Exposure assessment of Nanomaterials at production sites by a Short Time Sampling (STS) approach : Strategy and first results of measurement campaigns

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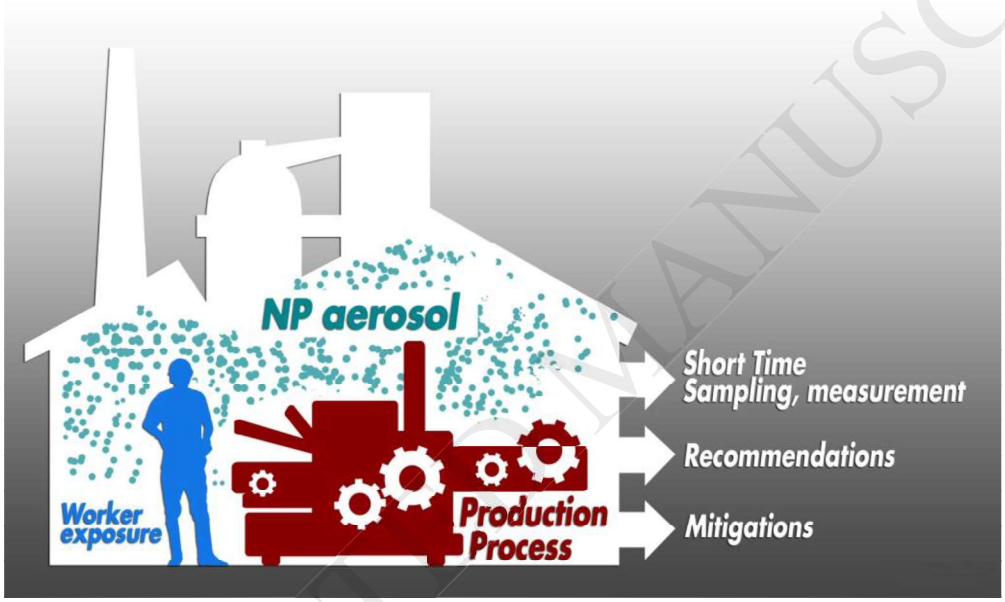
Graphical abstract



Highlights

- Characterization of the exposition to nanoparticles and –objects at workplaces is a huge technical challenge.
- Workplace exposure during short durations is particularly difficult to detect due to the low performances of the samplers.
- This article proposes a solution allowing for characterizing emissions at workplaces.
- By the developed technique, 9 out of 37 of the studied steps have been shown to exhibit exposures to nanoparticles and nano-objects.

Abstract

Characterization of the exposition to nanoparticles and nano-objects at workplaces is a huge technical challenge. Workplace exposure during short durations is particularly difficult to detect due to the low performances of the samplers. This article proposes a solution allowing for characterizing emissions at workplaces and presents the results obtained from a nanomaterials exposure measurement campaign

performed on six different process lines (PLs) distributed all over Europe. By using our Short Time Sampling (STS) approach, the emitted nanomaterials are characterized in terms of their number concentration, size, shape and chemical composition. The background noise without any production activity is first measured for each PL and then it is distinguished from the emitted nanomaterials during production. The PLs yield different nanomaterial emission levels: the PL using the extrusion of polymer composites shows high emission whereas the PL dealing with the electrospinning of polyamide nanofibers shows the least i.e. no significant change in the background noise during the process and no detectable nanofiber emission either. The nanomaterials get emitted in the form of nanoparticles or submicronic fibers, or their agglomerates and aggregates i.e. Nano Objects, Agglomerates and Aggregates (NOAA). By the developed technique, 9 out of 37 of the studied steps have been shown to exhibit exposures to nanoparticles and nano-objects. For nanosafety measures, the energetic processes like spraying, extrusion, transport and cleaning activities of the nanomaterials in the powder form require most attention.

Keywords: Nanoparticle, NOAA, Exposure, Measurement campaign, Short Time Sampling, Nanosafety, risk assessment and management

1. Introduction

The current work on assessing the hazards of engineered nanomaterials (ENMs) solely based on laboratory tests is time-consuming (Christophe Bressot, 2017; Shandilya et al., 2015), resource intensive (Bressot et al., 2016), and in the case of toxicological studies lengthy (Privalova et al., 2014) and constrained by ethical considerations (Chen et al., 2017). For this, various secondary studies are carried out, focusing on aspects such as cellular uptake of particles (Phuc and Taniguchi, 2017) or environmental release (Plazas-Tuttle et al., 2015; Salehi et al., 2017).

In the framework of industrial workplaces, the operations dealing with the processing of the nanomaterials, nanoparticles (NPs) or Nano Objects, Agglomerates and Aggregates (NOAA) can lead to potential exposures unless proper safety measures are taken (ISO, 2012; Pavlovska et al., 2016). Prior exposure studies have been performed in the real workplaces dealing with the production and handling of nanomaterials (Bello et al., 2008; Bello et al., 2009; Brouwer et al., 2009; Demou et al., 2008; Demou et al., 2009; Fujitani et al., 2008; Johnson et al., 2010; Kuhlbusch and Fissan, 2006; Lee et al., 2011; Pavlovska et al., 2016). These works have led to general recommendations for exposure measurement assessments (Consent Report, 2011; INERIS - CEA - INRS et al., 2012.; nanoGEM; Ramachandran et al., 2011). Moreover, recent reviews highlight the need for an extensive description of workplaces to facilitate the comprehension of the mechanisms involved in particle release (Ding et al., 2016), (Privalova et al., 2014). The practical consequences in an aerosol characterization have been the use Mixed Cellulose Ester (MCE) filter (Methner et al., 2010) and performing intensive campaign with SMPS or FMPS, respectively (Kaminski et al., 2015; Kuhlbusch et al., 2011).

In order to make these studies successful, whilst considering various background aerosols originating from the general work environment or the process itself, , the measurement campaigns are intensive and time consuming (Kuhlbusch et al., 2011). For such campaigns, the size and time-resolved instruments like APS, SMPS etc. are an obvious choice in which the aerosol particle detection principles are based on the particles' optical properties or electrical mobility.

