Worker exposure to airborne particles in industrial settings: evaluation of exposure assessment and modelling tool

Carla Ribalta Carrasco

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Worker exposure to airborne particles in industrial settings: evaluation of exposure assessment and modelling tools

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PhD Thesis
Barcelona, May 2019

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Abstract

Exposure to particulate matter in work environments has been linked to ischemic heart, cardiovascular and respiratory-related disease risk increase due to inhalation. Increased adverse health effects have been linked to nanoparticles (< 100 nm) due to their ability to reach the deepest sections of the respiratory tract and their longer retention time. Exposure monitoring is widely used method to assess worker exposure to airborne particles. However, other prediction tools have been explored such as the use of the dustiness index, mass-balance models, and health risk assessment tools. Discussions regarding the use and application of the latter tools are ongoing due to their relatively novelty for worker exposure assessment, the need to test their performance under real-world scenarios, and the need to understand the uncertainties related to critical parameters and limitations.

The main objectives of this PhD Thesis are to 1) assess worker exposure to particles (4 nm - 35 μm) in ceramic industry real-world workplace scenarios; 2) evaluate currently used exposure assessment metrics and decision-making approaches; 3) understand the relationship between material dustiness and worker exposure; 4) evaluate the performance of mass-balance models, and 5) compare health risk assessment tools.

Worker exposure was assessed during mechanical handling of powders in 6 different scenarios and for 15 materials as well as thermal spraying of ceramic coatings. Exposure monitoring was conducted using online and offline instruments which allowed for the characterization of particle mass and number concentrations, particle size and size distribution, particle morphology and chemical composition. In addition, some of these scenarios were also selected to assess relationship between the dustiness index and exposure concentrations as well as the ability of different particle metrics to represent worker exposure. Finally, decision making approaches, and the performance of mass-balance models and risk assessment tools were tested. Results evidenced clear impacts of industrial activities on workplace exposure to coarse, fine and nanoparticles.

Significant increases of inhalable and respirable particle mass concentrations (inhalable mass concentration 80-4000 μg m⁻³) were observed during mechanical handling of raw materials (d₅₀ 2.7-40 μm), when compared to background concentrations. The highest mean inhalable mass concentration (3700 μg m⁻³) was monitored during packing of ceramic materials, when mitigation strategies were inefficiently implemented.
Conversely, particle number concentrations were not influenced by mechanical handling of powders, but by driving of diesel-powdered forklifts, leading to concentrations up to 70000 cm$^{-3}$. Thermal spraying, on the other hand, increased particle number concentration up to $10^5$ cm$^{-3}$ in the worker area. After the application of the ICRP respiratory tract deposition model, airborne particles in the workplaces studied were seen to deposit mainly in the alveolar region (51-64%) during packing of powder materials and (54-70%) during thermal spraying by means of surface area. Source enclosure and modification of the energy settings were pointed out as useful strategies to minimize worker exposure.

The validity, performance and comparability of tools for exposure assessment were evaluated. Several decision-making approaches were tested to determine statistically significant impacts on exposure. Among them, the ARIMA models were seen to be the least conservative while the nanoGEM approach confirmed its usefulness for particle number but slightly underestimated exposure for particle mass concentrations when compared to traditional statistical tests. High degree of correlation was found between dustiness and measured exposure concentrations during mechanical handling of powders in a pilot plant ($R^2$ up to 0.97) and at industrial scale ($R^2$ up to 0.80). This correlation was stronger when material characteristics dominated over process characteristics, and an adequate methodology is applied, using the dustiness method which best mimics the activity under study.

Finally, one- and two-box models were used to model particles under high and low concentrations in terms of mass and particle number concentrations. Ratios between modelled and measured concentrations were 0.82-1.22 when modelling inhalable particle mass in the mechanical handling scenario, whereas ratios of 0.2-0.7 were obtained when modelling thermal spraying particles. Thus, model performance was poorer for the high nanoparticle concentration scenario. The addition of background and outdoor concentrations as input improved model performance. Risk assessment and control banding tools (ART, Stoffenmanager and NanoSafer) were tested for the scenarios under study, and it was concluded that the mechanical processes were estimated with higher accuracy and lower variability by Stoffenmanager (64% of the cases). Conversely, ART and NanoSafer showed higher flexibility for introducing more case-specific input data. A clear need for harmonization between risk assessment tools was evidenced.
L'exposició per inhalació de material particulat en ambients de treball ha estat relacionat amb l'augment del risc de patir malalties cardiovasculars y respiratòries. En el cas específic de les nanopartícules (< 100 nm), els efectes adversos han estat relacionats amb la seva capacitat per arribar a les regions més profundes del aparell respiratori i al seu major temps de retenció. Per tal de determinar els nivells d'exposició a material particulat, un mètode experimental àmpliament utilitzat és l’ús d'equips de mesura en continu de les concentracions. No obstant això, altres eines estan sent actualment explorades com per exemple l’ús del poder d’emissió de pols dels materials, models basats en balanços de masses per a la predicción de l’exposició, així com eines per a l'avaluació del risc per a la salut degut a l’exposició d’agent químics. No obstant això, degut a la seva relativa novetat, existeix la necessitat d’avaluar la validesa de totes aquestes eines en escenaris reals, així com de comprendre les incerteses relacionades amb els paràmetres i les seves limitacions. Per tant, el seu us i aplicació es troben actualment en debat.

Els principals objectius d’aquesta tesi doctoral són: 1) avaluar els nivells d'exposició laboral a material particulat d’entre 4 nm i 35 μm en escenaris de treball reals, 2) avaluar les diferents mètriques existents per a l’avaluació dels nivells d’exposició i els mètodes de presa de decisions utilitzats en la actualitat; 3) comprendre la relació existent entre el poder d’emissió de pols dels materials i els nivells d’exposició dels treballadors durant la seva manipulació; 4) avaluar la validesa del models basats en balanços de massa; i 5) comparar diferents eines d’avaluació dels riscos de l’exposició a agents químics.

En aquesta tesi s’han avaluat els nivells d’exposició laborals a material particulat, tant durant manipulació mecànica, concentradament de 15 materials pulverulents en 6 escenaris diferents, com durant projecció tèrmica de recobriments ceràmics, amb l’estudi de 2 escenaris amb tres materials per a l’obtenció de recobriments ceràmics sobre peces metàl·liques. El control experimental dels nivells d’exposició es va realitzar mitjançant l’ús d’equips de mesura de partícules en temps real i de la recol·lecció de mostres gravimètriques del material particulat emes, que va ser posteriorment analitzat per microscòpia electrònica. Tot això va permetre la caracterització de la concentració del material particulat en massa, numero de partícules, mida i distribució de mida de les partícules, la morfologia de les partícules i la seva composició química. Addicionalment, en els processos mecànics es va avaluar la relació entre el poder d’emissió de pols dels
materials i els nivells d’exposició, així com la capacitat de diferents mètriques, generalment utilitzades per a l’anàlisis de l’exposició a partícules (massa i numero), de representar l’exposició dels treballadors. Finalment, es van estudiar diferents mètodes per a la presa de decisions, es va avaluar la aplicabilitat en condicions industrials dels models basats en balanços de massa, així com de tres eines per a l’avaluació dels riscs per exposició a agents químics. Els resultats van evidenciar un clar impacte de les activitats industrial estudiades sobre els nivells d’exposició dels treballadors en els escenaris estudiats a partícules grolleres, fines i nanopartícules.

Durant la manipulació mecànica de matèries primeres ($d_{50}$ 2.7-40 μm) es van observar augmentes significatius de les fraccions màssiques de pols inhalable i respirable (concentració de massa inhalable 80-4000 μg m$^{-3}$) en comparació amb les concentracions de fons. La concentració mitjana més elevada per a la fracció màsica inahlable (3700 μg m$^{-3}$) va ser mesurada durant l’ensacat de materials ceràmics amb una implementació ineficient de mesures de mitigació. Per el contrari, les concentracions en numero de partícules no es van veure influenciades per la manipulació mecànica dels materials pulverulents, però si que es van registrar concentracions de numero de partícules de fins $7\times10^4$ cm$^{-3}$ degut a l’ús de carretons elevadors dièsel. Per una altra banda, en els escenaris de projecció tèrmica es va observar un augment de la concentració en numero de partícules de fins a valors del ordre de $10^5$ cm$^{-3}$ en l’àrea de treball. Mitjançant l’aplicació del model de deposició de partícules ICRP, es va observar que les partícules en suspensió en els llocs de treball estudiats es depositaven principalment en la regió alveolar tant durant l’ensacat (51-64%), com durant la projecció tèrmica (54-70%). L’aïllament de la font d’emissió així com la modificació de l’energia aplicada durant el procés es van detectar com a estratègies útils per a minimitzar l’exposició dels treballadors.

També es va avaluar la validesa, el rendiment i la comparabilitat de varies eines estadístiques per a avaluar la significança estadística de les dades d’exposició. D’entre els mètodes evaluats, els models ARIMA van ser considerats com als menys conservadors, mentre que la metodologia nanoGEM va confirmar la seva utilitat per a l’anàlisis de les concentracions en numero de partícules, però va subestimar lleugerament la significança estadística de les concentracions en massa en comparació amb les proves estadístiques tradicionals. Es van trobar alts graus de correlació entre el poder d’emissió de pols del materials i les concentracions d’exposició mesurades durant la manipulació mecànica.
Resum

dels materials en planta pilot ($R^2$ fins a 0.97) i en escala industrial ($R^2$ fins a 0.80). Aquesta correlació s'ha vist reforçada quan les característiques dels materials dominen sobre les característiques del procés, i quan una metodologia adequada per a la determinació del poder d' emissió de pols va ser utilitzada, aquella que millor simula el procés d'estudi.

Finalment, es van utilitzar els models basats en balanços de massa de una i dos caixes per a modelar dos escenaris diferents, un de baixa exposició a partícules grolleres (manipulació mecànica, ensacat de materials) y un altre d'altres concentracions de numero de partícules (projecció tèrmica). Les proporcions entre les concentracions modelades/mesurades van ser de 0.82-1.22 per a la modelització de la fracció màssica de pols inahalble en el cas de la manipulació mecànica, mentre que les proporcions van ser de 0.2-0.7 per a la modelització de la concentració en numero de partícules durant la projecció tèrmica. Per tant, la bondat dels models basats en balanços de massa va ser menor en l'escenari d'altes concentracions de numero de partícules. Al considerar les concentracions de fons i de l'aire ambient en els models, la bondat i la precisió dels models va augmentar. De les tres eines per a l'avaluació de riscos per exposició a agents químics (ART, Stoffenmanager i NanoSafer) que van ser provades, les concentracions mesurades durant els processos de manipulació mecànica van ser estimats amb una major precisió i menor variabilitat per Stoffenmanager (64% dels cases). Per el contrari, ART i NanoSafer van mostrar tenir una major flexibilitat per a introduir dades d'entrada específiques per a cada cas.
RESUMEN

La exposición por inhalación a material particulado en ambientes de trabajo se ha relacionado ampliamente con el aumento del riesgo de enfermedades cardiovasculares y respiratorias. En el caso particular de las nanopartículas (< 100 nm), los efectos adversos sobre la salud se ha postulado que se deben a su capacidad para llegar a las regiones más profundas del tracto respiratorio y a su mayor tiempo de retención. Para la determinación de los niveles de exposición a material particulado, un método experimental ampliamente utilizado es la monitorización en continuo de las concentraciones ambientales. Sin embargo, también se están explorando herramientas de predicción, como por ejemplo el uso del poder de emisión de polvo, modelos basados en la aplicación de balances de materia, así como herramientas de evaluación de riesgos por exposición a agentes químicos. No obstante, debido a su relativa novedad, existe la necesidad de evaluar la validez de todas estas herramientas en escenarios reales, así como de comprender las incertidumbres relacionadas con los parámetros y sus limitaciones. Por tanto, su uso y aplicación se encuentran actualmente en debate.

