Temporal Evolution of Nanoparticle Aerosols in Workplace Exposure

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The evolution in time of a nanoparticle (NP) aerosol released into a simulated workplace environment was investigated for different starting scenarios including (i) NP release into a particle-free atmosphere and (ii) release in presence of a pre-existing background aerosol. In each case, particle number distributions and total number concentrations in a 2 m³ aerosol chamber were monitored over several hours. On the time scale and under the conditions relevant for workplace exposure, collisions between NP within their own size class and, if present, with the background aerosol were identified as the most important mechanism driving the change in particle size and number concentration. A model has been formulated on the basis of well-known aerosol dynamic principles to predict the evolution of NP number concentration for a defined source and a defined environment (a given background aerosol concentration). A dimensionless number is introduced to scale the rate of NP concentration change relative to background aerosol concentration and particle size, which scales inversely with the concentration of free NP in the atmosphere. Beyond the physical change, the emergence of binary agglomerates constitutes a change in chemical composition of the aerosol. It is shown that the NPs are still chemically present in the aerosol after becoming attached to background particles, thus remaining airborne while being invisible in the size distribution.

Keywords: aerosol; coagulation; nanoparticle release; workplace environment

INTRODUCTION

Nanoparticles (NPs) are commonly used in many commercial products to improve their quality, change their handling or obtain new properties. The potential health hazards for workers involved in the production, handling or use in manufacturing of engineered nanoparticles (ENPs) are thus also subject to active research, although in many respects without definitive conclusions. While there is a strong focus on the physico-chemical properties of ENP made of a variety of materials, the effects of size and structure of such ENPs is of equal importance.

The metric most relevant for the assessment of exposure risk to ENP is still a much debated question (Wittmaack, 2007). Particle size, however, is directly related to the mode of deposition in the airways as well as the subsequent fate of particles in the biological environment. Particle number concentration and number size distribution further allow the estimation of the surface area and—provided the particle density is known—also the mass distribution (Lall and Friedlander, 2006; Lall et al., 2006). Therefore, these metrics can be used as relevant aerosol characteristics to estimate deposition and biological behavior.

Airborne NPs in an occupational setting undergo continuous changes in concentration, size distribution and particle structure from the point of release to the receptor (i.e. the entrance to the airways or surface of the skin). These parameters can be influenced by a variety of potential mechanisms, depending on the available time and in some cases on the available starting concentration at the source. A comparison of the required time scales for those conditions relevant in typical occupational settings leads to the identification of collisional growth of particles (coagulation) as a very important—if not the most important—mechanism of change.

Loss mechanisms to the system walls, such as particle deposition due to Brownian or turbulent diffusion or due to thermal gradients (thermophoresis), are rather slow processes. For example, Bémer et al. (2002) showed that for particles <5 µm, the
time scale for a significant change in aerosol concentration due to turbulent diffusion is in the range of one hour; for Brownian diffusion it is even longer. On the other hand, collisional growth, which is a function of number concentration, can produce a significant change in number concentration within minutes or seconds at common workplace conditions.

As opposed to powders, the size of an airborne ‘particle’ undergoing collisional growth is thus not a fixed parameter, but could—depending on age—range from an isolated NP to a large agglomerate. The fundamentals of such changes are basically a well-defined problem of aerosol dynamics (e.g. Hinds, 1999; Friedlander, 2000). The evolution of particle size distributions in indoor environments was subject of several studies (e.g. Jamriska and Morawska, 2002; Nazaroff, 2004; Park and Lee, 2002). However, the change of particle size between localized sources and a (human) receptor under conditions relevant for NP release in the workplace environment has to our knowledge not been studied before.

Experiments were conducted in a simulated atmosphere mimicking the real conditions in terms of time scales, mixing state and particle parameters. Particle characteristics monitored were the number size distribution and total particle number concentration. The evolution of these was monitored over periods of several hours providing a basis for the deduction of the governing kinetics. A chemical analysis of aerosol samples was conducted as well, to differentiate between ENP and background particles. It revealed the fate of ENP in the simulated workplace atmosphere.

