Nano-sized emission from commercially available paints used for indoor surfaces during drying

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ABSTRACT

Consumers worry about the presence of nano-particles in paints and the risk of exposure. As a result, the paint industry now omits marketing paints as containing nanoparticles. The industry claims that no nanoparticles are released into the indoor environment; this, however, has yet to be documented. In this study, the emission of nano-sized emission from four indoor paints was investigated. The emission was studied for both base and full-pigmented versions of the paints, which consisted of three water-borne acrylic paints and one solvent-borne alkyd paint. All experiments were performed twice in a 6.783 m^3 stainless-steel test chamber under standardized conditions (22.98 °C, 50.08% RH, air exchange rate 0.48 h^{-1}). Emissions during the paint-drying period were measured using a TSI Fast Mobility Particle Sizer (FMPS) measuring the number concentration of nano-particles and the size distribution in the range 5.6–560 nm.

The results from the solvent-borne paint showed the highest concentration, with a mean concentration of $3.2 \cdot 10^5$ particles/cm^3 and a maximum of $1.4 \cdot 10^6$ particles/cm^3. This paint also had the smallest particle size distribution, with 9.31 nm particles as the most dominant particle size. The results from this study showed that the exposure to nanoparticles for the residents evaluated over a 7 or 28 day period was low and that interior paints are probably not very important when it comes to identifying products that release nano-particles into indoor environments.

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1. Introduction

Most people in the industrialized world spend more than 90% of their time indoors (Klepeis et al., 2001). Minimizing exposure to potentially harmful substances in indoor and outdoor air is thus an important factor in establishing a healthy environment (Schneider et al., 2003; Agudelo-Castañeda et al., 2016, 2017). Nanoparticles, also referred to as ultrafine particles, are the smallest particle fraction measured, with diameters below 100 nm. It has been shown that we are exposed to ultrafine particles in the indoor air during activities such as cooking, toasting, candle burning and when using hairspray, as well as through infiltration of traffic pollution from outside (Schneider et al., 2004; Wallace, 2006; Sjaastad et al., 2008, 2010; Jørgensen et al., 2012; Bekô et al., 2013; Bluyssen et al., 2013). The level of exposure may vary between residences, and probably depends most on pollution in the outdoor air, the penetration across the building envelope and the behaviour of residents(Riley et al., 2002; He et al., 2004; Zhu et al., 2005; Bekô et al., 2013; Spilak et al., 2014; Gaspar et al., 2017). Most of the particles in the ultrafine range are produced naturally through hot processes and we have been exposed to them for a very long time (Kosk-Bienko, 2009). In contrast, engineered nanoparticles give rise to concerns regarding the human health consequences of exposure, as they have been produced to have specific characteristics and some have been shown to have negative health effects in animals (Poland et al., 2008; Larsen et al., 2009; Saber et al., 2012; Zhang et al., 2014; Schneider et al., 2016; Agudelo-Castañeda et al., 2017).

The focus on healthy indoor environments, together with a focus on environmental concerns, has forced the paint industry to develop paints with lower, or no volatile organic compounds (VOC) content. This development is also a result of legal regulations, such as the EU paint directive 2004/42/CE (European Union, 2004). Consumers demand high quality paint despite the low VOC content, which further has caused the development of new additives and adhesives designed for low VOC paints (Hovland, 2011). Nanotechnology is used during product development in the paint industry, for instance in the development of new binders (Abd El-Ghaffar et al., 2016) and antifungal additives for indoor water-borne paints (Bellotti et al., 2015). Consumers regard nanoparticles as innovative, but they are also worried about the consequences of using paints containing nanoparticles. Paint manufacturers are therefore concerned about the consequences of advertising the paint as a product containing nanoparticles, even though they believe the nanoparticles in the paint are chemically bonded to the dry paint surface, (Hovland, 2011). Nanoparticles have been used in paint products for years in titanium dioxide (TiO$_2$) and Carbon Black, which are powders used in large quantities as white and black pigments, respectively (Kaiser et al., 2013). However, novel, engineered nanomaterials are continuously introduced into the market, and we may expect nanoparticles to be included in paint

products (Kaegi et al., 2008, 2010; Larsen et al., 2009; Bellotti et al., 2015; Hincapié et al., 2015).

It is well known that nanoparticles are used in the production of indoor paints (Koponen et al., 2011) and we know that both silver nanoparticles (Kaegi et al., 2010), TiO_2 nanoparticles and SiO_2 nanoparticles are released from outdoor paint surfaces. We also know that nanoparticles used for paint production (such as TiO_2 nanoparticles) promote allergy sensitization and lung inflammation in mice (Larsen et al., 2009) and *in vitro* toxicity in lung cells (Smulders et al., 2015). 76Carbon Black is the other pigment often used as tinting colour for paints. Carbon Black has a primary particle size in the range of 20–60 nm, (Long et al., 2013). However, as a commercial product on the marked, Carbon Black is sold as pellets, which are compressed agglomerates. The size of the pellets generally falls between 100 nm and several micrometres. (International Carbon Black Association (u.a.). Studies among Carbon Black manufacturing workers suggests that nanoscale Carbon Black particles could be responsible for the reduction of lung function and pro-inflammatory cytokines secretion (Zhang et al., 2014). Immunotoxicity of Carbon Black nanoparticles has been studied in blue mussel hemocytes, where exposure induced inflammatory processes, (Canesi et al., 2008). This effect is also found in mammalian cells, where Carbon Black nanoparticles induce DNA damage in lung epithelial cells(Hiraku et al., 2017). Both Carbon Black and Titanium Dioxide dust are considered *possibly carcinogenic to humans* and classified as a Group 2B carcinogen(IARC, 2010). VOC emissions from paints are well documented (Xiong et al., 2013). However, the emissions of nanoparticles from paint to indoor air have yet to be investigated. As a precautionary measure, it is highly relevant to study the emissions of nanoparticles to indoor air in order to establish whether there is a risk of exposure to nanoparticles from interior paints.

The purpose of this work was to measure the number concentration and particle size distribution of the emissions from interior wall paints to room air during the first week post-application. Experiments with four different paints, with and without a tinting colour, were performed in a stainless steel test chamber. Both nanoparticles (<100 nm) and the particle ranging from 100 nm to 500 nm were studied as part of the size distribution analysis.