En este contexto, los principales objetivos de esta tesis doctoral son: 1) evaluar la exposición laboral a partículas de entre 4 nm y 35 μm en escenarios de trabajo reales; 2) evaluar las diferentes métricas de evaluación de la exposición y los métodos de toma de decisiones utilizados en la actualidad; 3) comprender la relación entre el poder de emisión de polvo de los materiales pulverulentos y la exposición de los trabajadores a material particulado durante su procesado; 4) evaluar la validez de los modelos basados en balance de materia para la predicción de la exposición, y 5) comparar diferentes herramientas de evaluación de riesgos de exposición a agentes químicos.

En esta tesis se ha evaluado la exposición laboral a material particulado, tanto en procesos mecánicos, -concretamente en la manipulación y envasado de 15 materiales pulverulentos en 6 escenarios industriales distintos- así como en procesos de proyección térmica, con el estudio de 2 escenarios con 3 materiales para la obtención de recubrimientos cerámicos sobre piezas metálicas. La monitorización experimental de la exposición se llevó a cabo utilizando instrumentos que miden la concentración de partículas en tiempo real, además se tomaron muestras, mediante sistemas de captación específicos, que posteriormente fueron caracterizadas por microscopía electrónica. Todo ello permitió la determinación de la concentración en masa y en número de partículas, el tamaño medio y la distribución del tamaño de las partículas, la morfología de las
partículas y su composición química. De forma adicional, en los procesos mecánicos se evaluó la relación entre el poder de emisión de polvo de los materiales pulverulentos y los niveles de exposición a material particulado, así como la capacidad de diferentes métricas (masa o número) para representar la exposición de los trabajadores. Finalmente, se probaron distintos métodos estadísticos para el tratamiento de datos y toma de decisiones, se evaluó la aplicabilidad en condiciones industriales de modelos basados en balances de materia, así como de tres herramientas reconocidas de evaluación de riesgos por exposición a agentes químicos. Los resultados evidenciaron un claro impacto de las actividades industriales sobre la exposición laboral a partículas gruesas, finas y nanopartículas.

Durante los procesos mecánicos de manipulación de materias primas ($d_{50}$ 2.7-40 µm) se observaron aumentos significativos de las fracciones másicas de polvo inhalable y respirable (concentración de polvo inhalable 80-4000 µg m$^{-3}$) en comparación con las concentraciones de fondo. La mayor concentración media de polvo inhalable (3700 µg m$^{-3}$) se midió durante el ensacado de materias primas cerámicas, con un bajo nivel de implantación de medidas correctoras. Por el contrario, las concentraciones en número de partículas no se vieron influenciadas por el procesado mecánico de materiales pulverulentos pero sí se registraron concentraciones elevadas del número de partículas, hasta de $7\times10^4$ cm$^{-3}$ debido al uso de carretillas elevadoras con motores diésel en interiores. Por otro lado, en los escenarios de proyección térmica se observó un aumento significativo del número de partículas, hasta valores del orden de $10^5$ cm$^{-3}$ en el área de trabajo. Mediante la aplicación del modelo de deposición de partículas en el tracto respiratorio ICRP, se observó que las partículas en suspensión en los lugares de trabajo estudiados se depositaban principalmente en la región alveolar, tanto durante el ensacado (51-64%) como durante la proyección térmica (54-70%). Se detectó que el confinamiento de las fuentes y la reducción de la energía aplicada durante el procesado son estrategias útiles para minimizar la exposición de los trabajadores.

También se evaluó la validez, el rendimiento y la comparabilidad de varios métodos estadísticos para evaluar la significancia estadística de los datos de exposición. De los métodos evaluados, los modelos ARIMA se consideraron los menos conservadores, mientras que el método nanoGEM confirmó su utilidad para tratar datos del número de partículas, pero subestimó ligeramente la significancia estadística de las concentraciones en masa en comparación con las pruebas estadísticas tradicionales. Se encontraron altos
Resumen
grados de correlación entre el poder de emisión de polvo de los materiales y los niveles de exposición medidos durante la manipulación mecánica de dichos materiales pulverulentos en planta piloto ($R^2$ hasta 0.97) y a escala industrial ($R^2$ hasta 0.80). Esta correlación se ha visto reforzada cuando las características de los materiales predominan sobre las características del proceso y se aplica el método de caracterización del poder de emisión de polvo que mejor se asemeja al proceso estudiado.

Finalmente, se utilizaron los modelos basados en balances de materia, concretamente los de una y dos cajas, para modelizar dos escenarios distintos, uno de baja exposición a partículas gruesas (manipulación mecánica) y otro de altas concentraciones de número de partículas (proyección térmica). La relación entre las concentraciones estimadas por el modelo y las medidas experimentalmente fueron de 0.82-1.22 cuando se modelizó la concentración másica de polvo inhalable en el escenario de procesado mecánico, mientras que las proporciones fueron de 0.2-0.7 cuando se modelizó la concentración en número de partículas emitidas durante la proyección térmica. Por lo tanto, la bondad de los modelos basados en los balances de materia fue menor en escenarios de alta concentración de nanopartículas. Al considerar que las concentraciones de fondo y del aire ambiente exterior no eran despreciables, se aumentó significativamente la bondad del ajuste entre los datos experimentales y los calculados por los modelos. De las tres herramientas de evaluación del riesgo por exposición a agentes químicos (ART, Stoffenmanager y NanoSafer) probadas, la que con mayor precisión y menor variabilidad estimó la concentración en los procesos mecánicos fue el Stoffenmanager (64% de los casos). Por el contrario, ART y NanoSafer mostraron una mayor flexibilidad para introducir datos de entrada específicos para cada caso.
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1. INTRODUCTION

1.1. Air pollution

Air pollution is defined as the presence of substances in ambient air, due to natural or anthropogenic causes, and which are likely to have harmful effects on human health and/or the environment (Mészáros 1999, Directive 2008/50/EC). Atmospheric pollution is currently considered as a major environmental health issue affecting nearly 90% of the global population, including low, middle, and high-income countries (Gakidou et al. 2017, WHO 2016, Landrigan et al. 2018). Specifically, in Europe, 74-85% of the population is exposed to PM$_{2.5}$ in higher concentration than recommended by the World Health Organization (WHO) (EEA 2018). Air pollution caused by particles and gaseous pollutants is estimated to cause more than 4.2 million premature deaths worldwide, from which 92% occur in low- and middle-income countries (Landrigan et al. 2018), and 400000 in the EU-28 (EEA 2018). However, air pollution is not only limited to outdoors but also found indoors and in workplaces, with humans spending nowadays approximately 90% of the time in indoor environments (Monn 2001) and 50% in workplaces (Klepeis et al. 2001). Indoor and workplace air quality is determined by their own type of source, which depends on the type of environment (homes, workplaces, transport systems, hospitals, schools...), and outdoor infiltration and influence, affected by outdoor air pollution, air exchange rates, penetration factors, as well as deposition and resuspension mechanisms (Chen and Zhao 2011). Due to the vast variety of indoor and workplaces, and their complexity and heterogeneity these type of environments are in general less studied than outdoor air pollution (Viana et al. 2011, Weschler 2011). However, recently, numerous studies have focused on air pollution covering exposure in homes and schools (Morawska et al. 2003, 2017, Hussein et al. 2005, 2006, Mazaheri et al. 2014, Reche et al. 2014, Isaxon et al. 2015, Rufo et al. 2015, Klepeis et al. 2017, Zhang et al. 2018), in public transport systems and during commuting (Onat and Stakeeva 2014, Martins et al. 2016, Yan et al. 2015, Minguillón et al. 2018, Strasser et al. 2018), and in different workplaces such as offices, industries, mining and airports (Koponen et al. 2001, Koivisto et al. 2010, Möller et al. 2014, Morawska et al. 2017, Viitanen et al. 2017) among others. The present PhD Thesis focuses on the industrial workplace exposure as research topic, specifically focusing on particle pollutants.
1.2. Workplace exposure to airborne particles

1.2.1. Aerosol formation and exposure

Aerosols are a mixture of particles (single continuous unit of solid or liquid, or two or more held together by inter-particle adhesive forces, containing many molecules held together by intermolecular forces) suspended in the air (Steinfeld and Pandis 2006). Ambient air contains particle pollutants originated from natural (organic, e.g., pollen, bacteria or virus, or inorganic, e.g. mineral dust, sea salt or volcanic released aerosols), and anthropogenic sources (result of processes related to human activities). Airborne particles typically range between few nanometres up to approximately 100 µm (Figure 1.1). Therefore, exposure is generally assessed as a function of particle size and described as exposure to coarse (> 2.5 µm), fine (< 2.5 µm) and ultrafine particles (UFP) (< 100 nm) (Figure 1.2). It should be noted that in the aerosol research field particles < 100 nm are referred to as UFP and those < 50 nm as to nanoparticles (NPs), whereas in the nanotechnology field particles < 100 nm are referred to as NPs. In this Thesis we will use the term “nanoparticles, NP” as defined in the nanotechnology field (< 100 nm).

![Figure 1.1 Comparative schemes of objects size in a nanometer scale and common atmospheric pollutants sizes. Source: modified from Fonseca (2016), Jensen (2019) unpublished figure by Koivisto, AJ) and Savolainen et al. (2013).](image)
Particles behaviour in the air is dominated by formation and transformation processes. Aerosols are commonly divided by their formation mechanisms as follows (Figure 1.2):

- **Nucleation mode (< 20/30 nm)**: new particles formed from gaseous precursors (mainly $\text{H}_2\text{SO}_4$, $\text{NH}_3$ and VOCs) in a super-saturated environment without help of condensation nuclei (Kulmala *et al.* 2004, Kumar *et al.* 2010). They quickly tend to coagulate with other particles or grow by condensation (Charron and Harrison 2003, Rodriguez *et al.* 2005, Kumar *et al.* 2010). The nucleation mode also contains primary particles such as a fraction of exhaust vehicle emissions.

- **Aitken mode (20-100 nm)**: includes directly emitted combustion particles and soot, and those which evolve by coagulation and condensation (which implies particle growth) processes on pre-existing particles (Wehner and Wiedensohler 2003, Kulmala *et al.* 2004, Steinfeld and Pandis 2006).

- **Accumulation mode (0.1-1 µm)**: includes combustion, smog particles, marine organic and coagulated nucleation/Aitken mode particles (Hinds 1999, Steinfeld and Pandis 2006, Rodriguez *et al.* 2007). Particles coagulation kinetics is usually slow and they do not reach the coarse mode, hence, they have a relatively long lifetime in the atmosphere (Harrison *et al.* 2000, Kumar *et al.* 2010).

- **Coarse mode (> 2.5 µm)**: this mode is mainly composed by primary particles originated by mechanical processes. It includes windblown dust and mechanically generated

![Figure 1.2](image)

**Figure 1.2** Relationship between mass and number distribution of atmospheric aerosols by particle size, and particle formation and transformation processes. Source: modified from Watson and Chow (2007) and Fonseca (2016).
anthropogenic particles (e.g. agriculture or mining), large salt particles from sea spray, and pollen (Harrison et al. 2000, Raes et al. 2000, Steinfeld and Pandis 2006). Because of their large size, particles readily settle out or impact on surfaces, so their lifetime in the atmosphere is short (generally few hours or days).