**METHODS**

*Generation of NP aerosol*

The ‘primary release’ aerosol was emulated by platinum NPs generated on line by an evaporation/condensation method. This choice was driven mainly by practical considerations, such as narrow size distribution in the range of 10 nm, stability of the source during many hours, as well as ease in distinguishing the Pt particles chemically from almost any background aerosol. It should be noted, however, that the chemical nature of the particles has no importance for the present investigation because aerosol dynamic properties are governed entirely by size and concentration. Hence, the experimental results obtained for Pt are relevant for all materials producing roughly isometric particles. (Fibrous particles are expressly outside the scope of this study.)

The aerosol was generated with a self-built hot wire generator according to a design by Schmidt-Ott et al. (1980). The generator produces very narrow, approximately log-normal size distributions with median diameters of 7–8 nm and \( \sigma_g \approx 1.3 \) (Fig. 1). Particle concentrations could be varied over two orders of magnitude at almost constant particle diameters by adjusting the heating current and the carrier gas flow rate through the generator (Table 1). Since the

![Fig. 1. Pt aerosol size distributions measured by DMA at the exit of the hot wire generator with log-normal fit functions shown.](image-url)

Table 1. Pt aerosol size distribution parameters for different aerosol concentration settings. Variations of number concentration and particle size remained within 10% over the duration of an experiment. Total number concentrations are calculated on the basis of the fit functions in Fig. 1

<table>
<thead>
<tr>
<th>Aerosol 1</th>
<th>Aerosol 2</th>
<th>Aerosol 3</th>
<th>Aerosol 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Count median diameter/nm</td>
<td>7.9</td>
<td>7.3</td>
<td>8</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.33</td>
<td>1.35</td>
<td>1.33</td>
</tr>
<tr>
<td>Total concentration/cm</td>
<td>5.1E + 06</td>
<td>4.5E + 06</td>
<td>2.1E + 06</td>
</tr>
</tbody>
</table>
analytical technique used to measure the aerosol size distributions [a differential mobility analyzer (DMA)] had a lower detection limit of 5.5 nm, the total concentration was corrected on the basis of the log-normal fit functions shown in Fig. 1.

**Generation of background aerosols**

The selection of materials and generation methods for a suitable background aerosol was guided by the assumption that binary coagulation kinetics are independent of substance and solely depend on the geometrical and diffusional properties of the particles. The concentrations of the background aerosols were chosen to be representative of indoor aerosols with concentrations of typically $10^3$ to $10^4$ cm$^{-3}$ and particle sizes in the range of 0.1–1 μm. In atmospheric and indoor aerosols, this size range is called the accumulation mode, where particles are relatively abundant by number compared to the coarse mode which dominates by mass. Coarse mode particles are efficient scavengers due to their size but negligible overall in terms of aerosol dynamics due to their low number concentration.

The two types of aerosol selected were oil droplets in the submicron range and micron-sized monodisperse silica particles. Both materials are spherical in particle shape and thus avoid the complications of data analysis resulting from complex particle structures. The oil droplets were generated using a Collison atomizer, which generated sprays of di(2-ethylhexyl) sebacate (DEHS), an oily substance with low vapor pressure at the conditions used. Median diameters between 200 and 250 nm in the chamber were achieved (Fig. 2). The total number concentration was varied from a low value of $10^4$ cm$^{-3}$ up to approximately an order of magnitude higher. Monodisperse silica aerosol was generated by pulse dispersion of 1 μm Merck Monospheres® using compressed air (Fig. 3). The particle number concentration of the silica aerosol was $7 \times 10^3$ cm$^{-3}$, lower than in the case of DEHS.

**Exposure chamber**

A metallic aerosol chamber with a volume of 2 m$^3$ (dimensions 1 × 1 × 2 m) was fitted with a variable speed fan (located at the bottom of the chamber) and several inlet or outlet ports distributed over the chamber walls as shown in Fig. 3. The inlet ports were used to inject the Pt nano-aerosol (lower left port) and, optionally, a defined background aerosol (upper right port). Small sample flows were extracted from outlet ports located in the chamber walls and ceiling for the purpose of monitoring the aerosol size distribution, concentration and chemical composition as functions of time.