2. Materials and methods

2.1. Test facility

The experiments were carried out in a 6.783 m^3 test chamber (Vötch type VCE 8000/S, Vötch Industrietechnik GmbH, Germany). The chamber is a panel construction with an inner lining made of electro-polished stainless steel in a welded design. One side of the test chamber consists of a door hinged onto the left side with retightening hinges. The dimensions of the inner chamber are width: 1.7 *m*, depth: 2.28 *m* and height: 1.75 *m*. On one side of the test chamber there are five sampling ports of stainless steel, of Swagelok type. Only one port was used for sampling in this case; Swagelok caps closed the other four ports.

The test chamber is provided with compressed air from the laboratory, dried and cleaned by filtering. The airflow used for the test chamber was kept constant at 1 air exchange rate; the airflow could be regulated between 0.1 and 1.8 air exchange rates. The air exchange is continuously adjustable via the mass flow controller and is regulated by a SIMCON/32-NET system.

The chamber shows a leakage rate of <0.1% test space volume per minute at 1000 Pa overpressure (static test) and a leakage rate of <1% of carrier gas mass flow at 0.5 air exchange per hour for dynamic testing. Two internal fans mix the air in the chamber.

The temperature and relative humidity were kept constant during the test period. The relative humidity could be regulated between 30 and 70%, and the temperature between 18 °C and 30 °C. The control of the test chamber was managed with a microprocessor and the monitoring system (SIMCON/32-NET). Temperature, relative humidity and air exchange rate were measured during the experiments.

During long-term running, the stability of the chamber is very high. With set points for temperature at 23 °C, relative humidity 50% and air exchange rate 0.5 h^{-1}, the chamber produces 23.00 ± 0.08 °C, 50.01 ± 0.23% RH and 0.49 ± 0.003 h^{-1} air exchange rate, respectively.

Total desorption of pollution from the test chamber walls was ensured by increasing the inlet temperature to 250 °C and keeping the temperature there for 8 h before lowering to normal test conditions. This procedure was performed before the start of the experiments and it was repeated half-way through the experimental series.

2.2. Test materials

2.2.1. Eight paints were evaluated

A) Water-borne low-VOC-emission acrylic paint, tested and approved by The Norwegian Asthma and Allergy Association
B) Water-borne acrylic paint tested and approved as Eurofins Indoor Climate Gold
C) Water-borne acrylic paint (large sales volume paint)
D) Solvent-borne alkyd paint (maximum 300 g/l VOC)

Paints A-D were investigated both as a full-pigmented version (black/dark grey) and as a white base paint, without addition of tinting colour.

All tests were performed in duplicate, yielding a total of 16 experiments.

2.3. Test procedure

The test chamber was washed before each experiment. Extran® 2% was used as the detergent. The test chamber was rinsed with ultraclean water (Thermo Scientific Barnstead Smart2Pure 12 UV/UF, Ultrapure Water System, art. no. 50129845) and finally wiped with 99.9% ethanol. After cleaning, the chamber door was closed and the background level of the particle number concentration in the chamber was measured.

The aluminium plate was washed on both sides with dishwashing detergent, rinsed with ultraclean water and wiped with methylated spirit. Prior to the experiment, the amount of paint was calculated according to the recommendations from the supplier. The paint was stirred to a homogenous product, and the calculated amount of paint was applied to the aluminium plate using a paint roller. Three aluminium plates were used (two plates of 1.0 *m* × 2.0 *m* and one plate of 1.7 *m* × 1.0 *m*, both of thickness 0.002 *m*). The painting was performed as fast and smoothly as possible, and elapsed time was logged. The painted plate was placed into the test chamber immediately after application. Particle measurement was started immediately. The number concentration and particle size distribution were measured each second and the duration of the sampling period was one week.

The chamber background concentration was measured before and after each experiment.

The test procedure (including opening the door of the test chamber, placing of a clean aluminium plate without paint and

closing the door) was repeated 4 times in order to evaluate the method.

2.4. Test conditions

- Temperature: 23 °C
- Relative humidity: 50%
- Air exchange rate: 0.5 h^{-1}
- Loading: 1 m^2/m^3

Temperature, relative humidity and air exchange rate were measured during all experiments. The experiments were performed at a temperature of 22.98 ± 0.06 °C; the relative humidity was 50.08 ± 0.2% and the air exchange rate was 0.48 ± 0.03 h^{-1}.

2.5. Particle sampling

A TSI 3091 Fast Mobility Particle Sizer (FMPS, TSI, Shoreview, MN, USA) was used for measuring the particle size distribution and particle number concentration in the size range 5.6–560 nm. The FMPS was equipped with a 1 μm cyclone and the flowrate through the instrument was 10 l/min. Particle classification and counting were performed simultaneously through aerosol electrometers, with a time resolution of 1 s. The measurements were performed using a 0.59 *m* long flexible conductive silicone tube. Zeroing of the FMPS instrument was performed before the start of each experiment. After zeroing, the effect was controlled (zero-check) using a high efficiency particulate air filter (HEPA). No measurement was started before the zero check was satisfactory. Similar analytical procedures were previously reported ((Brand et al., 2013; Price et al., 2014; Kero and Jørgensen, 2016; Ragde et al., 2016).

2.6. Data analysis

The FMPS measurements were performed using the instrument software Fast Mobility Particle Sizer Software version 3.1.1. The particle number concentration within the size range 5.6–560 nm was measured in 32 channels. The number concentration of nanoparticles was calculated in Microsoft Excel as the sum of particles of the first 20 channels, resulting in a particle concentration in the range 5.6 nm–100.0 nm. The unit of the particle number concentration is the number of particles per cm^3 and the notation is #/cm^3

The measurements were performed with 1 s resolution; all results were calculated with concentrations calculated as 60 s mean values.

The total number of nanoparticles emitted from the paint from to the end of the emission period was obtained from the area under the curve (AUC). In this case, the AUC was calculated using the trapezoid method, as the sum of C·delta(t), where C is the total nanoparticle concentration.

The number of nanoparticles emitted to the chamber air per unit area (number of particles/m^2) over the 168 h of experiment is:

$$NP = \frac{AUC \cdot n \cdot V}{A}$$

where A is the area of the painted surface in m^2.

The particle size distribution of the entire measurement range (5.6–560 nm) is reported as a normalized concentration (dN/dlogDp):

$$\frac{dN}{d\ logD_p} = \frac{dN}{log\ D_{pu} - logD_{pl}}$$

where.

dN particle concentration
D_p midpoint particle diameter
D_{pu} upper channel diameter
D_{pl} lower channel diameter

The smallest channel had a midpoint of 6.04 nm; the largest channel a midpoint of 523.3 nm. On a logarithmic scale, the size widths of each channel were equal. The dominant mode of the particle size distributions was identified, and the count median diameter (CMD) and the corresponding geometric standard deviation (GSD) were calculated.

