.J., Fissan, H. and Neumann, S. (2004). Number Size Distribution, Mass Concentration, and Particle Composition of PM₁, PM_{2.5} and PM₁₀ in Bag Filling Areas of Carbon Black Production, ICBA-Study. *J. Occup. Environ. Hyg.* 1: 660–674.
- Kuhlbusch, T.A.J. and Fissan, H. (2006). Particle Characteristics in the Reactor and Pelletizing Areas of Carbon Black Production. *J. Occup. Environ. Hyg.* 3: 558–567.
- Kuhlbusch, T.A.J., Krug, H. and Nau, K. (2009). NanoCare: Health Related Aspects of Nanomaterials, Final Scientific Report, Frankfurt: DECHEMA e. V., ISBN 978-3-89746-108-6.
- Kuhlbusch, T.A.J., Asbach, C., Fissan, H., Göhler, D. and Stintz, M. (2011). Nanoparticle Exposure at Nanotechnology Workplaces: A Review. *Part. Fibre Toxicol.* 8: 22.
- Lee, J.H., Kwon, M., Ji, J.H., Kang, C.S., Ahn, K.H., Han, J.H. and Yu, I.J. (2011). Exposure Assessment of Workplaces Manufacturing Nanosized TiO₂ and Silver. *Inhalation Toxicol.* 23: 226–236.
- Liao, C.M., Chiang, Y.H. and Chio, C.P. (2009). Assessing the Airborne Titanium Dioxide Nanoparticle-Related Exposure Hazard at Workplace. *J. Hazard. Mater.* 162: 57–65.
- Ling, M.P., Chio, C.P., Chou, W.C., Chen, W.Y., Hsieh, N.H., Lin, Y.J. and Liao, C.M. (2011). Assessing the Potential Exposure Risk and Control for Airborne Titanium Dioxide and Carbon Black Nanoparticles in the Workplace. *Environ. Sci. Pollut. Res.* 18: 877–889.
- Maynard, A.D., Baron, P.A., Foley, M., Shvedova, A.A., Kisin, E.R. and Castranova, V. (2004). Exposure to Carbon Nanotube Material: Aerosol Release during the Handling of Unrefined Single-Walled Carbon Nanotube Material. *J. Toxicol. Environ. Health* 67: 87–107.
- Maynard, A.D., Aitken, R.J., Butz, T., Colvin, V., Donaldson, K., Oberdörster, G., Philbert, M.A., Ryan, J., Seaton, A., Stone, V., Tinkle, S.S., Tran, L., Walker, N.J. and Warheit, D.B. (2006). Safe Handling of Nanotechnology. *Nature* 444: 267–269.
- nanoGEM (2013). Tiered Approach for the Assessment of Exposure to Airborne Nanoobjects in Workplaces, SOP, http://www.nanogem.de/cms/nanogem/front_content.php?idcat=159&lang=10.
- Methner, M., Hodson, L. and Geraci, C. (2009). Nanoparticle Emission Assessment Technique (NEAT) for the Identification and Measurement of Potential Inhalation Exposure to Engineered Nanomaterials - Part A. *J. Occup. Environ. Hyg.* 7: 127–132.
- Patashnick, H. and Rupprecht, E.G. (1991). Continuous PM₁₀ Measurements Using the Tapered Element Oscillating Microbalance. *J. Air Waste Manage. Assoc.* 41: 1079–1083.
- Plitzko, S., Dziurawitz, N., Thim, C., Asbach, C., Kaminski, H., Voetz, M., Goetz, U. and Dahmann, D. (2013). Messung der Inhalativen Exposition gegenüber Nanomaterialien - Möglichkeiten und Grenzen. *Gefahrstoffe - Reinhalt. Luft* 73: 295–301.
- Ramachandran, G., Ostraat, M., Evans, D.E., Methner, M.M., O'Shaughnessy, P., D'Arcy J., Geraci C.L., Stevenson, E., Maynard, A. and Rickabaugh, K. (2011). A Strategy for Assessing Workplace Exposures to Nanomaterials. *J. Occup. Environ. Hyg.* 8: 673–685.
- Roco, M.C. (2005). Environmentally Responsible Development of Nanotechnology. *Environ. Sci. Technol.* 39: 106A–112A.
- Stahlmecke, B., Wagener, S., Asbach, C., Kaminski, H., Fissan, H. and Kuhlbusch, T.A.J. (2009). Investigation of Airborne Nanopowder Agglomerate Stability in an Orifice under Various Differential Pressure Conditions. *J. Nanopart. Res.* 11: 1625–1635.
- Tammet, H., Mirme, A. and Tamm, E. (1998). Electrical Aerosol Spectrometer of Tartu University. *J. Aerosol*

- Sci.* 29S1: S427–S428.
- Tsai, S., Ashter, A., Ada, E., Mead, J.L., Barry, C.F. and Ellenbecker, M.J. (2008). Airborne Nanoparticle Release Associated with the Compounding of Nanocomposites Using Nanoalumina as Fillers. *Aerosol Air Qual. Res.* 8: 160–177.
- VDI-Richtlinie 2463 Blatt 11 (1996). Messen der Massenkonzentration (Immission), Filterverfahren - Filterwechsler Digital DHA-80, VDI-Handbuch Reinhaltung der Luft, Band 4.
- VDI-Richtlinie 2463 Blatt 7 (1982). Messen der Massenkonzentration (Immission), Filterverfahren - Kleinfiltergerät GS 050, VDI-Handbuch Reinhaltung der Luft, Band 4.
- Wake, D, Mark, D. and Northage, C. (2002). Ultrafine Aerosols in the Workplace. *Ann. Occup. Hyg.* 46: 235–238.
- Witschger, O., Le-Bihan, O., Reynier, M., Durand, C. and Charpentier, D. (2012). Préconisation en Matière de Caractérisation et d'Exposition des Potentiels d'Emission et d'Exposition Professionnelle Aux Aerosols Lors d'Operations Nanomateriaux. *INRS, Hygiène et sécurité au travail* 226: 41–55.
- Yang, Y., Mao, P., Xu, C.L., Chen, S.W., Zhang, J.H. and Wang, Z.P. (2011). Distribution Characteristics of Nano-TiO₂ Aerosol in the Workplace. *Aerosol Air Qual. Res.* 11: 466–472
- Yeganeh, B., Kull, C.M., Hull, M.S. and Marr, L.C. (2008). Characterization of Airborne Particles during Production of Carbonaceous Nanomaterials. *Environ. Sci. Technol.* 42: 4600–4606.

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