Moreover various studies were had difficulties to distinguish process generated NPs or NOAA from ambient particles (Bekker et al., 2015; Brouwer et al., 2014b). In addition, many nanomaterial emissions occur for a very brief period (i.e. for a second or fraction of a second) and are observed as number concentration peaks (Pietroiusti and Magrini, 2014). In this case, the use of samplers,

requiring long sampling durations, becomes obsolete. Considering these critical points while carrying out the measurement campaigns, the Short Time Sampling (STS) approach presented in the present article may lead to a global improvement in NP exposure assessment at workplaces. Alternative samplers have been previously used but required a long-term exposure (Hedmer et al., 2014; Methner et al., 2012) or sample preparations (Asbach et al., 2014; Gorner et al., 2010; Hedmer et al., 2014; Koponen et al., 2015; Methner et al., 2012). The Micro Inertial Impactor (MINI) is an interesting short-term sampler used at workplace exposure assessments but the D50 cut-off at 0.05 and 0.9 µm aerodynamic diameter prevents a comprehensive inhalable study (Kandler et al., 2011; Kling et al., 2016).

The STS approach is illustrated in Figure 1. The first step is basic information gathering about the process and materials which may come from different sources (literature, Material Safety data Sheet, companies, etc). Although the presented method does not directly involve toxicological considerations, the knowledge of a material's toxicity is of great concern when it comes to the evaluation of the analytical detection limits and/or background noise level are appropriate for the substance under consideration. For this, any related available toxicological data is also documented in the proposed procedure and compared to these limits. In the case of unavailable data, detection limits are furthermore documented allowing for rapidly reevaluating the exposure levels once such toxicological data becomes available. This is then followed by a semi-quantitative exposure measurement campaign through visual observations, inventory of process and operations. If a step is potentially emissive, a sampling within or near the breathing zone of the worker is carried out systematically using Mini Particle Sampler, MPS (Bressot et al., 2015; R'mili et al., 2013). A short sampling duration is possible because of the high collection efficiency. The efficiency is minimum at 30 nm i.e. 15-18 % and maximum at 5 nm i.e. 70 % (R'mili et al., 2013).The subsequent offline microscopic characterization of the TEM grid can differentiate between the ambient particles and NP or NOAA. This methodology decision criterion is the key factor of the campaign strategy. The existing tiered approach requires a stable background counting for a threshold limit between emission and background counting. By contrast, the present approach only necessitates a simple comparison between the background and process generated NP which is done by an offline emission checking using MPS. If an average of one nanoparticle or NOAA is collected per TEM grid square (41µm x 41 µm) and the same holds true for a minimum of 10 squares on the grid, then we consider it in the present approach to be an effective exposure. That value approximately corresponds to a spherical nanoparticle concentration between 200 to 500 cm^{-3} for a 5 minute sampling duration.

A particle counter was also used in conjunction for a quantitative measurement. Considering the mobility and dominance of submicronic sized particle in the ambience of the workplaces, the exposure analysis was consequently performed using a Condensation Particle Counter (CPC 3007, TSI Inc.) which has a relevant accuracy in the frame of handheld CPC (Asbach et al., 2012).

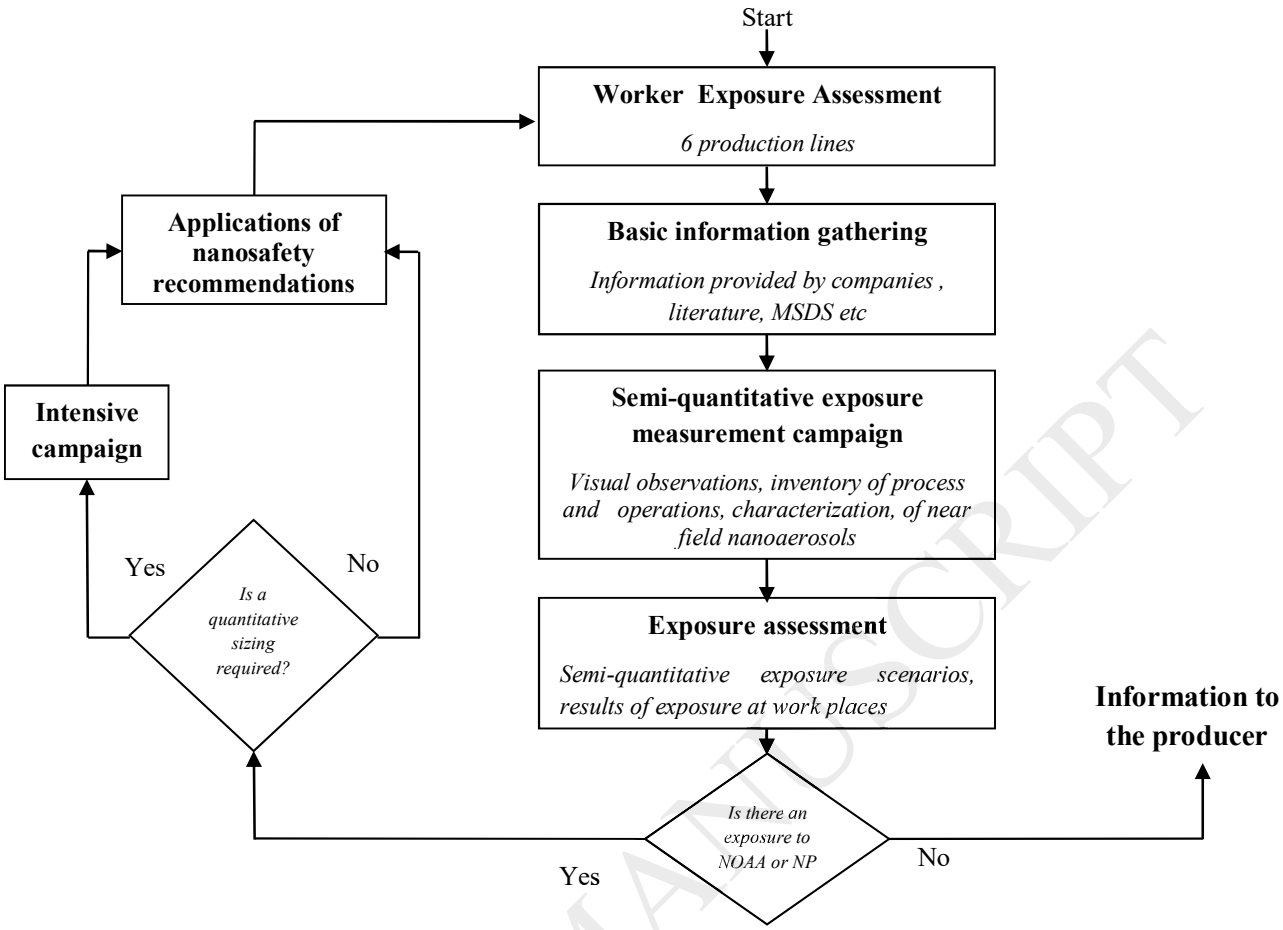


Figure 1: Schematic representation of the global approach for Exposure Assessment at work places through STS methodology integrating data gathering and measurement campaigns at workplaces. The near filed zone corresponds to vicinity of the worker.