Exposure is defined as the state or condition of being unprotected and open to damage, danger or risk. Exposure to particles can occur through dermal or oral inhalation route, the latter being regarded as the main exposure route. Standardization of worker exposure in occupational settings is very complex as workplaces are very diverse and particle sources are highly case-specific. In addition, industrial emissions have the added complexity of being extremely variable over time, shift and location, as they are influenced by a mixture of time changing processes (Ramachandran 2005). Thus, having exactly the same combination of sources in different periods of time is quite unlikely. Whereas the impact of particles on human health is linked to their physicochemical and functional properties (Oberdörster and Kuhlbusch 2018), particle size is one of the most important factors driving the potential adverse health effects of exposure to airborne particles (Aitken et al. 2004, Sánchez-Jiménez et al. 2011). For airborne particulate matter (PM), the most common metric generally used is mass concentration as occupational exposure limits (OELs) are established in terms of mass (NIOSH 2002, Aitken et al. 2004). However, particle number concentration and surface area are also used.

1.2.2. Exposure to micro-sized particles

Occupational exposure to PM, as established in ISO 7708:1995 and UNE-EN 481 1995, is usually reported in terms of (Figure 1.3):

- **Inhalable mass**, the mass fraction of total airborne particles which is inhaled through the nose and mouth. The inhalable criterion has 100% penetration for particles < 10 µm, dropping to 50% for 100 µm particles and has no median cut-off aerodynamic diameter.

- **Thoracic mass**, the mass fraction of inhaled particles penetrating beyond the larynx. The curve has a median diameter of 11.64 µm and geometric standard deviation (GSD) of 1.5.

- **Respirable mass**, the mass fraction of inhaled particles penetrating to the unciiliated airways, with a median aerodynamic diameter of 4.25 µm and 1.5 GSD.
Exposure to micron-sized airborne particles in occupational environments mainly occurs due to mechanical processes such as cutting, breaking and crushing, drilling, abrasive and sand blasting, digging or hammering, and during dry handling due to particle release and/or resuspension (pouring, cleaning, mixing or polishing, among others) (WHO 1999, Finlayson-Pitts and Pitts 2000, NIOSH 2002, Chiu Leung et al. 2012). Particle shape and chemical composition in occupational exposure are very diverse and highly dependent on the type of activity, e.g. farming (predominance of PM$_{10}$ particles, fibres and microorganisms with organic composition, feces, skin, and feed) (Cambra-López et al. 2010, Viegas et al. 2013), agriculture (mainly mineral particles such as silica and aluminium) (Schenker et al. 2009, Dewangan and Patil 2014) or mining (metals and inorganic components) (Dubey et al. 2012).

![Figure 1.3](image-url) Probability of aerosol penetration as a function of aerodynamic diameter, internationally agreed by CEN/ISO/ACGHI. Source: modified from Sánchez Jiménez et al. (2011).

In the case of the ceramic industry and related activities, the main type of materials handled are ceramic materials, which are inorganic, non-metallic materials made from metal and a non-metal compounds, and may be crystalline or partly crystalline (Barba et al. 2000). Traditional ceramic materials are clay, feldspar, silica (quartz), kaolin, dolomite, talc, calcite, and nepheline with main primary particle morphology being plate-like and prismatic, and $d_{50}$ values ranging from few µm up to hundred µm (Worrall 1982, Barba et al. 2000, López-Lilao et al. 2015, 2016, 2017). Their chemical composition is mainly SiO$_2$ and Al$_2$O$_3$ although other components can be present in lower amounts. Special attention is given to silica due to its health effects (see more in section 1.3.1) (Fang et al. 2010 and references therein, Chiu Leung et al. 2012). Activities which can lead to exposure to micron-sized silica dust are abrasive blasting with sand, sawing brick or concrete, sanding or drilling into concrete walls, grinding mortar, manufacturing

Occupational exposure to airborne particles has been reported during several mechanic and handling processes, e.g.; pouring and packing of paint pigments, fertilizers, ceramic and cement materials (Koponen et al. 2015, Notø et al. 2018, Ribalta, et al. 2019a, Ribalta et al. 2019b), cleaning, dry wiping and sweeping (Douwes et al. 2017, Notø et al. 2018), welding (Notø et al. 2018), and repair tasks, floor screed layers, tile setting and mechanical milling (Peters et al. 2008, Ribalta et al. 2019c). It is interesting to highlight that particle emissions of fine and coarse airborne particles have also been detected during NP handling due to agglomeration, e.g.; packing of carbon black, carbon nanofibers, TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} (Kuhlbusch et al. 2004, Evans et al. 2010, Koivisto et al. 2012a, Kaminski et al. 2015), sweeping (Yeganeh et al. 2008), storage, weighting and reactor areas (Fujitani et al. 2008, Cena and Peters 2011, Kaminski et al. 2015).

1.2.3. Exposure to nanoparticles

A nanomaterial is defined as a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm (Savolainen et al. 2013). However, currently there are 14 available definitions for nanomaterial (Boverhof et al. 2015).

In recent years, NPs have received special attention from the scientific community because of their larger surface area when compared to their non-nano counterparts, potentially toxic constituents, high alveolar deposition fraction, and therefore higher potential ability to penetrate into the blood vessels. Nanotechnology is currently present in our everyday life (electronics, cosmetics, drugs…) (Aitken et al. 2004), but exposure concentrations in work environments are from 60 to 450 times higher compared to non-occupational environments (Viitanen et al. 2017). NPs are usually divided in two groups, engineered and non-engineered NPs, both having an impact on worker exposure.

1.2.3.1. Engineered nanoparticles

Engineered or manufactured NPs (ENP/MNs) are intentionally engineered and produced particles with distinct properties and characteristics, affecting their physical, chemical

They are usually presented in spherical, regular or irregular shape (nanocrystals and cubes, quantum dots or dendritic forms), tubes, fibres and wires (ceramic and aluminium) (Aitken et al. 2004). In some cases, they can also be found in the form of aggregates (Kuhlbusch et al. 2004, Evans et al. 2010, Koivisto et al. 2012a, Kaminski et al. 2015).

Some of the most common chemical composition for engineered NPs are 1) nano-metals or nano-metal oxides such as SiO$_2$ (amorphous silica), TiO$_2$, Al$_2$O$_3$, Au and Ag, among others; 2) carbon based materials such as carbon black, carbon nanofibers, carbon nanotubes (CNTs), fullerenes or graphene; and 3) organic NPs or nano composites (Aitken et al. 2004, Ostiguy et al. 2010, Kaluza et al. 2013).

The worst scenario of risk of worker exposure to ENPs is during NP manufacture in dry state especially during production (when chambers are opened) capture, drying or packaging (handling) (Fujitani et al. 2008). Processes such as pouring and mixing, maintenance and cleaning, dust collection and ventilation, abrasive activities such as sanding and drilling composites, handling under fume hoods or at laboratory level, bagging, cleaning, weighting, spraying, and aerosol generators have been detected as activities with potential risk of worker exposure (Fujitani et al. 2008, Demou et al. 2009, Tsai et al. 2009, O’Shaughnessy 2013, Jensen et al. 2015, Mølgaard et al. 2015, WHO 2017, Fonseca et al. 2018, Jensen et al. 2019). Maximum mass levels were seen to range from few micrograms up to few thousand micrograms (O’Shaughnessy 2013). Conversely, maximum particle number concentrations were detected from thousands up to millions (Aitken et al. 2004, Brouwer 2010, Nazarenko et al. 2011, O’Shaughnessy 2013, Shepard and Brenner 2014).

1.2.3.2. Non-engineered nanoparticles

Non-engineered NPs in indoor workplaces originate from the background and from unintentional release from industrial activities (Brouwer et al. 2004, Viitanen et al. 2017). Background NPs are those coming from 1) outdoor, typically produced in high energy processes such as combustion (20-30 nm) (Viitanen et al. 2017), gas-to-particle conversion (Hämeri et al. 2009), nucleation processes or photochemical processes (Kulmala et al. 2004); and 2) generation inside the workplace but not related to any
specific activities, such as diesel engines e.g. forklifts, thermal processes or vacuuming among other processes (Maynard et al. 2004, Demou et al. 2008, Fujitani et al. 2008, Elihn and Berg 2009, Huang et al. 2010, Koivisto et al. 2012a, Ding et al. 2017). Thus, chemical composition may be very divers. In some workplaces, background concentrations have been reported to be higher than concentrations in urban environments what is generating current discussions (Viitanen et al. 2017).

Unintentionally-released NPs, also referred to as process-generated (PGNP) or incidental NPs, are primary or secondary nano-sized particles from industrial processes with or without relation to nanotechnology. Some examples are particles generated during thermal treatments, 3D printing, laser ablation, melting and combustion, soldering, welding, and metal grinding or abrasion processes among many others (Viitanen et al. 2017). Hence, their chemical composition is very variable, and particle morphology is mainly irregular or spherical (Fonseca et al. 2015, 2016, Viana et al. 2017, Salmatonidis et al. 2019). High risk of exposure to unintentional NPs has been observed during thermal spraying in pilot plant and industrial scenarios (Huang et al. 2016, Viana et al. 2017, Salmatonidis et al. 2019), ceramic tile sintering, ceramic firing and laser ablation (Voliotis et al. 2014, Fonseca et al. 2015, 2016, Salmatonidis et al. 2018), welding (Stanislawska et al. 2017, Viitanen et al. 2017), and ceramic dip coating and electrostatic spray deposition (Koivisto et al. 2018a, Koivisto et al. 2018b).

1.3. Particle-related health risk

1.3.1. Micro-sized particles

Exposure to PM as a result of air pollution is known as a risk factor for adverse health effects such as respiratory and cardiovascular diseases (WHO 2016, Gakidou et al. 2017, Landrigan et al. 2018). Specifically, particles are major causes of cardiovascular and respiratory morbidity (Fang et al. 2010, Ibfelt et al. 2010, Kreatsoulas and Anand 2010). The impact of particles on human health is related to particle size, size distribution, morphology and shape, surface area, agglomeration state, chemical composition and crystallinity (Hinds 1999, Aitken et al. 2004, Baron and Willeke 2011, Savolainen et al. 2013, Persons et al. 2014, Oberdörster and Kuhlbusch 2018) (Figure 1.4).
In occupational environments, exposure to PM differs from ambient air exposure in chemical composition, exposure frequency and duration, and particle concentration (which is usually higher than ambient air concentrations) (Fang et al. 2010). These differences require specific worker exposure assessments as they may have different health implications (Fang et al. 2010). Ischemic heart and increase on cardiovascular disease risk was observed to increase in, among other examples, mine workers, workers exposed to silica, diesel exhaust and inorganic dust, construction, metal and asphalt workers, and heavy equipment operators (Kuempel et al. 2003, Fang et al. 2010).

![Figure 1.4](image)

**Figure 1.4** Particles characteristics affecting human health. Source: modified from Persons et al. (2014) and Fonseca (2016).

In the case of the ceramic industry, no solid link between ceramic workers exposure to PM and cardiovascular diseases has been found (Fang et al. 2010); conversely, respiratory-related disease due to inhalable dust have been reported in several studies (Dehghan et al. 2009, Neghab et al. 2009, Alim et al. 2015). For example, inhalation of respirable crystalline silica (RCS) dust can cause silicosis, one of the major causes of morbidity and mortality worldwide, prevalent in low- and middle-income countries (NIOSH 2002, Chiu Leung et al. 2012). Moreover, RCS dust generate at workplaces has been recently classified as carcinogenic for humans (Directive 2017/2398/EC). Research is ongoing aiming to minimize RCS hazardous potential, through for example particle coatings using organosilanes (Ziemann et al. 2017). Other exposure impacts characteristic of the ceramic industry, driven by particle size and size distribution, are evident in the literature but their specifically health effects are not yet fully understood. This is why this kind of impact is the main focus of this Thesis.