The size distributions of the fine particles were measured using a scanning mobility particle sizer system (SMPS) consisting of a condensation particle counter (CPC, Grimm Series 5.400) and an intermediate length DMA (Grimm Vienna/Reischl type). Coarser particles were characterized by an optical particle counter Grimm portable aerosol spectrometer model 1.109 as required. A second CPC of the same type was used to monitor the total particle concentration in the chamber.

The flow pattern in the chamber was characterized with and without the fan by measuring the flow velocity at different sampling ports (Fig. 3). The corresponding Reynolds numbers with the fan turned on were roughly $10^4$ at all points sampled, which suggests turbulence and thus rapid mixing of the aerosols. The quality of mixing was also tested by consecutively measuring the temporal evolution of a NP aerosol from three different sampling ports, L3, R3 and OL. The three experiments agreed to better than 7% in particle number, which is within experimental uncertainty and shows good mixing of the chamber.

The chamber was also equipped with an external pump to flush it with filtered air in order to obtain a particle-free environment. The pump was shut off during experiments, while the filter-equipped air inlet remained open to prevent pressure build up in the chamber.

![Fig. 2. Size distributions of the DEHS oil droplets in the aerosol chamber measured by SMPS (left); SEM image of silica microspheres (right).](https://academic.oup.com/annweh/article-abstract/52/8/707/247912)
RESULTS

Evolution with time of the aerosol in the chamber

Two different ENP release scenarios were simulated. Scenario A represents the release of ENP from a moderately strong aerosol source (ca. $5 \times 10^6$ cm$^{-3}$) into a very clean environment, while Scenario B represents the release into a typical workplace atmosphere with varying background concentrations ($10^3$–$10^5$). Scenario A is intended to observe changes in the size distribution of the ENP aerosol by self-coagulation, while Scenario B shows the interaction of the ENP with background particles.

Scenario A—ENP release into a clean environment. In order to obtain a very low background aerosol concentration, the chamber was initially flushed with filtered air for several hours until the concentration measured with the CPC was <1 particle cm$^{-3}$.

Pt aerosol was then injected continuously for 3 h at a constant source flow rate $V_{S}$ of 5 l min$^{-1}$ into the well-stirred chamber. The source number concentration $n_{i,S}$ was $4 \times 10^6$ cm$^{-3}$; the particle size $d_{i,S}$ at the source was 7 nm. The size distribution was monitored over the entire duration of the experiment by SMPS (Fig. 4, left) from a sampling port located diagonally opposite the inlet port. Sixteen minutes after starting the ENP injection, when the first size distribution was measured, a single peak ~15 nm has appeared in the initially particle-free air. The following measurements at time intervals of 16 min each show the rapid emergence of a secondary peak which travels to larger particle sizes while continually decreasing in magnitude. These are ‘aged’ NPs consisting of large, loose agglomerates. During this time, the initial peak remains at 15 nm but decreases somewhat toward a stable concentration, fed continuously by fresh NP.

The evolution of the number concentration of each of these two modes is displayed in Fig. 4 (right), along with the mean particle size of the secondary mode. While the secondary mode continues to grow in size, the size of the primary NP mode is kept in place by the constant supply of fresh monomer from the NP source. The rapid increase in primary mode concentration (as well as total particle number concentration) during the first 30 min is due to the time required to fill the chamber with a sufficiently high aerosol concentration to initiate a substantial coagulation rate. The coagulation rate is proportional to $n^2$ and thus rises rapidly as the chamber fills, leading to the emergence of the observed secondary mode by homogeneous coagulation and to a slight decrease in chamber concentration.

The other contributor to the decline in primary mode concentration is the increased scavenging probability of the constantly growing particles in the secondary mode. Thus, the coagulation rate increases to a point where it outpaces the source rate, leading to a decrease in number concentration with time. Eventually, a steady state is reached when the coagulation rate equals the source rate, leading to a constant particle concentration.
Scenario B—ENP interactions with a background aerosol. This scenario was created by introducing a background aerosol (either DEHS droplets or SiO$_2$ particles) into the well-flushed chamber. The background particles were injected and allowed to mix and stabilize for several minutes. Then, the NP source was started and run continuously for several hours at a pre-selected concentration of $7 \times 10^4-5 \times 10^6$ cm$^{-3}$. Over this time period, size distributions of the source and the aerosol in the chamber were measured in 4-min intervals.