A systematic STS measurement campaign was carried out on six different process lines PL dealing with the production and manipulation of NMs to test the STS approach.

2. Materials and Methods

2.1 Instruments

A portable Condensation Particle Counter (CPC Model 3007; TSI Inc.) was used to carry out the measurement campaign. Its measurable particle size range is distributed from 10 nm to approximately 1 µm. A Mini Particle Sampler (MPS; Ecomesure Inc.) was used for the offline microscopic analysis of the sampled aerosol particles. It collects the particle on a porous copper mesh grid (Model S143-3; Quantifoil Micro Tools GmbH Germany) using a filtration technique. A Scanning Mobility Particle

sizer (SMPS Model 3936; including a CPC Model 3010; TSI Inc.) classifies the aerosol particles according to their electrical mobility diameter. The SMPS operates in the size range of 5 to 350 nm with a resolution of up to 64 channels per decade. With a sampling time or time resolution of 5 min 25 s, the air flow rate was kept at 0.3 l/min. A Fast Mobility Particle Sizer (FMPS Model 3091; TSI Inc.) measures aerosol particles in the size range of 6 to 523 nm with a resolution of 16 channels per decade. With a time resolution of 1 s, the FMPS is faster than SMPS. Both SMPS and FMPS were used to compare the observations obtained using CPC and MPS. The measurement ability of all these three instruments i.e. SMPS, FMPS and CPC are provided in the literature (Asbach et al., 2012; Kaminski et al., 2013). Due to a comparatively lower time resolution of FMPS, a discrepancy of size distribution between FMPS and SMPS is generally observed and is attributed to the manner of handling with particle size and morphology. The inaccuracy of the FMPS when measuring NOAA seems to be a known difficulty (Kaminski et al., 2013). To facilitate comparison, SMPS data are also favored in this paper.

2.2 Nanomaterials and their Process Lines

For this study, six pilot scale nanomaterial PLs concern the production and manipulation of seven nanomaterials: (a) ZrO_2 NPs, (b) Polyamide nanofibers, (c) TiO_2 nanofibers, (d) TiO_2 & Ag nanosols and (e) MWCNT, were selected. Table 1 summarizes the overall data of the production lines dealing with the production, using nanomaterials and comparison between short time sampling and, on PL1, three tiered approaches.

3. Results

Process Line 1

The PL1 is devoted to ZrO_2 NPs production from sol gel dispersion by drying in an oven. Before starting the PL1 operation, the ambient aerosol particles were examined to study the background noise (BG). Some particles were sampled at the fume hood containing the sol-gel reactor for their microscopic analysis.

The handling of the suspension involved *steps 1 and 2* (see Table 1). The results obtained during these two steps are mentioned in the Table 1. The number concentration of the ambient aerosol particles during the step 1 did not seem to be significantly influenced by these steps. No ZrO_2 particles, but soot, oil droplet and debris of building materials were detected.

The impact of opening the oven and transport (*step 5*) was studied. Both times a significant impact on the number concentration of the ambient aerosol particles was observed: a sudden increase to 200,000 cm^{-3}. It is important to note that the step 5 concerns only one product that has reached a solid state, but is not yet totally dry. The sampled particles with the size larger than 1 µm had two different compositions- metallic particles, and zirconium particles, constituting the majority (see Figure 3 a). Only one type of the particles dominated the size range of 0.1 to 1 µm- the ones that tended to degrade or "melt" under the microscope beam, and consisted of sodium, silicon and sulphur. Elements like calcium, carbon and silicon were present in the majority of the particles having size less than 100 nm.

The opening of the oven and the transport of the product (step 5) clearly led to a very significant increase in the number concentration of the ambient aerosol particles, going beyond the limit of the CPC display (200,000 cm^{-3}). This is a critical step clearly giving rise to the ZrO_2 NPs exposure in the laboratory workplace.

Process Line 1: STS-three tiered approach comparison

In order to verify the applicability of the STS approach vis-à-vis the three-tiered approach, CPC and MPS sampling results were compared with an intensive campaign carried out using SMPS and FMPS on PL1. The results are shown in Table 1. As per the three-tiered approach, an exposure is detected when the net number concentration of the aerosol particles (obtained after deducting the BG from the instantaneous particles number concentration) surpasses the two times of its standard deviation of BG. Using this criterion, all the steps involved in PL1 were found to be potentially emissive. However, considering the ubiquitous nature of the NPs, the sole use of reading instruments in this approach does not provide information on certain *specificities* such as morphology or composition. By contrast, the STS approach, which is capable of determining their morphology or composition, plays a *complimentary* role in this aspect. On the basis of the microscopic observations, it successfully refines the step 5 as potentially emissive as it is the only task where ZrO_2 NPs and sub-micron particles emission were detected. The particle size distributions (or size resolution) measured using SMPS and FMPS are shown in Figure 2 (a). The two instruments detect an almost unimodal size distribution of the emitted aerosol particles (initial aberrations for smaller sizes neglected) with the same size mode at 81 nm. The time resolution or the sampling time kept for SMPS was 5 min 25 s whereas for FMPS, it was 1 s.