1.3.2. Nanoparticles

Adverse health effects have been linked to particles < 100 nm (Oberdörster 2001) due to their ability to reach the deepest sections of the respiratory tract (alveolus) because of
their small size, the fact that they cannot be removed from the airways by mucociliary clearance and translocation to other organs (Figure 1.5). NPs are removed in the alveolus by macrophage clearance and they can be transferred to other body organs via the gastro-intestinal compartment more easily than non-nano particles (Behrens et al. 2002, Aitken et al. 2004). In addition, due to high NPs concentration and longer retention time, macrophages disruption occur, which induces inflammation (NIOSH 2002, Fang et al. 2010, Saber et al. 2014) and NPs penetration through epithelial cells to the bloodstream (Gilmour et al. 2004). Ultimately, this leads to translocation to other organs as for example the brain (Oberdörster et al. 2004, Donaldson et al. 2005, Knol et al. 2009) (Figure 1.5).

**Figure 1.5** Mechanisms of inflammation and translocation. Source: modified from Marianne Dybdahl in Vogel et al.(2018).

*In vivo* studies revealed that NPs can cross the alveolar barrier in much higher numbers than coarser particles and induce inflammation (Dybdahl et al. 2004, Hougaard et al. 2010, Fröhlich and Salar-Bezhadi 2014, Monsé et al. 2018) and cause cancer in mice and rats due to CNTs exposure (Kasai et al. 2016, Fukushima et al. 2018). There is evidence that pulmonary exposure to particles may increase cardiovascular risk by increasing plaque progression in the aorta (Thompson et al. 2018, Vogel and Cassee 2018) and lung damage such as fibrosis and plural granuloma (Hedmer et al. 2014).

Particle surface area has been found to correlate well with pulmonary response regardless of particle size. However, it seems that this may also be a function of the agglomeration state. Primary particles can form aggregates (strongly bonded) when
spherical primary particles stick together by van-der-Waal’s forces. These aggregates can then combine to form larger agglomerates (weakly bonded) (O’Shaughnessy 2013 and references therein). However, implications of agglomeration state on toxicity are currently under investigation (O’Shaughnessy 2013 and references therein) as they may have increased toxicity compared to larger particles (Oberdorster et al. 1994, Aitken et al. 2004).

1.4. Exposure assessment

Exposure assessment is the process of evaluating the exposures, accumulated doses and the derivate health effects to which a group of individuals is exposed (Ramachandran 2005). In order to assess worker exposure to airborne particles several strategies can be used. The sampling strategy should be effective in capturing the variability of workplace sources, feasible, efficient and should not require a large number of samples (Ramachandran 2005, Dahmann et al. 2008). For NP exposure, several authors (e.g., Methner et al. 2010, Ramachandran et al. 2011, Asbach et al. 2012, Brouwer et al. 2012, OECD 2015) have identified the need for a tiered approach to facilitate exposure assessment, which is described briefly below (Figure 1.6). This kind of approach is also typically used for exposure other types of workplace air pollutants such as micron-sized particles and chemical agents (UNE-EN-689 2019).

- **Tier I - Initial assessment**: the identification of potential particle emission mechanisms and worker exposure is qualitatively assessed by gathering as much information as possible regarding the site and the type of particles released. In order to complete this tier, risk assessment and control banding based tools such as ART, Stoffenmanager or NanoSafer may be used in the case of NPs and chemical agents. If particle release or exposure cannot be excluded a second tier level needs to be conducted.

- **Tier II - Basic exposure assessment**: the main focus of this tier is to conduct a basic release and exposure assessment on-site, by using easy-to-use and portable online and offline instruments (e.g. portable CPC, DiSCmini or OPC, see 3.3). Usually, the use of a combination of instruments is required. One of the main challenges is to quantify background particles in order to differentiate process particles from background particles and to decide whether or not measured concentration increases are statistically significant (Brouwer et al. 2009, Ramachandran et al. 2011). Background particles can be

Figure 1.6 Tiered approach flow chart recommended for workplace exposure assessment. Source: modified from OECD (2015) and UNE-EN 689 (2019). * Efficiency of applied measures is assessed going back to tier II and III. DiSCmini, OPC, CPC, SMPS and TEM are online and offline instruments and techniques used in exposure assessment (see section 3.3).
A specific approach using measured background concentrations to assess statistical significant increases of NPs has been designed in Asbach et al. (2012), which is also referred in this Thesis as the nanoGEM approach:

\[
\text{Mean concentration during packing} > \overline{BG} \pm 3 \cdot (\sigma_{BG}), \quad \text{Eq. (1.1)}
\]

where \( \overline{BG} \) is the mean temporal background (or pre-activity) concentration and \( \sigma_{BG} \) is the standard deviation of the background concentration.

In addition, recently, the ARIMA models, which are the most general type of models used for analyzing time series while considering the autocorrelation between samples, have been proposed in the EN 17058:2018 (standard for workplace exposure- assessment of exposure by inhalation of nano-objects and their aggregates and agglomerates) as the golden standard method for number concentration and other metrics analyses. However, for particle mass there is no specific method to determine statistically significant increases other than conventional statistical tests. This issue is discussed in detail in Chapter 4 (Publication III). In order to evaluate exposure to particle number concentrations, the Tiered approach recommends Eq. 1. Conversely, for particle mass concentration comparison with OEL values is recommended (UNE-EN-689 2019).

When significant particle emissions due to the process under evaluation are detected, tier III must be conducted.

- **Tier III - Expert exposure assessment**: the aim is to obtain as much information as possible on released NPs in the occupational environment in order to determine whether or not exposure can be excluded or if further risk management steps need to be implemented. In tier III all relevant instruments and techniques available should be used, including personal samplers and high-resolution instruments in order to provide a definitive conclusion regarding worker exposure. If a clear increase on particle exposure due to the process (significant increase over background and higher concentration than reference values) is observed, then risk management measures need to be implemented prioritizing reduction of exposure concentrations over increasing personal protection. Effectiveness of implemented measures needs to be further verified by conducting tier II and III again.

Traditionally, particle mass concentrations (usually expressed as \( \mu g \, m^{-3} \) or \( mg \, m^{-3} \)) have been the most commonly used metric to report human exposure to airborne particles. However, it is known that mass may not always be the most appropriate metric to report...
health effects on humans deriving from particle inhalation (Ramachandran 2005). This is especially true for NP exposure assessment, for which particle number and surface area have been suggested as more appropriate metrics for inhalation exposure assessment and are more widely used (Aitken et al. 2004, Brouwer et al. 2009, Hämeri et al. 2009). This is because contribution to particle mass concentrations of particles between 1 and 100 nm is negligible when compared to coarser particles. Direct links between total surface area of pulmonary deposited particles and cardiovascular risk have been found for example for TiO$_2$, black carbon NP and CNTs (Donaldson et al. 2002, Saber et al. 2014, Poulsen et al. 2016). Discussions are ongoing regarding the definition of the most appropriate metrics (Park et al. 2010, O'Shaughnessy 2013, Viitanen et al. 2017), which are in addition complex due to the variability of particle types and diameters in different microenvironments. For instance, studies have revealed that particles emitted during NP handling can be found in aggregate and agglomerate form (Kuhlbusch et al. 2004, Fujitani et al. 2008, Kuhlbusch et al. 2009, Stahlmecke et al. 2009), and therefore particle mass concentrations should also be considered a relevant metric when assessing NP exposures (Koivisto et al. 2012a).

Worker exposure monitoring can be conducted by using online (real-time) and offline instruments. Online instruments provide size resolved/integrated and time resolved (1 s up to 1 min) information regarding particle size and size distribution, surface area, and/or particle number and mass concentrations. However, they do not allow differentiating particles composition. Online instruments are generally divided in two types according to their portability (stationary and portable). Stationary instruments are those complex in terms of use and transportation, due to their size and weight but provide high-resolution measurements. Portable instruments, on the other hand, are useful for the detection of particle hotspots, personal monitoring, monitoring screening tasks, or testing the effectiveness of preventive measures (as they can be worn by the workers without influencing their work activity).

Offline instruments (size and time integrated), on the other hand, allow not only to gravimetrically determine particle mass concentrations but also physically and chemically characterise the collected particles. Offline techniques cover from simple open-face sampling solutions such as air sampling cassettes, to more complex equipment such as filtration, electrostatic or thermal precipitation instruments, or cascade impactors. The samples collected in the filters can be gravimetrically and chemically analysed. Additionally, morphology, geometry and optical size of particles and
agglomerates can be analysed by using electron microscopy techniques such as high resolution transmission electron microscopy (TEM) or scanning electron microscopy (SEM). Particles and agglomerates chemical composition and surface properties can be additionally identified by using energy dispersive X-ray spectroscopy (EDX) often coupled with SEM or TEM devices.

1.4.1. Exposure prediction tools: the dustiness index

During handling of a powdered material, particle emissions are driven, among other factors, by the material's dustiness index. The dustiness index is a measure of the tendency of a powdered material to release particles in response to a mechanical or aerodynamic stimulus (Plinke et al. 1992, Lidén 2006). The amount of emitted material mass (mg) per mass of handled material (kg) is ranked in different levels of emission. Dustiness is not an intrinsic property of powders, it depends on physic characteristics (e.g., humidity, surface coating, primary particle size and aggregate size), as well as on the mechanic or aerodynamic stimulus (e.g. type of method used and energy applied, and environmental conditions) (Plinke et al. 1995, Breum 1999, Evans et al. 2013).

Several methods are available to determine dustiness in the literature (Hamelmann and Schmidt 2003), such as the Vortex shaker (Dazon et al. 2017), the Venturi device (Evans et al. 2013) or the Heubach Dustmeter (Type 2000, Heubach GmbH, Germany), but only two are accepted as standard method (EN 15051): the Continuous Drop (C.D) and the Rotating Drum (R.D). The main difference between the two standard tests are that in the C.D fresh material is used continuously (dropped by gravitational forces) whereas in the R.D fresh material is placed inside the device at the beginning of the test and it is repeatedly agitated (drum rotation and drop of the material by gravitational forces). The method selected to quantify the dustiness of a given material should reproduce as closely as possible the type of mechanical stimulus and energy to which material would be subjected (CEN 2013, Evans et al. 2013).

Due to its ability to measure material’s tendency to generate airborne dust during handling, the use of dustiness has risen as a tool for occupational safety (Hamelmann and Schmidt 2003). The dustiness of a given material is determined under laboratory conditions and following standardized (CEN) methodologies, and is therefore a parameter which is relatively simple to obtain. As a result, dustiness of powders is frequently reported by manufacturers in the technical specifications.
Discussions are ongoing about the use of the dustiness index as a predictor of worker exposure (Brouwer et al. 2006, Evans et al. 2013, Levin et al. 2014, Fonseca et al. 2018, Ribalta et al. 2019b, 2019c). However, yet no clear direct relationship dustiness-exposure has been established as certain authors found no clear or limited relationship between exposure and dustiness (Brouwer, 2006; Class et al. 2001; Fonseca et al. 2018; Heitbrink et al. 1990), whereas other found statistically significant correlations (Heitbrink et al. 1989, Breum et al. 2003, Brouwer et al. 2006).

When establishing the relationship between dustiness and exposure, certain factors need to be considered: 1) material dustiness depends mainly on material particle size distribution, humidity, density, morphology and specific surface area (SSA) (Hamelmann and Schmidt 2003; Lidén 2006; López-Lilao et al. 2016, 2015); 2) dust emissions are known to depend on the amount of material handled, the process, and local controls (Fransman et al. 2011); and 3) the dustiness test methodology should mimic as closely as possible the actual process energy applied (CEN 2013, Evans et al. 2013), while the different methodologies are often not directly comparable (Hamelmann and Schmidt 2003).