3. Results

Fig. 1 shows the emissions of nanoparticles from the four different paints. Each subfigure shows the pigmented version and base version of each type of paint. Note that the concentration scale differs between the subfigures. The number concentration of nanoparticles from the paints was measured for 7 days in all experiments. Data analysis shows that the emissions only occur for 48 h for the solvent-based paints and for 24 h for the water-borne paints. Fig. 1 illustrates the emissions during the first 24 h only. For each measurement, the concentration is shown with the corresponding background concentration deducted.

The experimental results, including the maximum concentration and the average concentration in the test chamber during the emission period and the total number of particles emitted per area of painted wall during the experiment (NP), are presented in Table 1. All values are calculated for the first 24 h of the experiment, corresponding to the illustrations in Fig. 1.

The results from the empty chamber study is included in Table 1. In order to calculate comparable NP values, an identical area of material is used for the empty chamber and for the paint experiments.

The main difference between the emission levels was found to be between the solvent-borne alkyd paint D and the water-borne acrylic paints A–C. For paint D, the chamber concentrations reach a maximum number concentration of 1.09·10^6 particles/cm^3 for the pig-
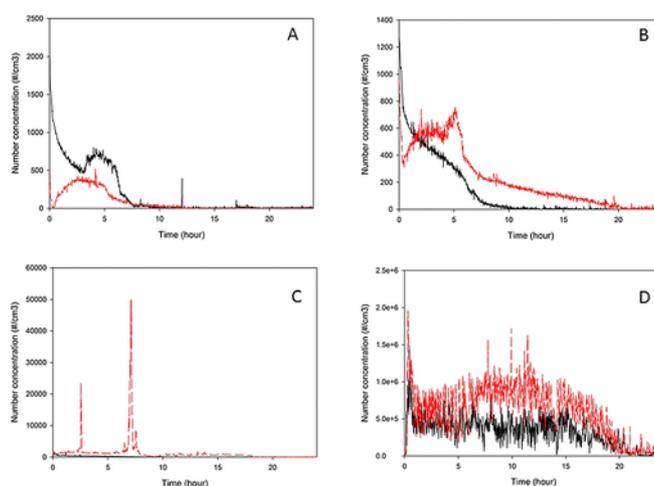
Fig. 1. Number concentration of emitted particles from waterborne acrylic paint marked "Low VOC emission" (A), waterborne acrylic paint marked "Eurofins Gold" (B), waterborne acrylic paint (C) and solventborne alkyd paint (D) during a test period of 24 h. Black full line represent the base version of the paint, red dotted version shows the pigmented version of the same paint. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Statistics for the experiments.

		AUC	Maximum	AM	NP
		#/cm³·min	#/cm³	#/cm³	#/m²
Paint A: acrylic paint	Base	278066	1994	194	2911
	Pigmented	118681	525	109	1242
Paint B: acrylic paint	Base	181278	1268	127	1898
	Pigmented	315095	1882	220	3298
Paint C: acrylic paint	Base	146728	1526	102	1536
	Pigmented	1745386	49949	1212	18270
Paint D alcyd paint	Base	468849674	1477746	325357	4907727
	Pigmented	463149988	1090099	321407	4848065
Empty chamber		67.896	921	122	711

AM: arithmetic mean, AUC: area under the curve, NP: number of particles emitted during the test period per area of material.

mented version of the paint, and $1.48 \cdot 10^6$ particles/cm³ for the base version, with a mean concentration of $3.25 \cdot 10^5$ particles/cm³ for the base version and $3.21 \cdot 10^5$ particles/cm³ for the pigmented version. These concentrations are substantially higher than the concentrations produced by the water-borne acrylic paints. The most important difference is the number of particles emitted during the test period per area of paint, where the solvent-based alkyd paint showed a factor of 10^3 higher NP values. Among the water-borne acrylic paints, paint C showed higher emissions compared to the others, especially for the pigmented version, which showed an arithmetic mean of $1.21 \cdot 10^3$ particles/cm³, caused mainly by a high emission period after 7 h of experiment and also an NP value that was 5–11 times higher than the other waterborne acryl paints. The remaining water-borne acrylic paints showed concentrations below 250 particles/cm³. No systematic difference between pigmented and base versions of the paints was found, but for paint C the difference is remarkable.

For paint D, a small emission occurred between 24 h and 48 h. The AUC values corresponding to 48 h of testing were $4.79 \cdot 10^8$ particles/cm³·min (base) and $5.00 \cdot 10^8$ particles/cm³·min (pigmented), and the NP values were $5.01 \cdot 10^6$ particles/m² (base) and $5.23 \cdot 10^6$ particles/m² (pigmented). The contributions between 24 and 48 h increases thereby the NP values after 24 h with 2% (base) and 8% (pigmented).

Fig. 2 illustrates the particle size distributions of the emission from the four paints for the first 24 h of each experiment; both the pigmented and the base versions of the paints are included.
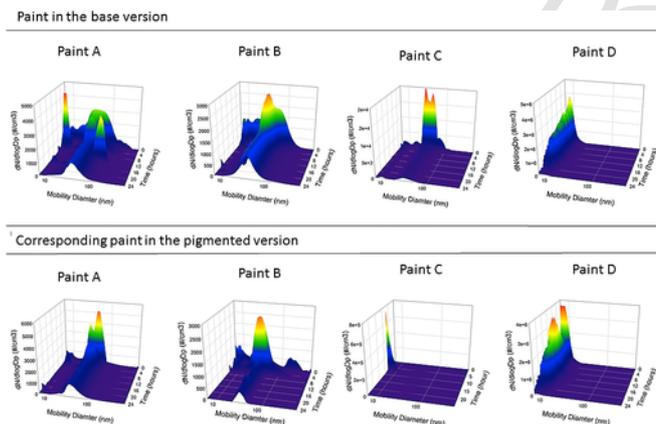
As seen from Fig. 2, paint D emits only small particles and shows an identical emission profile during the experiment in terms of the particle size of the emission. Paints A, B and their base versions showed identical emission profiles as well, but at a lower level and with a larger particle size. The pigmented version of paint C in contrast shows a short-term high concentration of very small particles between 6.5 and 7.5 h after start of the experiment.

Fig. 3 illustrates the mean particle size distribution for each paint emission experiment. Two different y-axes are used; paint D follows the left-hand axis, while the other experiments are following the right-hand axis.

The dominant modes, count median diameter and geometric standard deviations corresponding to the results in Fig. 3 are shown in Table 2.