Table 1: Summary of the production lines (PL) dealing with the production/handling/manipulation of the nanomaterials (NM) and comparison between short time sampling (STS) and three tiered approaches on PL1. **NPs**: Nanoparticles; **Vent**: Ventilation; **N/F**: Natural or Forced; **CA**: Co-activity; **Y/N**: Yes/No; **WS**: Workspace; **S**: Small (< 40m^2); **M**: Medium (≥ 40 and ≤ 100 m^2); **B**: Big (> 100 m^2); **SD**: Standard deviation; **Background** (**BG**): Average number concentration (obtained using CPC) and type of the particles (obtained using TEM of the sampled aerosol particles) present in the **BG** before starting the production or manipulation of the nanomaterials; **C_{net}**: Net particle number concentration obtained by subtracting the mean particle number concentration of **BG** from the mean of instantaneous number concentration; **N/A**: Not available; §: Exposure limit set to 1 particle per grid square on ten grid squares; §§: Indicative value, beyond the measuring limit of the CPC (i.e. 10^5 cm^{-3}); §§§: Exposure limit set to 3x**SD** > **C_{net}**; *: A range of **BG** values (**C_{net}** or **SD**) is given because the **BG** is evaluated for each step; **MWCNT**: Multiwalled Carbon Nanotubes

PL/NM	Facility type	Step no.	Step Bold: suspected source	Source type	Vent (N/F)	CA (Y/N)	WS (S/M/L)	CPC counting (TSI 3007)			TEM/EDS observation	Exposure § (Y/N)	3-tiered approach (SMPS TSI 3936)			
								CPC mean (cm^{-3})	SD (cm^{-3})	R= CPC /BG			C_{net} (cm^{-3})	SD (cm^{-3})	Threshold value = 3xSD (cm^{-3})	Exposure (Y/N) §§§
1/ ZrO_2 NP	R&D labor–atory-pilot scale	-	BG	Handling of ZrO_2 NP	F	N	S	5360	3214	1	Soot and building particles	-	1306-6933*	915-1322*	-	-
		1	**Suspension transfer**					10^4	784	1.86	Same as BG	N	N/A	N/A	N/A	-
		2	**Transport to oven**					$3x10^4$	4000	0.4	Same as BG	N	2680	154	462	Y
		3	**Oven warm-up**					2500	407	0.5	Same as BG	N	$1.1x10^{5§§}$	13222	79332	Y
		4	**Particles crystallization**					$8x10^4$	53847	15	Same as BG	N	N/A	N/A	N/A	-
		5	**Oven opening**					$7x10^4$	9225	13	NP and submicronic particles of ZrO_2	**Y**	$1.9\ x10^{5§§}$	1154	3462	**Y**
		6	**Powder handling**					3000	830	0.56	Same as BG	N	N/A	N/A	N/A	-
		-	Whole day					-	-	-	-	-	$3.6x10^4$	6545	19634	Y
		-	Empty warm oven door opened					-	-	-	-	-	6288	154	462	Y
2/ ZrO_2 NP	R&D labor–atory-pilot scale	-	BG	Spray drying of the ZrO_2 NP	F	N	S	4000	240	1	Soot and building particles	-				
		1	Weighing and Handling					$5x10^4$	745	12.5	Same as BG	N				
		2	Cleaning					6355	1380	1.6	Same as BG	N				
		3	Suspension transport					8800	1300	2.2	Same as BG	N				
		4	Suspension handling					4000	250	1	Same as BG	N				
		5	Oven opening and powder transfer					4400	360	1.1	Same as BG	N				
		6	**New powder production**					4530	340	1.1	Same as BG	N				
		7	**New powder recovery**					4100	200	1	One irregularly shaped particle with a fraction of Zr; below the defined limit.	N				
	R&D	-	BG	Production	F	N	M	3200	800	1	Soot and building	-				

3/ PA nanofibers	labor–atory-pilot scale			and mani–pulation of poly amide nanofibers through electro–spinning							particles	
		1	Solution pouring					3300	515	1	Same as BG	N
		2	Electrospinning					3450	620	1.1	Same as BG	N
		3	**Sheet cutting**					3610	273	1.1	Same as BG	N
		4	**Cleaning**					3600	440	1.1	Same as BG	N
4/ TiO_2 nanofibers	R&D laborato ry- pilot scale	-	BG	Production and manipulati on of TiO_2 fibers through electrospin ning	N	N	M	4650	260	1	Soot and building particles	-
		1	fibers recovery					4000	500	0.9	Same as BG	N
		2	fibers transfer					3000	244	0.6	Same as BG	N
		3	Calcination					2500	200	0.5	Same as BG	N
		4	**Nanofibers transfer**					3000	120	0.6	Same as BG	N
		5	**Grinding**					2740	100	0.6	Same as BG	N
		6	**fibers weighing and packaging**					3500	640	0.75	Same as BG	N
		7	**Cleaning**					5000	510	1.1	TiO_2 fibers (submicron length with diameter varying b/w 150 to 500 nm)	Y
5/ TiO_2 & Ag NP	Manu–facturer	-	BG	Spray of TiO_2 and Ag NP onto the ceramic or glass tiles	N	Y	M	$1.3x10^4$	760	1	Soot and building particles	-
		1	**TiO_2 dispersion spray**					$1.5x10^4$	1420	1.15	Particles with size < 1 μm: K, Si and low quantities of Ti (1 to 2%)	Y
		2	**Ag dispersion spray**					$2.8x10^4$	10^4	2.1	NOAA of Ag NPs (10-40 nm)	Y
		3	**Tiles transfer**					$2.7x10^4$	2700	2.1	Same as BG	N
		4	**Thermal treatment**					$2.4x10^4$	2540	1.85	NOAA containing low quantities (1-2%) of Ti with metal particles from CA	Y
		5	**Tiles recovered**					$2.1x10^4$	1740	1.6	NOAA containing low quantities (1-2%) of Ti or Ag with metal particles from CA	Y
		6	**Cleaning**					$2.3x10^4$	1500	1.8	NOAA containing low quantities (1-2%) of Ti with metal particles from CA	Y
	Manu–facturer	-	BG	Extrusion of	N	N	B	$1.2x10^4$	900	1	Soot and building particles	N

6/ MWCNT		1	PP granules weighing	polymeric matrix charged with MWCNT				4200	570	0.35	Soot and building particles	N	
		2	**MWCNT powder weighing**					4100	520	0.34	Soot and building particles	N	
		3	**Mixture shaking**					6320	1560	0.5	Soot and building particles	N	
		4	**Feeder opening**					5500	640	0.46	Soot and building particles	N	
		5	**Mixture pouring**					6750	1080	0.56	Soot and building particles	N	
		6	**Extrusion**					$2.6x10^4$	6100	2.1	Crossed over, free, CNT NOAA and protruding CNT from the polymer matrix	Y	
		7	**Cleaning**					$3.3x10^4$	$1.5x10^4$	2.75	Abundant CNT NOAA	Y	