As a result, dustiness is currently used as an input for exposure modelling (Levin et al. 2014; Schneider and Jensen 2007) and by material producers to modify products in order to reduce dust generation (Lidén 2006), rather than as a direct exposure predictor. Thus, it is important to continue working on dustiness test performance as well as to understand which the key factors to predict worker exposure are. This issue is addressed in detail in Chapter 4 (Publication I, II and III).

1.4.2 Exposure modelling: mass-balance models

Traditionally, exposure monitoring has been the most common method to evaluate worker exposure. However, due to the need to estimate exposure during a large variety of work micro-environments and materials under REACH regulation (EC 1907/2006), exposure prediction mass-balance models have been proposed as valuable risk assessment tools (Keil 2000, Ramachandran 2005, Spencer and Plisko 2007, Koivisto et al. 2019). In this context, models may contribute to understanding critical factors driving exposure and allow for more efficient risk mitigation strategies (Spencer and Plisko 2007, Hussein et al. 2015).
Different levels of complexity are available for exposure models, which are mostly based on mass-balance equations (Keil 2000, Ramachandran 2005, Jayjock et al. 2011, Ganser and Hewett 2017, Hewett and Ganser 2017). The simpler model is the saturation vapor pressure model, only applicable to gas and vapor exposure, and which provides the most conservative exposure estimates. More complex models are the one-box model (or well-mixed room) which includes ventilation (Hewett and Ganser 2017), and the two-box model (or near-field “NF” far-field “FF” model) (Ganser and Hewett 2017), which has also been expanded to more boxes, e.g. three-box model (Jensen et al. 2018). However, higher complexity implies higher input requirement and thus, more complex to parametrize, especially in real-world scenarios (Keil 2000, Jensen et al. 2018).

These tools aim to model particle exposure in one-, two- or more boxes in which particle emissions are generated by a source and where particle transport and removal is determined by airflows between the different compartments, structural elements (e.g. doors), the total air exchange through doors, and mitigation strategies (e.g. ventilation extraction systems).

The one- and two-box models (Figure 1.7) are based on a set of mass balance equations including information of the source (contaminant generation), and transport. Usually, and for the sake of simplicity models assume that 1) particles are fully mixed at all times; 2) mass is created by a source inside the limits of the model (NF in the two-box model) and initial concentrations are zero; and 3) particle losses are due to natural and mechanical ventilation (Ramachandran 2005, Ganser and Hewett 2017, Hewett and Ganser 2017, Koivisto et al. 2019). However, outdoor or incoming concentrations can be included in the models, as well as other particle removal mechanisms such as deposition or coagulation in order to improve model accuracy (Jensen et al. 2019, Ribalta et al. 2019a, 2019d).

In the one-box model there is the limitation that the effect of proximity to the source is not considered and, thus, exposure near the source is usually underestimated (Keil 2000, Ramachandran 2005, Arnold et al. 2017, Jensen et al. 2018). Conversely, in the two- or more box model the effect of source proximity on exposure is included but it comes at the cost of requiring measurements of the interzonal (NF-FF) flow rate (Ramachandran 2005, Jensen et al. 2019). The two-box model is a well-accepted exposure assessment tool in the risk assessment field as, even with its simplified assumptions, it is able to adequately simulate actual conditions for various processes.
including volatile compounds and PM emissions (Jayjock et al. 2011, Arnold et al. 2017). The fact of adding extra boxes was seen to increase model performance (Jensen et al. 2018). A number of other more complex and resource-intensive models are also available (Ramachandran 2005).

Since the initial application of exposure prediction models, several research papers have been published regarding their theoretical aspects (Nazaroff and Cass 1989, Nazaroff 2004, Hussein et al. 2005, Hussein and Kulmala 2008, Ganser and Hewett 2017, Hewett and Ganser 2017) and they have been tested in different environments (Nicas 2016; Sahmel et al. 2009 and references therein; Jayjock et al. 2011 and references therein; Boelter et al. 2009, Johnson et al. 2011, Jones et al. 2011, Koivisto et al. 2015, 2019, Lopez et al. 2015, Arnold et al. 2017). However, in order to implement exposure prediction models as trustworthy tools in the framework of risk assessment (Spencer and Plisko 2007), additional real-world cases need to be evaluated to test model performance and to understand the uncertainties related to critical parameters (determinants of exposure) (Mølgaard et al. 2014, Tielemans et al. 2008a) such as source characterization, local controls, and air mixing, which are not yet fully parametrized (Baldwin and Maynard 1998, Sahmel et al. 2009, Cherrie et al. 2011, Jayjock et al. 2011, Keil and Zhao 2017) and are often challenging to estimate (Zhang et al. 2009) in real-world scenarios.

Key parameters which drive model performance are (Fig 1.8):

- **Particle emission rate**: it can be estimated by using two different approaches depending on the type of process and information available: dustiness index and quantification of the emission rates from monitored concentrations. When modelling exposure to airborne particles due to handling of a dusty material, the most common method to
estimate the emission rate is by using the dustiness index. For modelling, dustiness is linked to the actual activity by an energy factor (H), which by definition links the energy applied during the process with the energy applied during the dustiness test (Schneider and Jensen 2007) and can range from 0 to 1 (Lidén 2006, Koivisto et al. 2015). The parameter H has been defined for the R.D dustiness test by Van Tongeren et al. (2011) for the Advanced REACH tool. However, currently the scaling of the source by using handling energy factor is not yet well understood and works are ongoing in order to parameterize the H factor. For those processes not including handling of dusty materials e.g. emission, or dustiness is unknown, equations to estimate emission rates have been described (Sachse et al. 2012, Hewett and Ganser 2017) and used on real scenarios by using mass balance equation and convolution theorem (Koivisto et al. 2018a, Koivisto et al. 2018b). However, literature regarding emission rates quantification is still relatively scarce (Koivisto et al. 2017).

![Figure 1.8 Modelling gaps and solutions.](image)

- **Local controls or protection factors**: all those actions preventing dispersion of the aerosolized particles or removing particles from air, e.g. enclosures or local extraction systems (Fransman et al. 2008), need to be included as well in the equations as an estimated or calculated factor of reduction. When having to consider extractions systems, local control values associated can be determined, by using relatively simple equations (Hewett and Ganser 2017), but in some cases key parameters are missing and they are not applicable. Fransman et al. (2008), revised by Goede et al. (2018), presents an exposure control efficacy library, which contains efficacy values for enclosure, local exhaust ventilation, general ventilation, suppression techniques and enclosure of the
worker, this values can be used when specific data is missing. Additional data are reported by Salmatonidis et al., (under review).

- Air exchange ratios (AER in air changes per hour, ACH) and air flow between near-field and far-field ($\beta$): need to be calculated or estimated. This should be a relatively easy to obtain parameter as only speed velocities are needed and box model sizes are required. However, in practice estimating $\beta$ can be challenging (Vernez et al. 2004, Spencer and Plisko 2007) as velocities may be unknown, and thus ventilation needs to be estimated from actual concentrations (Keil 2015, Keil and Zhao 2017) or assumed from literature (Baldwin and Maynard 1998).

1.5. Risk assessment

Risk assessment is a decision-making process to systematically evaluate potential exposures, risks associated to identified hazards and risk factors, and determine appropriate ways to eliminate the hazard or control the risk (CCOHS 2017). Traditionally, risk assessment is a result of a step paradigm including hazard identification and assessment, and exposure assessment (Savolainen et al. 2013). Overall risk of adverse health effects due to particle inhalation depends on their hazard (negative action in the organism and cells) and exposure (concentration in the inhaled air and deposition in the respiratory tract).

\[ \text{Risk} = \text{Hazard} \times \text{Exposure} \quad \text{Eq. (1.2)} \]

1.5.1. Inhalation deposition models for health risk assessment

The effects of particles on human health depend mainly on: particle chemical composition, deposition in the human respiratory tract as function of particle size (Heyder et al. 1986, Cousins et al. 2011) (Figure 1.9), and, especially in the case of NPs, the potential for translocation to other body organs.

While mean particle size can provide a general idea of the likely impact of inhaled particles in respiratory human health, detailed knowledge of particle size distribution can provide additional insights into particle deposition along the regions in the respiratory tract, irrespective of the chemical compositionof the particles.
Particle regional deposition in the human respiratory tract is inversely related to particle size and is mainly determined by 4 mechanisms: 1) inertial impaction (particles possess enough momentum to keep their trajectory and not follow the dominant airflow, and thus collide with the respiratory tract walls); 2) sedimentation (time dependent, the more time air is in the respiratory tract, the higher the particle deposition due to gravity); 3) diffusion (particles randomly collide with other objects and are trapped due to van-der-Waals forces); and 4) minor mechanisms such as electrostatic interception (Heyder et al. 1986, Carvalho et al. 2011, Hussain et al. 2011) (Figure 1.10).

Particles with sizes between 0.01 and 0.1 μm, and 1 and 5 μm mainly deposit in the tracheobronchial and alveolar regions, the deepest areas in the human respiratory system (Heyder et al. 1986, Madanchi et al. 2018) (Figure 1.9). Conversely, particles > 10
µm rarely penetrate into the respiratory tract, and particles between 0.1 and 1 µm have the lowest deposition rate in the human respiratory system with less than 20% of the inhaled particles depositing in the human respiratory system (Bailey and Roy 1994, Hinds 1999, Cousins et al. 2011) (Figure 1.9). Therefore, particles between 0.001 and 0.1 µm, and 1 to 10 µm, are of special concern from a deposition and also translocation perspective. However, regional deposition is not only ruled by the particle size and size distribution, but also affected to a great extent by inhalation flow rates, age and gender (Hussain et al. 2011). Other factors such as particle shape, charge, density and hygroscopicity, pulmonary physiology (breathing pattern, inspiration period, nasal or oral breathing and lung geometry) are known to affect particle deposition in the respiratory tract (Heyder et al. 1986, Dolovich 2000, Carvalho et al. 2011, Hussain et al. 2011). Finally, health hazardous consequences due to particle inhalation will also depend on particle chemical composition, uptake (transport to the blood stream), redistribution, storage and removal (clearance and excretion) and translocation (Hussain et al. 2011, Fernández Tena and Casan Clarà 2012).