As it is seen from Table 2, the particle size distribution shows that the dominant particle size emitted from paint D is 9.31 nm, while the dominant mode for the pigmented paint C is the lowest detected particle size at 6.04 nm. The remaining paints showed a maximum of particles in the size range 29.4–34 nm. No differences were found between base and pigmented versions of the same paint, except for paint C.
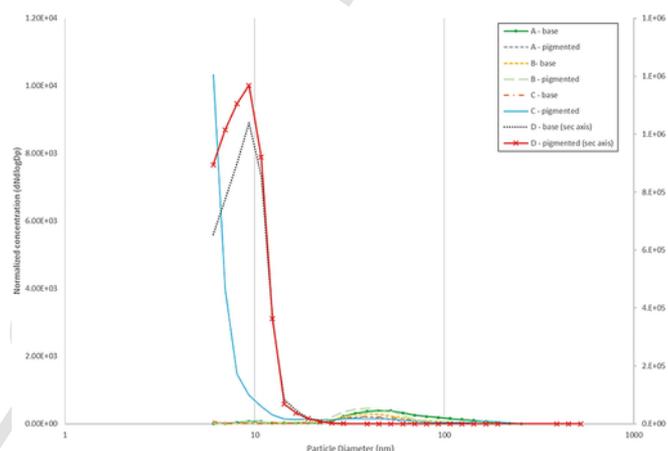
Fig. 3. Mean particle size distribution of particles emitted from four different paints, with and without pigment during 24 h of emission.

Table 2
Characterization of the size distribution of particles from the different paints.

		Dominating Mode[a] nm	CMD[b] nm	GSD[c]
Paint A: water-borne acrylic paint	Base	45.3	49.4	1.91
	Pigmented	39.2	31.0	1.89
Paint B: water-borne acrylic paint	Base	39.2	41.9	1.84
	Pigmented	39.2	38.2	1.80
Paint C: water-borne acrylic paint	Base	39.2	37.3	1.89
	Pigmented	6.04	6.8	1.32
Paint D: solvent-borne alkyd paint	Base	9.31	8.7	1.28
	Pigmented	9.31	8.5	1.27

[a] The dominant mobility diameter at peak particle concentration.

[b] geometric mean diameter.

[c] geometric standard deviation.

Fig. 2. Particle size distribution of the emission of particles emitted from four different paints with and without pigment.

4. Discussion

The amount of paint applied was within the range recommended by the supplier. Small differences between applied amounts in the two replicates of each experiment did however exist. No connection between the amount of paint applied and differences in the number of particles emitted was found during the test period.

The test chamber was well suited for the experiments. All experiments were performed with aluminium as the test substrate. The prior cleaning process and application by paint roller allowed the experiments to be carried out with consistency. The recommended amount of paint was applied and the adhesion was satisfactory. Aluminium plates are inert and do not affect the result. Even though aluminium is not a realistic material in reality, it is useful for comparison studies and has been used previously (Jørgensen et al., 1995).

As mentioned in the methods section, the test chamber was operated at a constant temperature and constant relative humidity during the experiment and the average values were consistent throughout the test period. Looking into the details of the measurements, we found an increase in humidity a short period after introduction of the painted test material to the test chamber. Within the first 30 min the humidity increased from 50 to 52% for the solvent-based paints, and from 50 to 54–57% RH for the water-based paints. The humidity in the test chamber decreased from this maximum level and back to the set point within 4 h. This was mainly due to the operation method of the test chamber, which compensated for the contribution from the paints to the humidity in the test chamber. In the same way, the temperature decreased within the first 30 min from 23 to 21–22 °C, thereafter the temperature increased to the set point (23 °C) over the next 3–4 h.

The emission was investigated during a 7 day period after application of the paint. The results showed that the water-borne acrylic paints only show emission during the first 24 h, while the solvent-borne paints shows emission for 48 h. This difference is probably due to the difference in drying time for the two types of paints. Compared to investigations of VOC emission, this is a very short emission period and the exposure of the residents is consequently short term. Paints A, B and D follow a decay curve similar to that known from VOC emission experiments. Paint C shows in contrast two separate peaks of nanoparticle emissions after 2.5 and 7.5 h of experiment. No explanation was found for these peaks, but they were repeated in both experiments.

The emission of nanoparticles from the water-borne acrylic paints was in general very low. The emission from the solvent-borne alkyd paint (D) was, in contrast, much higher. During the first 24 h of emission, a mean of $3.25 \cdot 10^5$ particles/cm^3 was found for the solvent-borne alkyd paint, with a peak of $1.47 \cdot 10^6$ particles/cm^3. The difference between the NP values confirms that this paint emitted a substantially higher number of particles during the experiment (a factor of 10^3) compared to the water-borne acrylic paints. The lowest emission was found for paints A and B with a mean of $1.1 \ 10^2$–$2.2 \ 10^2$ particles/cm^3 and a peak of $2.0 \ 10^3$ particles/cm^3. This is only slightly higher than the experiment with the empty chamber. No comparable results exist for emission from paints.

Wallace found a mean of 2500 particles/cm^3 in a US domestic building in periods where no activities took place (Wallace, 2006). Wallace and Ott reported less than 3500 particles/cm^3 (Wallace and Ott, 2011), and Bekô reported 5100 particles/cm^3 (Bekô et al., 2013), both results found when no activities took place. It is well known that activities such as cooking and candling result in higher concentrations (Afshari et al., 2005; Sjaastad et al., 2008), but compared to concentrations of particles in indoor air during periods without special activities, the emission of nanoparticles from solvent-borne paints exhibits a significant contribution to the pollution level, while the water-borne paint emissions are insignificant.

The emissions from all paints showed a short duration, of 24 h for the water-borne paints and 48 h for the solvent-borne paints. This means that even though the arithmetic mean (AM) and the maximum emission of the solvent-borne paint is high, the total exposure to the resident is low. Occupational exposure limits for nanoparticles are set to $4.00 \cdot 10^4$ particles/cm^3. European labelling schemes evaluate the emission of products after 28 h, while US labelling schemes such as Greenguard evaluate after 7 days of testing. If the nanoparticle emission is evaluated as a mean value representing a 7 day mean, the AM would be $1.15 \cdot 10^4$ for both versions of Paint D; evaluated after 28 days the AM would be 553 particles/cm^3 for the base version and 547 particles/cm^3 for the pigmented version. Evaluated for a longer period, the exposure would be correspondingly lower. The exposure to the residents is consequently far below the threshold limits for engineered nanoparticles. No short-term limits for nanoparticle exposure exits.