There is a higher particle size measurement range in the case of FMPS which allows detection of more particles than SMPS but here the difference is low because the aerosol size is mainly nanometric. Time resolved distributions of the emitted aerosol particles which were measured by the two sizers i.e. SMPS and FMPS and one counter i.e. CPC are shown in Figure 2 (b). The aim of this comparison is to validate the number concentrations obtained using CPC which are already shown in the Table 1. All the changes observed in the number concentration measured by CPC are also present in the cases of FMPS and SMPS, *e.g.* the increase in the number concentration as soon as the oven starts warming up and maximum concentrations when the oven attains the temperature set-point. The number concentration measured by FMPS illustrates short-term peaks whereas SMPS counting corresponds to an approximate average of these peaks (see Figure 2 (b)). However, there are differences in their measured values. These differences can be due to two facts: (i) the difference in the measurable size ranges of the three instruments; (ii) different conditions in the workplace during which these measurements were taken.

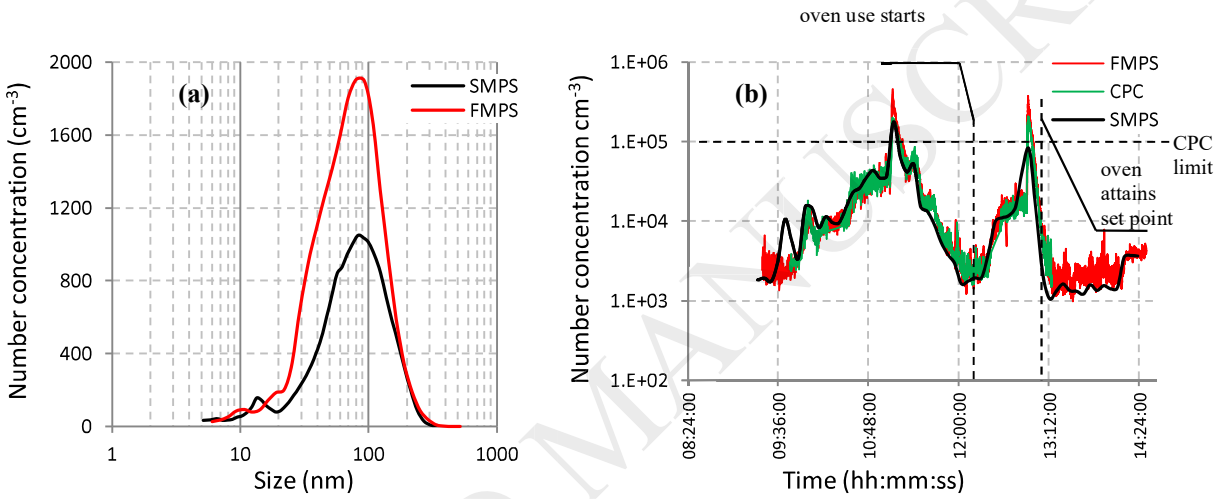


Figure 2: Comparison between (a) averaged particle size distributions of the emitted aerosol particles measured by SMPS and FMPS during the entire operation of PL1 (std. dev. for SMPS: 4 to 2094 cm^{-3} and for FMPS: 0.4 to 3615 cm^{-3}); (b) total number concentrations measured by SMPS and FMPS with the number concentration measured by CPC during the entire operation of PL1

Process Line 2

PL2 uses a confined spray drying chamber to generate aggregated or agglomerated powders of ZrO_2 NPs. The operation to test the BG was carried out in the solution preparation room before starting the spray drying process of the ZrO_2 NPs (see Table 1). The number concentration of the BG particles in the room was about 4,000 cm^{-3}. The fluctuations observed, once the process started, are provided in the Table 1. Apart from a single micronic NOAA of ZrO_2 (during step 7), no significant emission was detected. Since no particle containing Zr was found over other ten grid squares, this emission can be neglected.

Process Line 3

PL3 produces polyamide nanofibers using an electrospinning process. While doing the BG characterization for the PL3, the absence of a chemical element that can act as a polyamide nanofiber tracer (a reference to identify the presence of polyamide nanofibers) for its detection complicated the task. Indeed, carbon and oxygen, which are main constituents of polyamide nanofibers, were commonly detected in the particles present in the ambient air. Nitrogen was the only element present in the nanomaterial that was less commonly detected in the ambient air particulates collected on the TEM grids. The task therefore got oriented towards the search of fibers in the ambient air samples that contained nitrogen. As detailed in the Table 1, no exposures were detected obtained during the entire PL.

Process Line 4

PL4 uses an electrospinning process to generate TiO_2 nanofibers. Five minutes prior to turning on the oven, the background particles analysis was carried out. The results, provided in the Table 1, account from the point when the electrospinned fibers calcination starts, i.e. when the fibers were placed in an oven at 240°C for a few minutes and were then collected, ground and weighed. The number concentration variation with time, during these steps, is summarized in Table 1.

The TEM images of the aerosol particles, which were sampled during the manipulation processes are shown in Figure 3 (a) and (b). Out of the twenty TEM grid squares analyzed, all contained at least two fibers with a maximum of 14 fibers and an average of nearly 8 fibers per quadrant. As a result, the cleaning step of the PL4 led to an exposure of submicronic fibers (see Table 1).

Process Line 5

The dispersion spraying on tiles is a common process to modify their surface properties. PL5 aims to produce such modified tiles by using pulverized dispersions of TiO_2 and Ag NPs respectively. Prior to the PL operation, no Ti or Ag objects were detected in collected samples during BG sampling (see Table 1).

The spraying step was performed in two stages. The first stage consists of spraying a dispersion containing 1 wt% of TiO_2 NPs onto a first batch of tiles. Twenty minutes later, the operator sprays a similar dispersion of Ag NPs on another batch of tiles of the same type. The Table 1 shows the results. Throughout the entire period, a slow increase in the count was observed, followed by a sharp increase in the particle concentration a few minutes after the silver-based aqueous dispersion was sprayed. The microscopic images of the particles sampled during cleaning, filling and spraying steps are shown in Figure 3 (e) – (g). Five out of six steps of PL5 were found to be prone to an exposure (see also Table 1).