Due to the intrinsic complexity of particle deposition along the human respiratory tract, in vivo studies present limitations to understand deposition mechanisms, and thus modelling approaches have been developed (Hussain et al. 2011, Koivisto et al. 2012b). Currently, the two main types of empirical models used are single and multiple path models (Ramachandran 2005). In single path models the human respiratory tract is considered a series of symmetrical compartments where all pathways are identical and have equal linear dimensions. Conversely, in multiple path models the asymmetry of the lung branching pattern is considered, thus providing more realistic deposition dose fractions. Two of the most widely used empirical deposition models are the International Commission on Radiological Protection (ICRP) single path model, and the multiple path particle dosimetry model (MPPD). Even though empirical models have been widely used and improved, it should be noted that they do not include NP-specific effects (Fröhlich and Salar-Bezhadi 2014), particle morphology, chemical composition or translocation, factors which impact human health. The focus of these models is on particle deposition along the human respiratory tract as a driver of respiratory health risk, but not cardiovascular risk (as they do not include translocation to other organs). Particle deposition modelling is discussed and applied in Chapter 4 (Publication II and III).
1.5.2. Risk assessment tools

The Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) regulation implemented by the European Chemical Agency (ECHA) requires producers and importers of substances (including nanomaterials) to ensure the safety of any product brought to the market (EC 1907/2006) by analyzing their impact on human health and the environment. A large number of empirical models, based on dimensionless exposure modifying factors to calculate an exposure score which is further converted to an exposure value by using calibration factors (e.g. Schinkel et al. (2011)), have been developed in order to provide risk assessment of chemical hazards under the REACH regulation (Fransman et al. 2011; Kristensen et al. 2010; Tielemans et al. 2008b; Jensen et al. in preparation). ECHA recommended quantitative exposure inhalation tools for risk assessment are the ECETOC TRA (ECETOC targeted risk assessment, 2004, 2009, 2012), MEASE (EBRC, 2010) and EMKG-Expo-Tool (EMKG, BAuA, 2008, 2016) as Tier I, and Stoffenmanager (Marquart et al. 2008) and the Advanced REACH tool (ART) (Fransman et al. 2011) as higher tier tools (ECHA 2016b). Stoffenmanager (Marquart et al. 2008) and ART (Fransman et al. 2011) have been tested in different scenarios including dust emissions (Landberg et al. 2015, 2017, Riedmann et al. 2015, Bekker et al. 2016, Savic et al. 2018) and were seen to both over and underestimate actual exposure concentrations (Landberg et al. 2017, Savic et al. 2017, Van Tongeren et al. 2017). In addition, the exposure modifying factors are not always clearly described which makes the models challenging to evaluate (Koivisto et al. 2018, Koivisto et al. 2019). Therefore, there is controversy regarding their use with regulatory purposes and whether or not their results are sufficiently robust (Raul 2003, Koivisto et al. 2019). ECHA recommends using measurement data in exposure assessment for substances with high hazardous potential (ECHA 2016a, 2016b).

However, all previously mentioned risk assessment tools present important limitations when it comes to exposure and risk assessment of nanomaterials (Liguori et al. 2016). Risk assessment based on control banding represents an alternative approach based on “computational” hazard and exposure for the control of workplace exposure to agents with unknown or uncertain toxicological properties, and lack of quantitative exposure estimations (Liguori et al. 2016). Thus, control banding tools, which are frequently user-friendly and have low input requirements, are used to guide the assessment and management of workplace risks due to nanomaterials with the final goal to assess the levels of precaution required to control their risks by grouping them into control
categories or bands (Zalk and Heussen 2011, Hristozov et al. 2016). Examples of control banding tools in literature are Stoffenmanager nano-module (TNO, Van Duuren-Stuurman et al. (2012)), CB NanoTool (Lawrence Livermore National Institute by Paik et al. (2008)), Precautionary matrix (TEMAS, Höck et al. (2013)), IVAM guidance (Cornelissen et al. 2011), NanoSafer (NRCWE, Kristensen et al. (2010) and Jensen et al. in preparation), and GUIDEnano tool (LEITAT). However, due to their novelty, control banding tools have not yet been thoroughly tested and compared, and thus they are recommended to be used with care (Sánchez Jiménez et al. 2016).

In general it was found that risk assessment and control banding tools comparison and standardization is complex as their input and output data vary considerably (Hristozov et al. 2016, Liguori et al. 2016, Sánchez Jiménez et al. 2016). In addition, many of them still have not been fully validated and/or calibrated (Hristozov et al. 2016).

1.6. Legislation: worker exposure to airborne particles

The European Union (EU) has set air quality limit values for ambient air PM and other pollutants (Directive 2008/50/EC). However, there are no direct limit values established for indoor air quality. For occupational exposure, each European member state has to establish its own limits based on the Commission directives of indicative OELs 2000/39/EC (2017/164/EU) and binding OELs 98/24/EC for chemical agents. In Spain, it is the (Real Decreto 374/2001) which transposes to the Spanish law the directives from the Commission, making reference to the limit values published by the “Spanish National Institute for Health and Safety at Work”, Instituto Nacional de Seguridad y Trabajo (INSHT). The INSHT publishes annually a list of daily OELs (value to which workers can be exposed during 40 h a week, 8 h a day, during their entire life without suffering any adverse health effects) and short term OELs (period of 15 minutes or less, depending on the chemical, during the work shift) (Table 1.1).

Table 1.1 INSHT 2018 limits, OEL (occupational exposure values) for inhalable and respirable particles not otherwise specified and respirable crystalline silica.

<table>
<thead>
<tr>
<th>Description</th>
<th>OEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhalable fraction (particles not otherwise specified)</td>
<td>10 mg m$^{-3}$</td>
</tr>
<tr>
<td>Respirable fraction (particles not otherwise specified)</td>
<td>3 mg m$^{-3}$</td>
</tr>
<tr>
<td>Respirable crystalline silica: quartz and cristobalite</td>
<td>50 µg m$^{-3}$</td>
</tr>
</tbody>
</table>
Currently, discussions are ongoing regarding OEL limits for low-toxicity dusts, with some authors believing they are too high (Koponen et al. 2015; commentary by Cherrie et al. 2013 and response letter by Kuempel et al. 2014). Additionally, in an analysis of occupational standards in Germany (the maximum workplace concentrations or the MAK values) it was found that these values were also not purely health-based (Ramachandran 2005). Therefore, further studies regarding toxicity and exposure to airborne particles are required to ensure worker health and safety.

1.6.1. Nanoparticle exposure legislation

In October 2011, the European Commission published a recommendation for a definition of a nanomaterial. However, different definitions are available and nanomaterials are not regulated by a separate legislation. Integration of the nanomaterial definition and consequences to specific sectors and regulations has already been implemented for biocides (EU 528/2012), food (EC 2015/2283) and (EU 1169/2011), medical devices (EU 2017/745), cosmetics (EC 1223/2009), and recently for chemical agents (REACH 2006, EC 1907/2006).

Currently, OECD test guidelines for nanomaterial characterization are being developed, as well as other measurements for standardization (CEN EN 17058:2018 for occupational nanomaterial exposure assessment and Zhao et al. (2018) for indoor/outdoor measurements). However, the lack of 1) systematic and detailed information on the potential hazards; 2) scientific and reliable knowledge on risk assessment; and 3) in vivo studies with systematic short- and long-term toxicity tests, which are required for risk assessment (Van Broekhuizen et al. 2012, Savolainen et al. 2013); are main reasons why regulatory limits are still not available for nanomaterials.

Thus it is essential to gather data regarding toxicity and workplace exposure for risk assessment which can be later used for further development of regulatory decision making, risk management and governance of engineered nanomaterials.

Several guidelines including recommended values for nanomaterials are published by different organizations (Table 2). The REACH (ECHA 2015) proposed a derived no-effect level (DNEL), the National Institute for Occupational Health and Safety (NIOSH 2011, 2013) proposed recommended exposure limit (REL), and the Social and Economic Council of the Netherlands (SER 2012) proposed nano-reference values (NRV), which are background corrected 8h TWA concentrations, based on the German Institute for
Occupational Safety and Health of the German Social Accident Insurance (IFA, 2009) particle number based approach for recommended benchmark limits.

Additionally, permissible exposure limits (PELs) are published by the US Occupational Safety and Health Administration (US-OSHA), and threshold limit values (TLVs) are issued by the American Conference of Governmental Industrial Hygienists (ACGIH), a voluntary organization with members from federal, state, and local bodies as well as industry and academia, since 1946 (Ramachandran 2005).

As a result it becomes evident that a multitude of non-binding targets, thresholds and recommended values is available to benchmark occupational exposures to nanomaterials. However, no common, standardized or legally-binding limit value is currently available for NPs (Table 1.2).

Table 1.2 Recommended occupational exposure limits proposed by different international organizations: *SER (2012); *NIOSH (2011); *NIOSH (2013); *ECHA (2015). NRV background-corrected 8h TWA concentrations. REL (recommended exposure limit) 8h TWA concentration during a 40-h workweek. DNEL derived no-effect level. Source: modified from Fonseca (2016).

<table>
<thead>
<tr>
<th>Description</th>
<th>Recommended limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Rigid, biopersistent, insoluble, fiber form nanomaterials for which effects similar to those of asbestos are not excluded</td>
<td>0.01 fibres cm(^{-3}) (NRV)</td>
</tr>
<tr>
<td>• SWCNT or MWCNT or metal oxide fibres</td>
<td></td>
</tr>
<tr>
<td>a Non-biodegradable granular nanomaterials in the range of 1–100 nm and density &gt; 6 kg/L</td>
<td>20 000 cm(^{-3}) (NRV)</td>
</tr>
<tr>
<td>• Ag, Au, CeO(_2), CoO, CuO, Fe, FeO(_y), La, Pb, Sb2O(_5), SnO(_2),</td>
<td></td>
</tr>
<tr>
<td>a Non-biodegradable granular nanomaterials in the range of 1–100 nm and density &lt; 6 kg/L</td>
<td>40 000 cm(^{-3}) (NRV)</td>
</tr>
<tr>
<td>• Al(_2)O(_3), SiO(_2), TiN, TiO(<em>2), ZnO, nanoclay, Carbon Black, C(</em>{60}), dendrimers, polystyrene, nanotubes, nanofibers and nanowires (asbestos-like effects are excluded)</td>
<td></td>
</tr>
<tr>
<td>a Biodegradable/soluble granular nanomaterials in the range of 1–100 nm</td>
<td>Applicable OEL (NRV)</td>
</tr>
<tr>
<td>• e.g. NaCl-, fats, flower, siloxane particles</td>
<td></td>
</tr>
<tr>
<td>b Fine (&lt;2.5 (\mu)m) and ultrafine (10-100 nm)TiO(_2)</td>
<td>2.4/0.3 mg m(^{-3}) (REL)</td>
</tr>
<tr>
<td>c Carbon nanotubes (CNTs) and nanofibres</td>
<td>0.001 mg m(^{-3}) (REL)</td>
</tr>
<tr>
<td>d SiO(_2) fumes (&lt;100 nm)</td>
<td>0.3 mg m(^{-3}) (DNEL)</td>
</tr>
</tbody>
</table>
1.7. Gap analysis

As a result of the above literature review the following research needs were identified.

1.7.1. Gaps in exposure monitoring

Work environment characteristics are highly variable, and thus particle emission mechanisms and patterns are location and activity specific. Additionally, the study of particle emission patterns of different industrial activities can be useful to test the validity of risk management tools and models. The ultimate goal of these tools is to mitigate exposure by facilitating the implementation of efficient mitigation strategies. Special efforts should be placed in order to understand unintentional NP emission mechanisms.

As a result, a larger number of real-world exposure assessments in occupational settings would further the current understanding of industrial particle emission sources, mechanisms and impacts on human health. The need to establish a standardized exposure assessment methodology, which includes metrics improving our understanding of measurement locations and of the definition of statistically significant impacts has been detected.

Further research is necessary to understand the metrics or combination of metrics which better represent particle emissions, taking into account particle diameter, toxicity and agglomeration mechanisms, among others.

Finally, standardized, efficient and quantitative testing of the effectiveness of exposure mitigation strategies from e.g. personal protective equipment (PPE) to general extraction system and local exhaust ventilation systems (LEV) is needed in order to provide users (e.g. industries) with robust and useful information to mitigate and prevent particle exposures.

1.7.2. Gaps in exposure prediction models

Mass-balance models for exposure prediction, e.g. the one- and two-box models, have been tested in different controlled environments. However, model performance in real-world environments, especially in environments where certain parameters are unknown, still needs to be better understood. Specifically, input parameters which are key to enhance model performance and their limitations are:
1) Local controls: reduction of the emission rate due to local controls can be quantified when extensive experimental data are available. When they are not available, literature reviews on rough estimations regarding efficiency should be used, increasing model uncertainty.