In the presence of background particles, the nano-aerosol evolves very rapidly into a quasi-steady state, shown in Fig. 5. At the high end of the selected background concentrations, almost the entire primary NP peak $\sim$15 nm vanishes by attachment onto the larger background particles. (Note that the NP aerosol is fed continually.) Similar to what was shown before in Fig. 5, a significant concentration of NP is still present. Then, the background concentration was raised rapidly by injecting a pulse of DEHS aerosol in the chamber while monitoring the change in the NP concentration. As seen in Fig. 6, the rapid change in the DEHS concentration is followed instantly, meaning within the 4-min interval, by a drop in NP concentration. This indicates that the coagulation processes between the NP and the background are very fast, an upper limit given by the 4-min interval.

Figure 6 also illustrates the sensitivity of the NP concentration to a subsequent change in the background aerosol concentration. The gradual decrease in the DEHS concentration after the pulse caused mainly by dilution is paralleled by an equally gradual increase in the NP concentration. Since NPs are continuously supplied, a decrease in the DEHS concentration leads to a reduction in the heterogeneous coagulation rate and thus to an increase in the NP concentration.
Chemical and morphological analysis of sampled particles

After sufficient interaction time between NP and background aerosols, particles were sampled from the chamber by a size-selective impaction technique. The device used for this purpose was a single-stage low-pressure impactor (described in more detail e.g. by Fernandez-de la Mora et al. 1990) with variable cut point. At a given setting, the impactor samples all particles with aerodynamic diameters above a given threshold value onto a substrate such as a transmission electron microscope (TEM) grid for further analysis. The aerodynamic diameter of a sphere of diameter $d$ and density $\rho$ is given by the equation $d_{ae} = \frac{d}{\sqrt{1 + \frac{16\rho C(d)}{\rho_0 C}}} = \frac{d}{\sqrt{1 + 16\rho C(d)/\rho_0 C}}$, where $\rho_0$ is the unit density. Hence, the aerodynamic diameter of a sphere is larger than its physical diameter by roughly the factor $(\rho/\rho_0)^{1/2}$, which is ~4.6 for Pt and 1.6 for silica.

Analyses were performed for mixed aerosols of NP with both silica monospheres and DEHS droplets. The silica was interesting because it represents the low end of background concentrations (where the attached fraction of Pt NPs should be small, according to Fig. 5), while DEHS represents the high end where essentially all Pt should be attached. The purpose of this physical analysis was thus to determine whether it would indeed be possible to find the Pt in the expected size range.

Silica monospheres were collected at various pressures. Pressure variation allows the control over the collected particle size (cutoff diameter) by changing the conditions of flow and deposition. By decreasing the cutoff size of the impactor in the range of agglomerated Pt NPs, the sampling of free NP was also possible, while for higher pressures (larger cutoff diameter) only the larger silica spheres were in the right size range for deposition. Thus, the separation of ‘free’ Pt particles and the background aerosol, potentially with scavenged NP, was possible. Samples from the platinum–silica system were analyzed by TEM for particle

Fig. 5. NP aerosol size distributions as a function of the DEHS background aerosol concentration in the chamber. The background concentration is quasi-stable during the entire experiment.

Fig. 6. Reaction of the concentration of the NP aerosol to a rapid change in the background concentration: no delay visible on the experimental timescale.
morphology as well as for the mass ratio of the two materials. (The mass ratio was estimated by image analysis of the respective particle volumes. While this procedure is not extremely accurate, it does give representative information about the presence of Pt.)

The data show that in the size range where most of the silica particles were deposited (cutoff diameter > 1 μm), only a small amount of Pt was found, while the amount of Pt increased with decreasing cutoff diameter, reaching the size range of larger Pt agglomerates (Fig. 7).