For the purpose of interpreting the results, information regarding nanoparticle inclusion and type was obtained from the paint suppliers upon completion of the experiment. The suppliers indicated that only Carbon Black was used during production of the pigmented paints (as a tint). The binder did not consist of nanoparticles and TiO$_2$ was not used in the bases. Therefore, the only possible contribution to the experimental results was from Carbon Black particles and they would only affect the results for the pigmented paints.

No systematic difference between the emission of nanoparticles from the pigmented and the base versions was found. The pigmented version was full pigmented, which means that it had the darkest possible colour (black or dark grey). This indicates that the tinting colour in general does not contribute to the emission. For paint C, the difference between pigmented and base versions however is remarkable, no explanation has been found for this difference, but the cause is the high emission of 6.04 nm particles after 7 h of experiments, which only is found for the pigmented version of the paint.

The particle size distribution shows that the dominant particle size emitted from paint D is 9.31 nm, while the dominant mode for the pigmented paint C is the lowest detected particle size at 6.04 nm. The remaining paints showed a maximum of particles in the size range 29.4–34 nm. No difference was found between base and pigmented versions of the same paint, except for paint C, where only the pigmented paint showed a high emission of 6.04 nm sized particles. For the pigmented paint C, a high concentration of particles at 6.04 nm was found in both repetitions of the experiments. The very small size of the particles emitted from paints C and D is remarkable; these are smaller particles than those emitted by most other particle sources. Particles emitted from a gas stove when not cooking are comparable (Jørgensen et al., 2012), but most other sources emit larger particles, Carbon Black, even as a primary particle is in a size range of 20–50 nm, which not is reflected in the results in this study.

The design of the study was inspired of the design of emission studies of volatile organic compounds. It was found to be more challenging to study low levels of particle emission, since opening the test chamber leads to a certain penetration of particles from the surrounding laboratory air. The opening procedure was performed as quickly as possible, but as seen from Table 1, a certain number of particles entered the chamber in any case.

The background concentrations before and after each experiment were deducted from the results but the empty chamber level, which corresponds to opening the test chamber door, was not deducted. The

emission measurements showed a high level of fluctuation, especially for paint D; this is also found in nanoparticle emission studies of 3D-printers (Azimi et al., 2016). No modelling of the emission was performed, but the area under the curve was calculated together with the number of particles emitted to the air during the experiment per painted area. The emission from paints A and B show low concentrations, comparable to the level of the empty chamber study, even though the number of particles emitted during the tests were higher than the empty chamber study.

Paint D was the only solvent-borne paint in this study. The emission of volatile organic compounds was expected to be higher from paint D compared to paints A–C. The FMPS instrument measures volatile, semi-volatile and solid particles, which means that it not was possible to determine whether the emission measured from paint D consisted of volatile, semi-volatile or solid particles. This is obviously a weakness of this study, the choice of nanoparticle instrument made it however possible to identify the very small particles emitted from the solvent-borne alkyd paint, with particle diameters as low as 6.04–9.31 nm. A high-temperature condensation counter could have looked into the question if the emitted particles were engineered nanoparticles or particles resulting from condensation of solvent from the paint emission (Collings et al., 2014), as indicated by Wallace (Wallace et al., 2017), another approach could have been to collect aerosol samples and analysing them by GC-MS for organics, ICP-MS for metals and Transmission electron microscopy (TEM). It would be relevant to investigate this further. The results of this study showed however, that exposure to nanoparticles from paints for indoor use, irrespective of their origin, was low from a resident's perspective. It is not very well defined how to evaluate exposure for residents; calculation is performed for a 28 day period, which is the most used time period for evaluation employed by the labelling schemes.

Paint A is marketed as a special, low-emitting paint, and is recommended by the Norwegian Asthma and Allergy Association as suitable for their members. This paint showed very low levels of emission of nanoparticles, but not remarkably much lower than paint C, which does not have the same label. The explanation is that the low-emitting-paint designation only relates to the emission of volatile organic compounds, and that the label does not show any evaluation of the emission of particles from the paint.

The only labelling scheme including particle emissions in the evaluation is the Greenguard scheme (Institute, 2005). The method used by Greenguard is measurement of $PM_{2.5}$; this is a mass-based particle fraction that in principle includes nanoparticles, but insofar as the nanoparticles have very low mass even when the number of particles is high, this means that they do not influence the measurement of $PM_{2.5}$. In this study, measurement of $PM_{2.5}$ was tested, but the concentrations found were below the detection limit of the instrument used. Methods for determining emission of particles for the purpose of labelling products should be investigated further, given that low-emitting materials are recommended for achieving good indoor air quality, especially in low-energy buildings (Kaunelienė et al., 2016).

Introduction of nanoparticles in the formulation of paints means that these particles are either released during application or bound to the painted surface. What happens to the nanoparticles in the paint during the remaining life cycle is only partly investigated. It has been shown that Ag, SiO_2 and TiO_2 nanoparticles are released from outdoor surfaces exposed to ambient weather conditions, and are discharged into natural receiving waters (Kaegi et al., 2008, 2010; Al-Kattan et al., 2015). The composition of paints intended for indoor surfaces differs from outdoor paints, and the surfaces are not exposed to rain or high humidity. What is more relevant for indoor exposure is the influence during sanding, wrecking and re-usage of painted sur-

faces. Koponen has looked into sanding of nanoparticle-doped walls, including indoor wall paints, outdoor wall paints, fillers and lacquers, and points out that the material characteristics of different products appear to be highly significant to the potential for particle generation during sanding. Koponen and co-authors found it difficult to conclude whether engineered nanoparticles reduce or increase the exposure risk to dust particles during sanding(Koponen et al., 2011). Mikkelsen investigated the oxidative stress potential of sanding dust from nanoparticle-containing paint and found that this dust did not generate more oxidative stress or expression of cell adhesion molecules than sanding dust from paint without nanoparticles (Mikkelsen et al., 2013); they also found that paint sanding dust generated less response than primary particles of TiO_2 and carbon black.

As Quadros and Marr discuss in their article from 2014, it is important to investigate the exposure to nanoparticles in air during use and disposal of products containing nanoparticles (Quadros and Marr, 2010). Nanoparticles in aqueous phase have been intensively studied, but human health risk is related more to conditions under which nanoparticles could become airborne. This study is a contribution to this field, and is also carried out using a very realistic exposure scenario, as requested by Vance (Vance and Marr, 2015). The results from this study show that the waterborne acrylic paints exhibited very low emission levels, and that the solvent-borne alkyl paint showed significant emissions, but only for 48 h, which means that the exposure to the residents is low from an indoor relevant perspective. Interior paints are probably not very important when it comes to identifying products releasing nanoparticles into indoor environments.