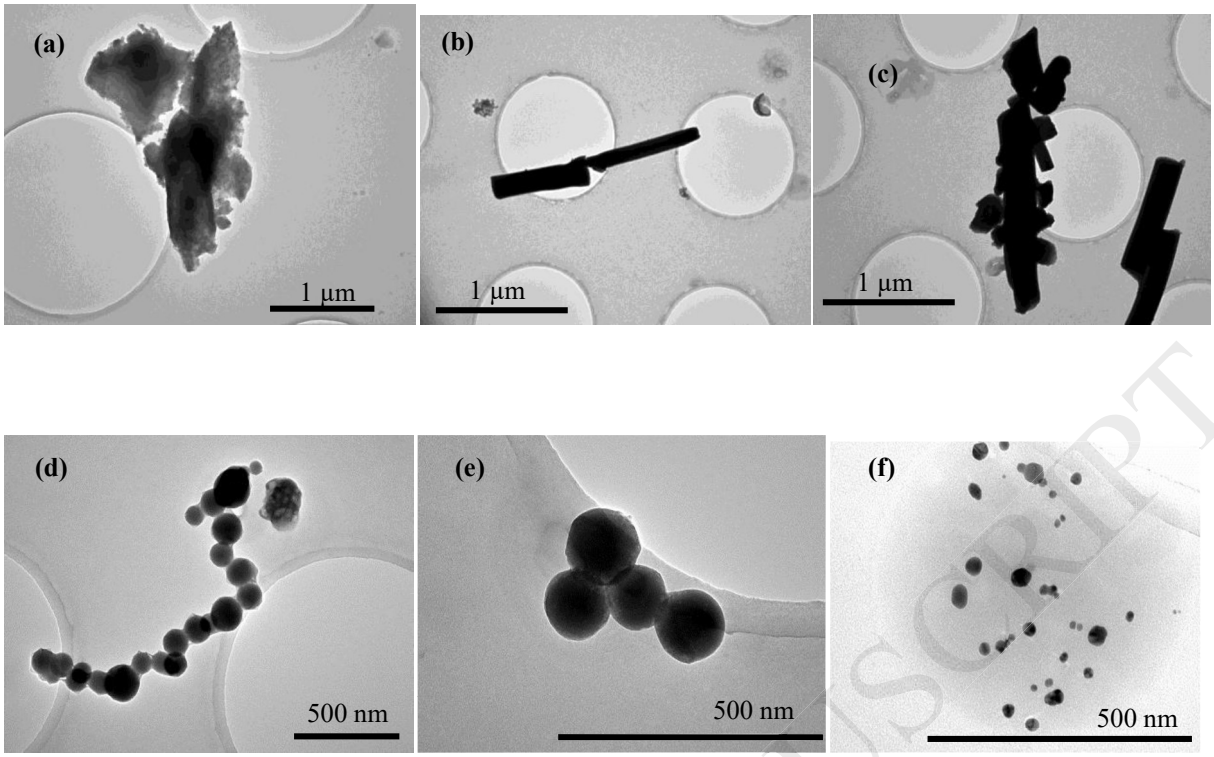


Figure 3: (a) TEM image of a particle containing Zr observed during opening of the oven and transport of the dried powder. (b) & (c) TEM image of the sampled aerosol particles during PL4 operation. (d) & (e) TEM images of the particles sampled during cleaning and filling steps; TiO_2 content: 1-2%; (f) Examples of NOAA of Ag and their clusters sampled during Ag based dispersion spray

Process Line 6

PL6 is based on extrusion of a MWCNT reinforced polymer matrix. No NOAA of CNT were identified during BG sampling (see Table 1). The extrusion produced a slow increase in the number concentration with short peaks particularly in the cleaning step (see Table 1). CNT objects collected during extrusion (Figure 4 (a-e) and cleaning (Figure 4 (f)) highlight these two steps as emissive one. Two steps out of seven, i.e. the extrusion and the cleaning, were identified as emissive. Both free CNT as well as inhalable NOAA (bundles or submicronic objects), made of CNT and polymeric matrix, were detected in this emission.

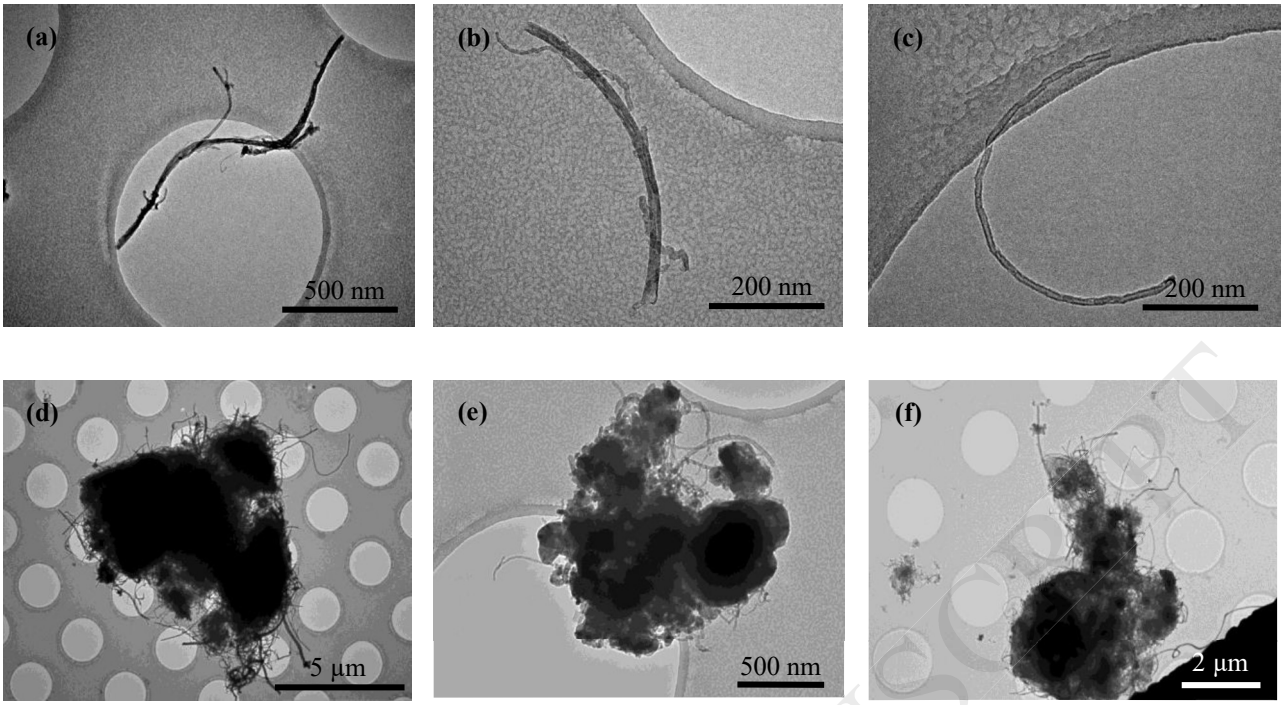


Figure 4: (a) - (d) Different forms of the sampled CNTs during extrusion process; (e) submicronic NOAA made of CNT and polymeric matrix (f) CNT bundle sampled during cleaning step of the PL6