2) Emission rate: in the case of handling of powders, emission rate can be relatively easily calculated by means of the material dustiness index. Dustiness is a frequently used tool in occupational exposure; however its direct correlation with exposure concentrations is still not fully understood and works are ongoing in order to understand which the key factors to predict worker exposure are. When used as model emission rate input, the difference between the dustiness test energy and the actual process energy needs to be included as an additional “energy” factor, which is not yet fully parametrized, thus, introducing uncertainty to the modelling. On the other hand, when emission rate cannot be estimated using the dustiness index, several options are available to calculate them based on measured particle concentrations. Furthermore, emission rate libraries are also potentially useful. As a result, the different approaches available for emission rate quantification require testing under real-world conditions. This last point is especially relevant if models are to be used for exposure scenarios impacted by unintentional released NPs (non-engineered).

1.7.3. Gaps in health risk assessment

Worker exposure assessments for several occupational environments have been reported in literature. However, in order to provide a complete human health risk assessment from exposure to airborne particles, not only concentration levels need to be monitored at the workplaces but detailed data are also required on particle deposition along the respiratory tract which can be linked to respiratory disease. The study of particle inhalation and deposition in exposure assessment studies is still often not included, and needs to be further studied and applied.

Risk assessment and control banding tools are promising tools which can help to assess worker exposure risk, especially at industrial level given that they are relatively easy to use. However, in practice, their application is complex, differences between similar processes are difficult to be included in the tools, they do not consider all types of processes (e.g. unintentional NPs are still not included), and there are many different tools available, which are similar in principle but include different parameters and provide different results not only in terms of total concentration but also type of
measure. In addition, their lack of transparency regarding certain functions has been pointed out (Koivisto et al. 2019). Two main gaps may be pointed out 1) validation of the different tools in real world scenarios; and 2) standardization of these tools would highly benefit the user communities.
Chapter 2

Objectives and Structure

- 45 -
2. OBJECTIVES AND STRUCTURE

Based on the gaps and research needs identified in the previous chapter, the objectives of this PhD Thesis were defined as follows.

2.1. Objectives

The main objectives of this work are:

1) To assess worker exposure to coarse, fine and NPs in different workplace scenarios at, industrial and pilot-plant scales. Pilot plant studies are easily controllable and therefore allow for the identification of the influence of different process parameters on particle emissions, whereas industrial studies are representative of real-world scenarios.

2) To evaluate, with the aim to contribute to the standardization of worker exposure assessment:

   i. decision making approaches for the determination of statistically significant impacts of emitted particles due to a specific process

   ii. current available metrics to report worker exposure (mass, particle number concentrations and surface area)

3) To understand the relationship between material dustiness and worker exposure concentrations, with the final goal to contribute to a better understanding of particle emissions patterns, the role of dustiness as an exposure predictor model input, and its standardization for modelling purposes.

4) To evaluate the performance of mass-balance models (one- and two-box models) as worker exposure prediction tools under industrial settings, in order to contribute to model application and parametrization in real-world scenarios.

5) To evaluate some of the existing tools for health risk assessment as users such as the inhalation deposition dose ICRP model, and risk assessment and control banding tools.

2.2. Structure

After the introductory chapter leading to the identification of gaps in the occupational exposure research field and definition of this PhD’s objectives, the methodology applied is described. In it details of the measurement sites, instruments, techniques and data processing tools are provided. The results are presented in chapter 4, structured as four
research publications, which are subsequently discussed in chapter 5. In this chapter, the most important findings are integrated into a joint discussion. Finally, in chapter 6 the conclusions of this Thesis are summarized. Additional scientific contributions are listed in Annex C.

The publications which are part of this Thesis are referenced and briefly described below:

- Research Publication I:


  In this study, worker exposure during mechanical handling of ceramic powdered materials in a pilot plant was monitored. Seven materials with different compositions, particle shape and characteristics were assessed, as well as different intensities of handling energy. Exposure concentrations were evaluated according to process and materials characteristics. The relationship between materials dustiness and evaluated exposure concentrations was assessed.

- Research Publication II:


  In this work, worker exposure concentrations were monitored during packing of 5 widely used ceramic materials, under three levels of source containment (low, medium and high mitigation strategies applied). Monitored worker exposure concentrations are discussed as a function of the degree of source containment, and material’s dustiness index. Health risk assessment is performed by using the inhalation and deposition ICRP model. This case study was used to evaluate the performance of three risk assessment/control banding tools as well as to test different strategies for decision making with regard to the
identification of statistically significant impacts of particle emissions on particle mass concentrations.

- Research Publication III:


Exposure concentrations during packing of a fertilizer in a real-world industrial scenario were monitored in two packing lines (small and big bags). Worker exposure risk assessment was completed with the application of the inhalation and deposition ICRP model, and chemical risk was assessed by using the Stoffenmanager risk assessment tool. This scenario was used to test the performance of the one- and two-box prediction models when challenged with low particle mass concentrations. Emission rates were estimated using the dustiness index, and special attention was given to in model parametrization.

- Research Publication IV:


Worker exposure concentrations to unintentional NPs were evaluated at an industrial-scale workshop where thermal spraying of ceramic coatings was applied. Occupational exposure evaluation and health risk assessment is presented and thoroughly discussed in Salmatonidis et al., (2019). The data from this study (Salmatonidis et al., 2019) were subsequently processed in the framework of this PhD to test the one-box models when challenged with high concentrations of unintentionally-released NPs. Emission rates were estimated by two different methods, and the results obtained were compared for this real-world setting.
Chapter 3

Methodology
3. METHODOLOGY

3.1. Exposure scenarios and monitoring sites

Worker exposure to airborne particles (micro- and nano-sized) was monitored in this Thesis for two main types of industrial processes; 1) mechanical, assessed at pilot plant and industrial level; and 2) thermal, assessed at industrial level. A total of five different locations were assessed (Table 3.1).

Table 3.1 Description of the studied processes.

<table>
<thead>
<tr>
<th>Paper No</th>
<th>Type of site</th>
<th>Type of process (activity)</th>
<th>Type of material</th>
<th>Sampling locations</th>
<th>Location and date</th>
<th>Objectives</th>
<th>Tools</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Pilot plant</td>
<td>Mechanical (handling)</td>
<td>5 micron-sized ceramic raw materials (+2 materials in “4.1.1”)</td>
<td>Worker area</td>
<td>Castellón (Spain), October 2016</td>
<td>1 and 3</td>
<td>Particle monitoring Dustiness</td>
</tr>
<tr>
<td>II</td>
<td>Industrial packing facility 1 and 2</td>
<td>Mechanical (packing)</td>
<td>7 micron-sized ceramic raw materials</td>
<td>Worker area Breathing zone</td>
<td>Onda (Spain), February 2018</td>
<td>1, 2, 3 and 5</td>
<td>Particle monitoring Dustiness Risk assessment tools</td>
</tr>
<tr>
<td>III</td>
<td>Industrial packing facility 3</td>
<td>Mechanical (packing)</td>
<td>1 granulated micron-sized inorganic fertilizer</td>
<td>Worker area</td>
<td>Castellón (Spain), January 2017</td>
<td>1, 3, 4 and 5</td>
<td>Particle monitoring Dustiness Mass-balance models Risk assessment tools</td>
</tr>
<tr>
<td>IV</td>
<td>Industrial thermal spraying</td>
<td>Thermal (spraying)</td>
<td>Micron-sized materials</td>
<td>Booth Worker area</td>
<td>Blanes (Spain), April 2017</td>
<td>4</td>
<td>Particle monitoring Mass-balance models</td>
</tr>
</tbody>
</table>

3.1.1. Mechanical processes

Mechanical handling of different powdered raw materials was monitored at pilot plant and industrial scales (Figure 3.1).

Pilot plant experiments were conducted at the Institute of Ceramic Technology (ITC) (Castellón, Spain) (Publication I) during a process which included feeding of the materials to a dry pendular mill and extracting the powders from it (Figure 3.1 (a) and (b)). Because the primary particle size was not modified by the mill, this activity was considered to be representative of handling of materials (as opposed to milling), at
industrial scale. Seven ceramic materials were studied, at two levels of mechanical energy.

At industrial level, exposure to packing of eight materials was assessed in three different ceramic-related packing facilities (Publication II and III). In the three industries different activities were carried out, each of them being conducted in a specific and independent hall. In the packing areas, packing was the main activity.

![Mechanical handling processes studied](image)

**Figure 3.1** Mechanical handling processes studied. (a) and (b) pilot plant mechanical handling, (c) and (d) ceramic materials packing at facility 1, and (e) and (f) inorganic fertilizer packing at facility 3.

In facilities 1 and 2, exposure during packing of seven ceramic materials was monitored (Publication II). In facility 1 packing was carried out in two lines of big bags (1200 kg), with low and medium mitigation strategies applied (Figure 3.1 (c) and (d)). The packing line with low mitigation strategies was not enclosed and had no closing system to attach the bag to the feed funnel, and the packing line with medium mitigation strategies was not enclosed but had a partially closing system to attach the bag to the feed funnel. Both packing lines were equipped with a local exhaust ventilation system (LEV), with an operational flow rate of 18000 m$^3$/h, and a subsequent bag filter. Facility 2 contained only one small bags (20-25 kg) packing line with high mitigation strategies. Packing was carried out automatically through a lateral cylindrical opening, and it was not enclosed.
but the bag was completely attached to the feed funnel during the filling process. This packing line was equipped with a LEV system (operational flow rate of 2400 m$^3$ h$^{-1}$) with a subsequent bag filter.

In facility 3, packing of a fertilizer was monitored (Publication III) in two different packing lines, small (25 kg) and big (600 kg) bags. In small bags (Figure 3.1 (e)), packing was carried out through an opening fitting the bag width and subsequently mechanically sealed. The packing process was fully automated and the process area was partially enclosed. In the case of the big bags (Figure 3.1 (f)), packing was carried out through a cylindrical opening, and the bag was manually closed by the worker.

3.1.2. Thermal processes

The thermal process assessed was thermal spraying, a thermal technique used to produce thermally and mechanically-resistant coatings. Monitoring of thermal spraying was carried out at an industrial-scale precision engineering workshop (Publication IV), equipped with three thermal spraying rooms (Figure 3.2 (a)).

In the workshop, two types of thermal spraying were carried out: atmospheric plasma spraying (APS), used to project oxides and metals by using high temperatures (5000–20 000°C) and projection velocities of 200–500 m s$^{-1}$, and high velocity oxy-fuel coating spraying (HVOF) (Figure 3.2 (b)), which is characterized by higher velocities (425–1500 m s$^{-1}$) and lower temperatures (2900°C). Due to the lower temperatures applied HVOF is frequently used to project carbides and metals. Parallel works such as cooling and sanding of metal pieces were occasionally carried out, but not during spraying process.

Figure 3.2 (a) Layout of the thermal spraying workshop, and (b) image of the HVOF booth.
3.2. Materials physical characterization

The following measurement and analytical techniques were used in this Thesis to characterize the physical properties of the materials under study.

3.2.1. Particle size distribution

Particle size distribution (PSD) of powdered materials was determined by laser diffraction (dlaser) wet method (ISO 13320-1, 2009) using the Mastersizer 2000 and by X-ray gravitational sedimentation using the Sedigraph method from Micrometrics (dstockes). The Mastersizer 2000 (size resolution of 0.02 - 2000 μm) analyses are based on the theory of Fraunhofer and Mie, using wave lengths 632.8 and 470 nm.

3.2.2. Flowability

Material flowability was assessed using the Hausner ratio (HR). It was calculated as the quotient of the bulk density of the packed particle bed (by tapping) and the aerated bulk density of the particle bed, obtained by dropping powder into a container without stirring or vibration (Amoros 1987). Dry materials with low cohesiveness and with mostly spherical shape show high compaction by gravitational drop, and therefore, the difference between the apparent density by gravitational drop and by tapping is small (HR close to 1). Thus, the lower the flowability, the higher the HR (Mallol et al. 2008).