This study was limited to studying indoor climate related conditions. The importance of nano-particles in outdoor air and accompanying environmental performances have been previously determinded (Hower et al., 2013; Ribeiro et al., 2013; Silva et al., 2013), thus potential emissions from paint for outdoor use were not included in this work.

5. Conclusion

The emission of nanoparticles has been measured in a 6.79 m^3 stainless steel test chamber. The emissions from four different paints, with and without tint, were evaluated by duplicate experiments together with the emission of the empty chamber during the same procedure.

The emission was evaluated according to particle number concentration of the emission, duration of the emission period and the particle size distribution of the particles emitted. The solvent-borne alkyd paint showed the highest concentration, with a mean of 3.2 10^5 particles/cm^3 and a peak of 1.4 10^6 particles/cm^3, the longest decay and the smallest particle size distribution, with 9.31 nm particles as the dominant particle size. Due to the short emission period of only 48 h, the resulting exposure to the residents is low from an indoor perspective.

Evaluation of the emission from water-borne acrylic paints showed particle size distributions and number concentrations comparable to background concentrations. The water-borne acrylic paints seem not to influence the particle concentration of nanoparticles in room air.

With the exception of one of the water-borne paints, no general differences were found between emissions from base versions and pigmented versions of the paints, which indicates that Carbon Black, used as paint pigments, do not cause emission of nanoparticles.

In order to investigate whether the nanoparticles identified from the solvent-borne paint (D) are volatile organic compounds or solid nanoparticles, it is recommended that the experiments be repeated

with a high temperature condensation particle counter. Another approach to distinguish organic compounds from solid nanoparticles would be to collect aerosol samples and analyse them by GC-MS for organics, IPS for metals and TEM.

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References

Abd El-Ghaffar, M.A., Sherif, M.H., Taher El-Habab, A., 2016. Novel high solid content Nano Siliconated poly (VeoVa-acrylate) Terpolymer latex for high performance latex paints. Chem. Eng. J. 301, 285–298. https://doi.org/10.1016/j.chemosphere.2014.02.005.

Afshari, A., Matson, U., Ekberg, L.E., 2005. Characterization of indoor sources of fine and ultrafine particles: a study conducted in a full-scale chamber. Indoor Air 15, 141–150. https://doi.org/10.1111/j.1600-0668.2005.00332.x.

Agudelo-Castañeda, D.M., Teixeira, E.C., Schneider, I.L., Pereira, F.N., Oliveira, M.L.S., Taffarel, S.R., Sehn, J.L., Ramos, C.G., Silva, L.F.O., 2016. Potential utilization for the evaluation of particulate and gaseous pollutants at an urban site near a major highway. Sci. Total Environ. 543, 161–170. https://doi.org/10.1016/j.scitotenv.2015.11.030.

Agudelo-Castañeda, D.M., Teixeira, E.C., Schneider, I.L., Lara, S.R., Silva, L.F.O., 2017. Exposure to polycyclic aromatic hydrocarbons in atmospheric PM1.0 of urban environments: carcinogenic and mutagenic respiratory health risk by age groups. Environ. Pollut. 224, 158–170. https://doi.org/10.1016/j.envpol.2017.01.075.

Al-Kattan, A., Wichser, A., Vonbank, R., Brunner, S., Ulrich, A., Zuin, S., Arroyo, Y., Golanski, L., Nowack, B., 2015. Characterization of materials released into water from paint containing nano-SiO2. Chemosphere 119, 1314–1321. https://doi.org/10.1016/j.chemosphere.2014.02.005.

Azimi, P., Zhao, D., Pouzet, C., Crain, N.E., Stephens, B., 2016. Emissions of ultrafine particles and volatile organic compounds from commercially available desktop three-dimensional printers with multiple filaments. Environ. Sci. Technol. 50, 1260–1268. https://doi.org/10.1021/acs.est.5b04983.

Bekô, G., Weschler, C.J., Wierzbicka, A., Karottki, D.G., Toftum, J., Loft, S., Clausen, G., 2013. Ultrafine particles: exposure and source apportionment in 56 Danish homes. Environ. Sci. Technol. 47, 10240–10248. https://doi.org/10.1021/es402429h.

Bellotti, N., Romagnoli, R., Quintero, C., Domínguez-Wong, C., Ruiz, F., Deyá, C., 2015. Nanoparticles as antifungal additives for indoor water borne paints. Prog. Org. Coating. 86, 33–40. https://doi.org/10.1016/j.porgcoat.2015.03.006.

Bluyssen, P.M., Alblas, M.J., Tuinman, I.L., 2013. In Vitro Exposure of Human Lung Cells to Emissions of Several Indoor Air Sources Created in a Climate Chamber, Retrieved from http://resolver.tudelft.nl/uuid:dfbc91cb-6f2a-464a-89da-3e56bb2ba7d3.

Brand, P., Lenz, K., Reisgen, U., Kraus, T., 2013. Number size distribution of fine and ultrafine fume particles from various welding processes. Ann. Occup. Hyg. 57, 305–313. https://doi.org/10.1093/annhyg/mes070Canesi.

Canesi, L., Ciacci, C., Betti, M., Fabbri, R., Canonico, B., Fantinati, A., Marcomini, A., Pojana, G., 2008. Immunotoxicity of carbon black nanoparticles to blue mussel hemocytes. Environ. Int. 34, 1114–1119. https://doi.org/10.1016/j.envint.2008.04.002.

Collings, N., Rongchai, K., Symonds, J.P.R., 2014. A condensation particle counter insensitive to volatile particles. J. Aerosol. Sci. 73, 27–38. https://doi.org/10.1016/j.jaerosci.2014.03.003.

European Union, 2004. Directive 2004/42/CE of the European Parliament and of the Council on the Limitation of Emissions of Volatile Organic Compounds Due to the Use of Organic Solvents in Certain Paints and Varnishes and Vehicle Refinishing Products and Amending Directive 1999/13/EC. European Union.

Gaspar, F.W., Maddalena, R., Williams, J., Castorina, R., Wang, Z.-M., Kumagai, K., McKone, T.E., Bradman, A., 2017. Ultrafine, fine, and black carbon particle concentrations in California child care facilities. Indoor Air https://doi.org/10.1111/ina.12408, n/a-n/a.

He, C., Morawska, L., Hitchins, J., Gilbert, D., 2004. Contribution from indoor sources to particle number and mass concentrations in residential houses. Atmos. Environ. 38, 3405–3415. https://doi.org/10.1016/j.atmosenv.2004.03.027.