Process Lines Ranking

Based on the results in Table 1 and the microscopic observations, the six PLs are ranked in Table 2. An exposure is declared in case of NP or NOAA on the sample obtained in the PL. The emission levels ratio is then estimated using a ratio between the emissive step counting and the BG counting.

Table 2 Ranking of the PL based firstly on presence of objects from PL origin on TEM grids and secondly on R' ratio; $\boldsymbol{CPC'_{mean}}$: Mean of individual $\boldsymbol{CPC_{mean}}$ of the emissive steps in a PL from Table 1 *(emissive step in PL1: step 5; no emissive step in PL2 and 3; emissive step in PL4: step 7; emissive steps in PL5: steps 1, 2, 4, 5 and 6; emissive steps in PL6: steps 6 and 7)*; $\boldsymbol{BG}$: Average number concentration of the particles present in the background before starting the production or manipulation of the nanomaterials; $\boldsymbol{R' = CPC'_{mean}/BG}$;

PLs	Exposure level	Remarks on exposure from sampling analysis	BG (cm^{-3})	CPC'_{mean} (cm^{-3})	R' (#)

1	High exposure	Emission of NP of ZrO_2 particles during its powder retrieval and transport	5360	$7x10^4$	13
6	High exposure	High number concentration of the free, entangled and bundled CNT during extrusion and cleaning	$1.2x10^4$	$3x10^4$	2.5
5	Exposure	Emission of some NOAA containing low quantities of Ti and Ag during spray, thermal treatment and cleaning	$1.3x10^4$	$2.2x10^4$	1.7
4	Exposure	Emission of free TiO_2 submicronic fibers during cleaning	4650	5000	1.1
2	No exposure detected	No emission of ZrO_2 particles (except one NOAA of ZrO_2 during powder retrieval and transport which is considered to be negligible as per the STS approach criterion)	4000	-	-
3	No exposure detected	No emission of the polyamide nanofibers	3200	-	-

4. Discussion

The present article deals with the results of a semi-quantitative exposure assessment campaign which was carried out at six different PL concerned with the production and manipulation of nanomaterials. Apart from ZrO_2 nanoparticles, the types of the nanomaterials chosen for the present study belong to the pool of the most widely-used nanomaterials in Europe and the world (Piccinno et al., 2012). The typical workplaces involved with the nanomaterials production and their manipulation i.e. R&D laboratories and commercial manufacturing sites with varying surface sizes (from 20 to 300 m^2) are also considered in this study. Some of these workplaces had natural ventilation systems. We were also able to track and characterize NP or NOAA emission in workplaces having diverse characteristics like co-activities (*e.g.* welding) different air flow patterns, or dimension variability.

Data gathering

Before starting the semi-quantification of the aerosol particles, a step-wise information gathering about the processes, materials and workplaces is required and done through preliminary visits. Once all the information is gathered and analyzed, the exposure assessment campaign is then carried out. Such a campaign provides a visual perception of the workplaces (process and work practices). At the same time, the information collected during this visit could provide useful inputs like exposure scenarios, process information, details regarding ventilation and the need of the personal protection equipment to carry out the risk assessment studies.

Approach comparison in PL1

The number concentration results obtained by the CPC, SMPS and FMPS on the PL1 were validated by showing a good agreement between the three. The PL1 was chosen for the comparison purpose because the conditions like forced ventilation in the absence of a co-activity and small size of the production facility were ideal to do so A prior increase in the number concentration (during steps 1 to 4), attributed to the incidental emission of particles during production process, was observed. This can be proved by noting the corresponding value of $C_{net\text{-}BG}$ equal to 6288 cm^{-3}, in the Table 1 during the

opening of an empty warm oven door. This value of $C_{net\text{-}BG}$ can be explained on the basis of (i) an ambient air agitation due to the warming up of the oven, and (ii) drying of the material with the contained residual moisture in the oven by the evaporation of residual moisture which in turn produces water droplets counted as particles by FMPS, SMPS or CPC. Nevertheless, the detected particles on the TEM grid are solely solid objects. These two facts can also explain the high particle number concentrations during steps 3 and 4 but with a total absence of ZrO_2 particles in the sample particles population. The specific cases of incidental emissions due to oven warming-up or water droplets generation are regularly observed at workplaces and perturb a precise assessment (Dolez and Debia, 2015). The STS and three-tiered approaches are in accordance with each other, thus confirming the exposure in the PL1. But the results included in the Table 1 illustrate that the STS approach can specifically detect a NP emission by identifying a huge number of ZrO_2 particles (confirmed by EDS analyses), during a unique step *i.e.* step 5 of oven opening in the PL1 in the middle of incidental emissions.

Hence, while employing the three-tiered approach on PL1, we identified the inherent complimentary nature of the STS approach to the three-tiered. The three-tiered approach is an important tool to identify and evaluate the potential exposure sources. However, the STS approach gives the opportunity to refine these potential sources because of short-term exposure distinctions. This is of utmost importance to the Small or Medium Enterprise (SME) which represented 75 % of the EU companies dealing directly with nanotechnology and manufactured nanomaterials in 2012 (EU OSHA, 2012). Identifications of exposure sources becomes also easier for them and can lead to the opportunity to modify the certain identified steps rather than the entire PL.