For the DEHS droplets, samples of collected material were analyzed by inductively coupled plasma optical emission spectroscopy. The aerosol size distribution did not show any particles in the NP regime and the chemical analysis, however, detected Pt in the size range corresponding to the background aerosol. Assuming binary coagulation, the detected mass corresponded to 60% of the expected value. These two chemical speciation experiments support the conclusions drawn from the size distribution measurements. In the case of the very low background concentration represented by silica, the homogeneous coagulation of the NP among each other is dominant and binary coagulation is relatively rare. At high concentrations, however, as in the case of high DEHS concentrations, the NPs coagulate with the background aerosol and remain airborne attached to the coarser particles, even though they may be invisible in the size distribution.

An aerosol dynamics model to predict the NP concentration for a constant source and a pre-existing background aerosol

To support the preceding qualitative discussion of the evolution of the NP size distributions with a more solid theoretical analysis, the binary system consisting of a constant NP source plus an aerosol background was modeled based on the principles of aerosol dynamics. While there have been elaborate approaches to aerosol dynamics related to radioactive aerosols and the fate of particles in the indoor environment (e.g. Nazaroff and Cass, 1989), these models are very complex and can only be solved numerically. For our purpose, a simple analytical model was more useful to test the hypothesized modifiers in their influence on NP number concentration in the chamber.

The balance equation (1) was set up for the change in NP number concentration \( n_i \) as a function of the source flow rate \( \dot{V}_S \), the ventilation flow rate \( \dot{V}_V \) (i.e. the flow of air out of the chamber in response to the source flow minus any sampling flow to measurement instruments) and coagulation rate, both by collisions within the species \( i \) as well as by collisions with background particles \( j \) of concentration \( n_j \):

\[
\frac{dn_i}{dt} = \frac{\dot{V}_S}{V} n_{i,S} - n_i \frac{\dot{V}_V}{V} - K_{ii} n_i^2 - n_i n_j K_{ij}.
\]

(1)

\( V \) is the chamber volume, \( n_{i,S} \) is the NP number concentration at the source; \( K_{ii} \) and \( K_{ij} \) are the respective coagulation rate constants for homogeneous and heterogeneous collisions

\[
K_{ii} = \frac{4kT}{3\eta}, \quad K_{ij} = \frac{2kTd_j}{3\eta d_i^2},
\]

(2)

with the Boltzmann factor \( kT \) and the gas viscosity \( \eta \) (e.g. Hinds, 1999). The heterogeneous coagulation coefficient \( K_{ij} \) depends on the ratio of the particle sizes \( d \) of the NPs and the background, which therefore has a strong influence on the coagulation rate.

Assuming that the chamber is completely mixed at all times, the solution to equation (1) is given by

\[
n_i(t) = \frac{(ab - 2bK_{ii}n_{i,0}) \exp\{ct\} - (ab - 2aK_{ii}n_{i,0})}{2aK_{ii} - 2bK_{ii}n_{i,0} \exp\{ct\}},
\]

(3)

with

Fig. 7. Ratio of Pt: SiO_2 mass found in aerosol particles of respective cutoff diameter.
\[ a = 2K_{0i}n_{i,0} + n_jK_{ij} + \frac{\dot{V}_S}{V} - c \]
\[ b = a + 2c \]
\[ c = \sqrt{4K_{0i}\frac{\dot{V}_S}{V}n_{i,0} - \left[ n_jK_{ij} + \frac{\dot{V}_S}{V} \right]} \]

\( n_{i,0} \) is again the initial NP concentration in the chamber and \( n_{i,S} \) the concentration of the source. All the model parameters are accessible to measurement, so no fit is necessary.

The model can be used to predict the steady-state concentration of unattached NP, given the knowledge about the NP source and the characteristics of the background aerosol. In steady state, equation (1) turns into an easy to solve algebraic equation in \( n_i \)

\[ \frac{dn_i}{dt} = \frac{\dot{V}_S}{V}n_{i,S} - n_i \left[ n_jK_{ij} + \frac{\dot{V}_S}{V} \right] - K_{0i}n_i^2 = 0, \quad (4) \]

which was solved for different combinations of source concentration \( n_{i,S} \), and background aerosol concentration \( n_j \). Such data were available to us from various experiments at a constant source flow rate \( \dot{V}_S = 2 \text{ l min}^{-1} \); the chamber volume \( V \) was always 2 m³. The particle size ratio was 30 for the DEHS aerosol and 130 for the silica monospheres. In Fig. 8, the steady-state concentrations predicted from equation (4) are plotted against the measured ones. The correlation is generally reasonable, given the simplicity of the model. The slope of the linear regression is 1.14, indicating a slight overprediction by the model, presumably because losses to the chamber walls, fan blades etc. are neglected.