Hincapié, I., Künniger, T., Hischier, R., Cervellati, D., Nowack, B., Som, C., 2015. Nanoparticles in facade coatings: a survey of industrial experts on functional and environmental benefits and challenges. J. Nanoparticle Res. 17, 287. https://doi.org/10.1007/s11051-015-3085-3.

Hiraku, Y., Nishikawa, Y., Ma, N., Afroz, T., Mizobuchi, K., Ishiyama, R., Matsunaga, Y., Ichinose, T., Kawanishi, S., Murata, M., 2017. Nitrative DNA damage induced by carbon-black nanoparticles in macrophages and lung epithelial cells. Mutat. Res. Genet. Toxicol. Environ. Mutagen. 818, 7–16. https://doi.org/10.1016/j.mrgentox.2017.04.002.

Hovland, K.M., 2011. Dare Not Promote Nano. Technical Magazine (Teknisk Ukeblad). http://www.tu.no/artikler/industri-tor-ikke-markedsfore-nano/249721.

Hower, J.C., O'Keefe, J.M.K., Henke, K.R., Wagner, N.J., Copley, G., Blake, D.R., Garrison, T., Oliveira, M.L.S., Kautzmann, R.M., Silva, L.F.O., 2013. Gaseous emissions and sublimates from the Truman Shepherd coal fire, Floyd County, Kentucky: a re-investigation following attempted mitigation of the fire. Int. J. Coal Geol. 116, 63–74. https://doi.org/10.1016/j.coal.2013.06.007.

IARC, 2010. Carbon black, titanium dioxide and talk. IARC Monogr. Eval. Carcinog. Risks Hum. 93, Retrieved from: http://monographs.iarc.fr/ENG/Monographs/vol93/mono93.pdf.

Greenguard Institute, 2005. Indoor Air Quality Guide, http://www. greenguard. org/.

International Carbon Black Association, Particle Properties of Carbon Black. Retrieved from http://carbon-black.org/files/ICBA-Particle-CB-Factsheet-111413.pdf.

Jørgensen, R.B., Bjørseth, O., Malvik, B., 1995. Emission from wall paints - the influence of the wall material. Proc. Healthy Build. 95 (2), 6, Milano.

Jørgensen, R.B., Strandberg, B., Sjaastad, A.K., Johansen, A., Svendsen, K., 2012. Simulated restaurant cook exposure to emissions of PAHs, mutagenic aldehydes, and particles from frying bacon. J. Occup. Environ. Hyg. 10, 122–131. https://doi.org/10.1080/15459624.2012.755864.

Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M., Boller, M., 2008. Synthetic TiO2 nanoparticle emission from exterior facades into the aquatic environment. Environ. Pollut. 156, 233–239. https://doi.org/10.1016/j.envpol.2008.08.004.

Kaegi, R., Sinnet, B., Zuleeg, S., Hagendorfer, H., Mueller, E., Vonbank, R., Boller, M., Burkhardt, M., 2010. Release of silver nanoparticles from outdoor facades. Environ. Pollut. 158, 2900–2905. https://doi.org/10.1016/j.envpol.2010.06.009.

Kaiser, J.P., Zuin, S., Wick, P., 2013. Is nanotechnology revolutionizing the paint and lacquer industry? A critical opinion. Sci. Total Environ. 442, 282–289. https://doi.org/10.1016/j.scitotenv.2012.10.009.

Kaunelienė, V., Prasauskas, T., Krugly, E., Stasiulaitienė, I., Čiužas, D., Šeduikytė, L., Martuzevičius, D., 2016. Indoor air quality in low energy residential buildings in Lithuania. Build. Environ. 108, 63–72. https://doi.org/10.1016/j.buildenv.2016.08.018.

Kero, I., Jørgensen, R., 2016. Comparison of three real-time measurement methods for airborne ultrafine particles in the silicon alloy industry. Int. J. Environ. Res. Public Health 13, 871. https://doi.org/10.3390/ijerph13090871.

Klepeis, N.E., Nelson, W.C., Ott, W.R., Robinson, J.P., Tsang, A.M., Switzer, P., Behar, J.V., Hern, S.C., Engelmann, W.H., 2001. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. J. Expo. Anal. Environ. Epidemiol. 11, 231–252. https://doi.org/10.1038/sj.jea.7500165.

Koponen, I.K., Jensen, K.A., Schneider, T., 2011. Comparison of dust released from sanding conventional and nanoparticle-doped wall and wood coatings. J. Expos Sci. Environ. Epidemiol. 21, 408–418. https://doi.org/10.1038/jes.2010.32.

Kosk-Bienko, J., 2009. Workplace exposure to nanoparticles. Work, E.A.f.S.a.H.a.. In: European Agency for Safety and Health at Work, Retrieved from: https://osha.europa.eu/en/tools-and-publications/publications/literature_reviews/workplace_exposure_to_nanoparticles.

Larsen, S.T., Roursgaard, M., Jensen, K.A., Nielsen, G.D., 2009. Nano titanium dioxide particles promote allergic sensitization and lung inflammation in mice. Basic Clin. Pharmacol. Toxicol. 106, 4. https://doi.org/10.1111/j.1742-7843.2009.00473.x.

Long, C.M., Nascarella, M.A., Valberg, P.A., 2013. Carbon black vs. black carbon and other airborne materials containing elemental carbon: physical and chemical distinctions. Environ. Pollut. 181, 271–286. https://doi.org/10.1016/j.envpol.2013.06.009.

Mikkelsen, L., Jensen, K.A., Koponen, I.K., Saber, A.T., Wallin, H., Loft, S., Vogel, U., Møller, P., 2013. Cytotoxicity, oxidative stress and expression of adhesion molecules in human umbilical vein endothelial cells exposed to dust from paints with or without nanoparticles. Nanotoxicology 7, 117–134. https://doi.org/10.3109/17435390.2011.641604.

Poland, C.A., Duffin, R., Kinlock, I., Maynard, A., Wallace, W.A.H., Seaton, A., Stone, V., Brown, S., MacNee, W., Donaldson, K., 2008. Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. Nat. Nanotechnol. 3, 423–426. https://doi.org/10.1038/nnano.2008.111.

Price, H.D., Stahlmecke, B., Arthur, R., Kaminski, H., Lindermann, J., Däuber, E., Asbach, C., Kuhlbusch, T.A.J., BéruBé, K.A., Jones, T.P., 2014. Comparison of instruments for particle number size distribution measurements in air quality monitoring. J. Aerosol. Sci. 76, 48–55. https://doi.org/10.3109/17435390.2011.587900.