STS Approach Advantages

Thanks to the MPS-TEM couple, the major advantage of the STS approach is the opportunity to distinguish easily NP or NOAA from BG. The emission determination is hugely facilitated (as shown in Table 1). In this case, even the emissions with very short durations are observable and can be characterized, as done, for instance, in the step 7 (cleaning) of the PL4, all spraying related steps of the PL5 and steps 6 and 7 (extrusion and cleaning) of the PL6. The cleaning steps are crucial to the exposure assessment (Ham et al., 2012; Kaminski et al., 2015; Zimmermann et al., 2012). Similarly, the spraying step is known as one of the highest emission sources (Bekker et al., 2015; Wake et al., 2002). Regarding the extrusion process, previous studies highlight the difficulties to assess an emission (Brouwer et al., 2014a; Dahm et al., 2013).

The STS approach offers an opportunity to characterize an emission of the nanomaterials or inhalable objects with any size or shape. Their emissions may even occur without any increase in the aerosol particles number concentration. The exposure in the case of PL4's step number 7 illustrates such condition. The sampled TiO_2 fibers were of submicron length with diameters varying from 150 to 500 nm. Despite these dimensions, an exposure has been clearly detected while the corresponding number concentration level was close to the BG number concentration (5000 cm^{-3}, R=1.1; see Table 1).

The STS approach has led to characterize free CNTs as well as different inhalable NOAA like CNT bundles or CNT composites, nano-Ag and nano-TiO_2. Moreover, the relative magnitude of such an emission as well as the emission's capacity to reach the breathing zone of workers can also be easily determined using the STS approach.

The easy NOAA distinction from the stray particles is another potential advantage of the STS approach as confirmed by the results obtained in the cases of PL5 and PL6 (see Table 1).

In this context, some previous studies describe NOAA characterization at workplaces (Bekker et al., 2015; Brouwer et al., 2014b; Brouwer et al., 2013). The more recent paper uses nickel coated polycarbonate filters in the IOM sampler followed by SEM characterization in the absence of step-by-step information (Bekker et al., 2015).

Emissions from the PL

The ranking proposed in Table 2 shows that the PL1 (oven opening in particular) renders highest emission followed by the PL6 (extrusion and cleaning) and then the PL5 (spraying and curing). Regarding the PL4, the unique emission is a cleaning step. The spray drying process (i.e. PL2) and the production of polyamide nanofibers (i.e. PL3) are considered as non-emissive because of the absence of NP / NOAA or nanofiber upon sampling. In our study, 8 out of 37 steps were found to be prone to a NP or NOAA exposure. Only one of the 37 steps highlights solely NP exposure (i.e. oven opening of PL1). This observation confirms the important part of NOAA exposure at workplace instead of NP one in accordance with recent literature (Bekker et al., 2015; Brouwer et al., 2014a; Brouwer et al., 2014b; Brouwer et al., 2013). In addition, one step leads to an exposure of submicronic fiber (cleaning, step 7 of PL4). In other words, 24 % (9 out 37) of the steps highlight exposures whatever the emitted materials i.e. submicronic fiber, NOAA or NP but two thirds of the PLs are implicated in almost one exposure step. Some of these nine steps giving rise to an exposure (*e.g.* cleaning step of the PL4) were not accompanied with a significant number concentration increase. The interest of our STS approach is thus confirmed by the possibility to distinguish an exposure in such conditions.

A complementary approach yet to be improved

Apart from these added values, the STS approach does suffer from some limitations. The first worthy of mention is the absence of the information on size resolved number concentration.

Sizing (using three-tiered approach) has been performed on the PL1 but limited to the comparison purpose. The use of counters in this approach allows the integration of the exposure, reducing measures quickly and cheaply into any production or manipulation step.

Quantitative sizing measurement could improve emissions data to provide a more precise assessment of NP fraction of the aerosol. Another limitation noted during the exposure evaluations involved the upper dynamic measurement range of the CPC which is equal to 10^5 cm^{-3}. Therefore, all data exceeding this value (as shown in figure 2 (b) and Table 1) should be interpreted with caution because an underestimation of the true particle number concentration will result (Asbach et al., 2012). Another drawback of this approach shows is the absence of long-term exposure assessment. As a result, the data presented here cannot be used for a thorough toxicological assessment or control banding.

5. Conclusions

The study presented here aims at verifying the applicability of the STS approach in a representative set of European SME's dealing with nanomaterials, which is today needed in industry (De Rademaeker et al., 2014) on the basis of interdisciplinary approaches (Gehin et al., 2016). A comparison has been performed with the three-tiered approach. The results confirm exposures at some workplaces. The STS approach identified eight steps prone to short-term exposures of nanoparticles or NOAA out of total 37 steps distributed in six process lines (PL). Another additional exposure of submicronic fibers of TiO_2 has been characterized thanks to TEM sampling and despite a low counting increase. During the entire study, the leading potential exposure sources were found to be the steps like manipulation (e.g. PL1, 4, 5 and 6), spraying (e.g. PL5) and cleaning (e.g. PL4 and 6). In addition, high emissions observed in the handling steps are consistent with the large amounts of nanoparticles reported in the basic information gathering of the PL1, 4, 5 and 6.

The process like spray drying (i.e. PL2) or electrospinning (i.e. PL3) are generally performed in a complete confinement and therefore exhibited no detectable emissions. The low intrinsic emissivity of the nanofibers or the containment of the machines producing the nanofibers effectively prevented their emission in the workplace. As a result, the handling of ZrO_2 NP (i.e. PL1) was observed to impart maximum potential exposure and minimum for the polyamide nanofiber production (i.e. PL3). In most cases where the exposure was detected, it was seen that no free primary particles but only NOAA (both > and < 100 nm) got emitted (e.g. PL5). In the case of fibrous materials, like fibers of TiO_2 (i.e. PL4) and MWCNT (i.e. PL6), their emission was found to be intermittent. The presence of their free strands as well as their bundles was detected in the ambience. As long as the nanomaterials existed in the form of suspension (e.g. PL2 and 3), no exposure was detected. The use of an oven (as in the cases of PL1 and 5) was also found to be critical in the terms of exposure.

Author contribution

Bressot, Christophe directed, prepared and performed the experiments with the assistance of Shandilya, Neeraj, who also edited parts of the manuscript. Jayabalan, Thangavelu, Le Bihan, Olivier, Voetz, Matthias and Meunier, Laurent contributed to the measurement campaings. Fayet, Guillaume provided input to the assessment method. Morgeneyer, Martin and Aguerre-Chariol, Olivier contributed to the scientific analysis of the measurement data and to the conceptual implementation of the method.

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