The change of \( n_i \) with time after a sudden increase of the background concentration was calculated from equation (3), using the parameters for the experiment shown in Fig. 6. The function rapidly approaches a steady-state value. After 200 s, the number concentration already reached a value within 5% of the steady-state value, close to the one found experimentally.

**A dimensionless number for the scaling of steady-state NP concentrations in an enclosure with NP sources of different strength**

While aerosol dynamic models are very powerful, it is often desirable to scale systems behaviors based on simple laws of similarity. A case in point for workplace environments is the steady-state concentration of unattached NP attained in an enclosure with a constant NP emission source. The concentration will depend on the size of the chamber \( V \), the source strength (\( n_{i,S} \) and \( \dot{V}_S \)), the initial concentration \( n_{i,0} \) of any background aerosol, as well as the collision frequency \( K_{ij} \) between the particles.

Dimensional analysis provides the following answers: for a total of six parameters (including the steady-state NP concentration \( n_i \) in the enclosure) and two independent equations (the parameters only contain length and time), we have four independent non-dimensional numbers.

We propose to scale the non-dimensionalized NP concentration \( \tilde{n}_i \) by a non-dimensional parameter

\[ Z = \frac{K_{0i} \dot{V}_S}{Vn_j - n_{i,S}} \]

based on the ratio of the loss rate by coagulation \( K_{ij}n_j - n_{i,S} \) and the source rate \( \dot{V}_S n_{i,S} \).

To test the usefulness of this approach, the non-dimensionalized concentrations of free NP in the aerosol chamber for four separate sets of data from independent experiments were plotted versus \( Z \) in Fig. 9. Clearly, the parameter groups the experimental data in a meaningful way, by assigning relatively low chamber concentrations to relatively high

![Fig. 8. Correlation between steady-state concentrations calculated from equation (4) and experimental values.](https://academic.oup.com/annweh/article-abstract/52/8/707/247912/download?download_selected=true)
background concentrations (i.e. high loss rates) and low source strengths, i.e. large values of $Z$.

The data points in Fig. 9 can be fitted reasonably well to a linear function

$$\frac{n_i}{n_{i,S}} = \frac{\text{const}}{Z}.$$  

Additional measurements may provide more accurate correlations in the future. Such a fit function can be used to predict the concentration of free NP in a workplace environment, provided one knows the mean particle sizes of NP and background aerosol (for the calculation of $K_{ij}$), the volume flow and concentration of the source and the concentration of the background aerosol.

CONCLUSIONS

The theoretical and experimental analysis of the evolution of NP aerosols in a simulated workplace atmosphere from the point of release to the receptor yielded results with far-reaching implications for the generation of representative test aerosols for the use in toxicological studies, the testing of protective equipment and the suitable metrics.

NPs do not reach the receptor in the form of the primarily released aerosol. They change their size and number concentration by coagulation, homogeneously by coagulation within the NP size class or heterogeneously by interaction with the background aerosol. The extent of these processes relative to each other depends on the concentration and particle size of the background aerosol and the number concentration of the NP aerosol. In addition to these changes of the aerosol characteristics, binary particles consisting of background particles decorated with NP evolve, constituting a change in chemical composition of the NPs.

Thus, if the toxicological effects of NP in the workplace are to be studied, protective measures are to be designed or a relevant metric for workplace exposure with NP is sought, the physical changes and the changes in chemical composition have to be taken into account.

Predictions of the dispersion state of NP and their number concentration after release in a workplace environment is possible using the mathematical model or the dimensionless number $Z$ introduced in this work. The limited accuracy of both methods should at least allow an estimation of the governing scenario for a certain workplace environment.

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