Quadros, M.E., Marr, L.C., 2010. Environmental and human health risks of aerosolized silver nanoparticles. J. Air & Waste Manag. Assoc. 60, 770–781. https://doi.org/10.3155/1047-3289.60.7.770.

Ragde, S.F., Jørgensen, R.B., Føreland, S., 2016. Characterisation of exposure to ultrafine particles from surgical smoke by use of a fast mobility particle sizer. Ann. Occup. Hyg. 60, 860–874. https://doi.org/10.1093/annhyg/mew033.

Ribeiro, J., DaBoit, K., Flores, D., Kronbauer, M.A., Silva, L.F.O., 2013. Extensive FE-SEM/EDS, HR-TEM/EDS and ToF-SIMS studies of micron- to nano-particles in anthracite fly ash. Sci. Total Environ. 452, 98–107. https://doi.org/10.1016/j.scitotenv.2013.02.010.

Riley, W.J., Mckone, T.E., Lai, A.C.K., Nazaroff, W.N., 2002. Indoor particulate matter of outdoor origin; importance of size-dependent removal mechanisms. Environ. Sci. Technol. 36, 200–207. https://doi.org/10.1021/es010723y.

Saber, A.T., Jensen, K.A., Jacobsen, N.R., Birkedal, R., Mikkelsen, L., Møller, P., Loft, S., Wallin, H., Vogel, U., 2012. Inflammatory and genotoxic effects of nanoparticles designed for inclusion in paints and lacquers. Nanotoxicology 6, 453–471. https://doi.org/10.3109/17435390.2011.587900.

Schneider, T., Sundell, J., Bischof, W., Bohgard, M., Cherrie, J.W., Clausen, P.A., Dreborg, S., Kildesø, J., Kjærgaard, S.K., Løvik, M., Pasanen, P., Skyberg, K., 2003. Europart Airborne particles in the indoor environment. A European interdisiplinary review of scientific evidence on associations between exposure to particles in buildings and health effects. Indoor Air 13, 38–48. https://doi.org/10.1034/j.1600-0668.2003.02025.x.

Schneider, T., Jensen, K.A., Afshari, A., Gunnarsen, L., Wåhlin, P., Glasius, M., Palmgren, F., Nielsen, O.J., Clausen, P.A., 2004. Prediction of indoor concentration of 0,5-4 um particles of outdoor origin in an uninhibited apartment. Atmos. Environ. 38, 6349–6359. https://doi.org/10.1016/j.atmosenv.2004.08.002.

Schneider, I.L., Teixeira, E.C., Agudelo-Castañeda, D.M., Silva e Silva, G., Balzaretti, N., Braga, M.F., Oliveira, L.F.S., 2016. FTIR analysis and evaluation of carcinogenic and mutagenic risks of nitro-polycyclic aromatic hydrocarbons in PM1.0. Sci. Total Environ. 541, 1151–1160. https://doi.org/10.1016/j.scitotenv.2015.09.142.

Silva, Luis, F.O., Fdez- Ortiz de Vallejuelo, S., Martinez-Arkarazo, I., Castro, K., Oliveira, M.L.S., Sampaio, C.H., de Brum, I.A.S., de Leão, F.B., Taffarel, S.R., Madariaga, J.M., 2013. Study of environmental pollution and mineralogical characterization of sediment rivers from Brazilian coal mining acid drainage. Sci. Total Environ. 447, 169–178. https://doi.org/10.1016/j.scitotenv.2012.12.013.

Sjaastad, A.K., Svendsen, K., Jørgensen, R.B., 2008. Sub-micrometer particles: their level and how they spread after pan frying of beefsteak. Indoor Built Environ. 17, 230–236. https://doi.org/10.1177/1420326X08091186.

Sjaastad, A.K., Jørgensen, R.B., Svendsen, K., 2010. Exposure to polycyclic aromatic hydrocarbons (PAHs), mutagenic aldehydes and particulate matter during pan frying of beefsteak. Occup. Environ. Med. 67, 228–232. https://doi.org/10.1136/oem.2009.046144.

Smulders, S., Luyts, K., Brabants, G., Golanski, L., Martens, J., Vanoirbeek, J., Hoet, P.H.M., 2015. Toxicity of nanoparticles embedded in paints compared to pristine nanoparticles, in vitro study. Toxicol. Lett. 232, 333–339. https://doi.org/10.1016/j.toxlet.2014.11.030.

Spilak, M.P., Frederiksen, M., Kolarik, B., Gunnarsen, L., 2014. Exposure to ultrafine particles in relation to indoor events and dwelling characteristics. Build. Environ. 74, 65–74. https://doi.org/10.1016/j.buildenv.2014.01.007.

Vance, M.E., Marr, L.C., 2015. Exposure to airborne engineered nanoparticles in the indoor environment. Atmos. Environ. 106, 503–509. https://doi.org/10.1016/j.atmosenv.2014.12.056.

Wallace, L., 2006. Indoor sources of ultrafine and accumulation mode particles: size distributions, size-resolved concentrations, and source strengths. Aerosol. Sci. Technol. 40, 348–360. https://doi.org/10.1080/02786820600612250.

Wallace, L., Ott, W., 2011. Personal exposure to ultrafine particles. J. Expo. Sci. Environ. Epidemiol. 21, 20–30. https://doi.org/10.1080/02786820600612250.

Wallace, L.A., Ott, W.R., Weschler, C.J., Lai, A.C.K., 2017. Desorption of SVOCs from heated surfaces in the form of ultrafine particles. Environ. Sci. Technol. 51, 1140–1146. https://doi.org/10.1021/acs.est.6b03248.

Xiong, J., Wang, L., Bai, Y., Zhang, Y., 2013. Measuring the characteristic parameters of VOC emission from paints. Build. Environ. 66, 65–71. https://doi.org/10.1016/j.buildenv.2013.04.025.

Zhang, R., Dai, Y., Zhang, X., Niu, Y., Meng, T., Li, Y., Duan, H., Bin, P., Ye, M., Jia, X., Shen, M., Yu, S., Yang, X., Gao, W., Zheng, Y., 2014. Reduced pulmonary function and increased pro-inflammatory cytokines in nanoscale carbon black-exposed workers. Part. Fibre Toxicol. 11, 73. https://doi.org/10.1186/s12989-014-0073-1.

Zhu, Y., Hinds, W.C., Krudysz, M., Kuhn, T., Froines, J., Sioutas, C., 2005. Penetration of freeway ultrafine particles into indoor environments. J. Aerosol. Sci. 36, 303–322. https://doi.org/10.1016/j.jaerosci.2004.09.007.