3.2.3. Specific surface area

Specific surface area (SSA) was assessed by measuring the adsorption isotherms according to the BET method by nitrogen absorption (ISO 9277:1995) (Brunauer et al. 1928).

3.2.4. Aspect ratio

A particle shape factor defined as the ratio of the particle’s major and minor dimension was determined by the Parslow-Jennings method for oblate spheroids (Otterstedt and Brandreth 1998, Jennings and Parslow 2006). This method is based on the fact that dlaser (diameter of a sphere of same diameter as the cross-sectional area of the particle μm) and dstokes (diameter of a sphere of same diameter as the cross-sectional projection area of the particle μm) have different dependence on aspect ratio and, therefore, it can only be obtained the same diameter in the case of spherical particles. This factor is a measure of the irregularity of particle shape, i.e. the deviation from a spherical shape. For
prismatic, platy, and ribbon-like particles the aspect ratios are 1 - 5, 4 - 15, and 5 - 100, respectively (Otterstedt and Brandreth 1998).

3.2.5. Dustiness

Dustiness is a measure of the tendency of a powdered material to release particles in response to a mechanical or aerodynamic stimulus (Plinke et al. 1992, Lidén 2006).

The two standard methods, the rotating drum (R.D) and the continuous drop (C.D) EN 15051 (CEN, 2013) (Figure 3.3), were used in order to determine the materials dustiness index.

**Method**

**Rotating drum (R.D)**

1. Inlet
2. Dust generation section (drum)
3. Dust collection
4. Foams and filter for inhalable, thoracic and respirable fractions

**Continuous drop (C.D)**

1. Sample tank
2. Metering device
3. Drop pipe
4. Sampling head for the respirable aerosol fraction
5. Sampling head for inhalable aerosol fraction

*Figure 3.3* Description of the two methods used for dustiness determination, rotating drum (R.D) and continuous drop (C.D).

The R.D test as described in the standard EN 15051 (part 2), consists of introducing a known volume of material (35 ml) inside a rotating drum which rotates at 4 revolutions per minute. The dust generated inside the drum is collected onto a three-body sampling system, in which the emitted dust cloud is drawn by the air current generated by a vacuum pump at a flow rate of 38 l min\(^{-1}\). The dust sampling system consists of two
sections of selective foam per particle size (one metal coated PE foam of 20 ppi and one metal coated PE foam 80 ppi) followed by a glass fiber filter, to gravimetrically analyze inhalable ($W_I$), thoracic ($W_T$) and respirable ($W_R$) fractions.

The C.D device EN 15051 (part 3), made of stainless steel, consisted of a cylindrical pipe through which air circulated in an upward direction with a volume flow rate of 53 l min$^{-1}$. Concentric to the cylindrical pipe there was an inner pipe, slightly shorter, through which material was dropped at a flow rate of 6 to 10 g min$^{-1}$, so that the powdered material was released into a counter-current airflow (López-Lilao et al. 2015). The total material drop height during the test was approximately 1.2 m, with a total duration of 10 minutes. Two sampling heads for inhalable (approximately total suspended particles, or TSP; designed by Institut für Gefahrstoff-Forschung-IGF) and respirable (approximately PM$_{4;}$ FSP-2, BGIA) fractions were located slightly above the discharge position of the material. Samples for gravimetric measurements of inhalable and respirable fractions were collected on cellulose thimbles, single thickness, 10x50 mm 25/pk and PVC filters of 37 mm and 5 µm of porosity, respectively. Each experiment lasted for 10 minutes.

The standard methods establish three repetitions for each sample in order to ensure repeatability of the results for the R.D test, and four for the C.D test. Between repetitions, cleaning the devices is not necessary while at the end of the test the device has to be thoroughly cleaned.

Considering gravimetrically sampled fractions ($W_I$, $W_T$ and $W_R$), the EN 15051 establishes 4 categories to classify material’s dustiness level (Table 3.2).

<table>
<thead>
<tr>
<th>Dustiness method</th>
<th>Category, classification</th>
<th>$W_I$</th>
<th>$W_T$</th>
<th>$W_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R.D</strong></td>
<td>Very Low</td>
<td>&lt; 300</td>
<td>&lt; 80</td>
<td>&lt; 10</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>300-650</td>
<td>80-300</td>
<td>10-60</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>&gt; 650-3000</td>
<td>&gt; 300-1000</td>
<td>&gt; 60-210</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>&gt; 3000</td>
<td>&gt; 1000</td>
<td>&gt; 210</td>
</tr>
<tr>
<td><strong>C.D</strong></td>
<td>Very Low</td>
<td>&lt; 1000</td>
<td>-</td>
<td>&lt; 20</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1000-4000</td>
<td>-</td>
<td>20-70</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>&gt; 4000-15000</td>
<td>-</td>
<td>&gt; 70-300</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>&gt; 15000</td>
<td>-</td>
<td>&gt; 300</td>
</tr>
</tbody>
</table>
### 3.3. Particle monitoring techniques and instrumentation

#### 3.3.1. Online instrumentation

The online instruments deployed during the experimental campaigns are summarized in Table 3.3.

**Table 3.3** Online instrumentation used during the experimental campaigns. N: number concentration \((\text{cm}^{-3})\). M: mass concentration \((\mu g \text{ m}^{-3})\). PSD: particle size distribution. LDSA: lung deposited surface area.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Manufacturer</th>
<th>Flow rate ((1 \text{ min}^{-1}))</th>
<th>Metric</th>
<th>Particle size range</th>
<th>Concentration range</th>
<th>Time resolution</th>
<th>Article</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Particle Sizer (OPS, TSI Model 3330)</td>
<td>TSI Inc., Shoreview, MN, USA</td>
<td>1</td>
<td>N and PSD</td>
<td>0.3-10 µm (16 channels)</td>
<td>0-3x10^5 cm^{-3}</td>
<td>1-min</td>
<td>II, IV</td>
</tr>
<tr>
<td>Mini Laser Aerosol Spectrometer (Grimm Mini-LAS)</td>
<td>Grimm Aerosol Technik, Ainring, Germany</td>
<td>1.2</td>
<td>M (occupational and PM)</td>
<td>0.25-32µm</td>
<td>0.1 – 10^4 µg m^{-3}</td>
<td>6-s</td>
<td>I, II, III, IV</td>
</tr>
<tr>
<td>Light scattering laser photometer (DustTrak™ DRX aerosol monitor TSI Model 8533)</td>
<td>TSI Inc., Shoreview, MN, USA</td>
<td>3</td>
<td>M (PM)</td>
<td>PM_{10}, PM_{2.5} and PM_{1}</td>
<td>0.001-150 mg m^{-3}</td>
<td>1-min</td>
<td>I, II, III, IV</td>
</tr>
<tr>
<td>Butanol Condensation Particle Counter (CPC TSI Model 3775)</td>
<td>TSI Inc., Shoreview, MN, USA</td>
<td>1.5</td>
<td>N</td>
<td>4-1500nm</td>
<td>&lt;10^7 cm^{-3}</td>
<td>1-s</td>
<td>I, II</td>
</tr>
<tr>
<td>Electrical Mobility spectrometer (NanoScan SMPS TSI Model 3910)</td>
<td>TSI Inc., Shoreview, MN, USA</td>
<td>0.7</td>
<td>N and PSD</td>
<td>10-420nm (13 channels)</td>
<td>100-10^5 cm^{-3}</td>
<td>1-min</td>
<td>I, III, IV</td>
</tr>
<tr>
<td>Diffusion Size Classifier Miniature (DiSCmini Matter Aerosol AG)</td>
<td>Testo, Wohlen, Switzerland</td>
<td>1</td>
<td>N, Size, LDSA</td>
<td>10-700nm</td>
<td>10^2-10^6 cm^{-3}</td>
<td>1-s</td>
<td>I, II, III, IV</td>
</tr>
<tr>
<td>Mini Wide Range Aerosol Spectrometer (Mini-WRAS 1371)</td>
<td>Grimm Aerosol Technik, Ainring, Germany</td>
<td>1.2</td>
<td>N,PSD and M (occupational and PM)</td>
<td>10nm-35µm</td>
<td>0.1 – 10^7 µg m^{-3}</td>
<td>1-min</td>
<td>I, II, III, IV</td>
</tr>
</tbody>
</table>

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Particle mass and number concentration, size and particle size distribution (PSD) were monitored by using portable and stationary instruments, based on different measurement principles:

- **Optical detection**

Optical particle sizer (OPS), laser aerosol spectrometer (Mini-LAS) and light-scattering laser photometer (DustTrak™ DRX).

Optical techniques are based on the detection of the light scattered by particles after interacting with a light source. They are based on the Mie scattering theory; the light scattered by a particle (0.3-0.6 µm) is proportional to its squared diameter. In optical particle counters, particles in the range between 0.3 up to 32 µm (depending on the instrument) are detected when going through a cell lit up by a lamp or laser beam. The particle size distribution is calculated comparing its scattered light with a calibration curve.

![Optical detection schematic operational principle](image)

**Figure 3.4** Optical detection schematic operational principle. Source: modified from TSI, OPS and DustTrak manual.

In optical instruments, the beam is generated by a laser diode, and passed through a lens to create a thin sheet of light which illuminates the aerosol. The light scattered by the aerosol particles is then captured by a mirror, which focuses the light on a photodetector. Finally, the scattered light pulse of every single particle is counted and the intensity of its signal classified to a certain particle size (single particle side scattering technology) (Figure 3.4). The photodiode signal can be separated into two components 1) the single particle pulses, to size discriminate; and 2) the photometric voltage, to
measure mass concentration (as voltage is proportional to mass concentration) (McMurry 2000).

- **Condensation particle counter (CPC)**

Condensation particle counters are designed to optically detect small particles (< 300 nm) (Liu 1976, Stolzenburg and McMurry 1991), although they can detect particles up to 3 μm. They are based on liquid (e.g. butanol, water) condensation on to the particles in order to increase their size up to a point where they can be optically detected (Agarwal and Sem 1980). The CPC used in this Thesis was butanol based and provided time-resolved and size-integrated particle concentration data.

The aerosol enters through the sample inlet and reaches a heated, butanol-soaked wick. The wick is dipped into the butanol reservoir and continuously absorbs butanol. Afterwards, when passing into the vertically cooled condenser, the vapour becomes supersaturated and condenses on to the particles, which act as condensation nuclei, forming larger droplets which can be optically detected. The liquid condensed on to the walls runs back down and is removed by the removal system (Figure 3.5).

![Figure 3.5 Butanol CPC schematic operational principle. Source: modified from TSI, CPC 3775 manual.](image)

- **Scanning Mobility Particle Sizer (SMPS)**

A SMPS is composed by a differential mobility analyser (DMA) and a CPC. The DMA classifies particles according to their electrical mobility, which is based on the fact that a particle with one charge inside an electric field migrates only according to its size and structure (Knutson and Whitby 1975a). Electrical mobility can be used to obtain particle size distributions of particles < 100 nm with high resolution and it is defined as:
\[ Z_p = \frac{neC_C}{3\pi \mu d_p} \]

where \( n \) is the number of charges, \( e \) is the charge of an electron, \( C_C \) Cunningham number, \( \mu \) air viscosity and \( d_p \) the particle diameter. Particles are charged by using two main mechanisms, diffusion or by presence of an electrical field. Particles get in contact with positive and/or negative ions (bipolar/unipolar charger) gaining ions and electrical charge. Ionization sources can be corona or radioactive.

In a stationary SMPS ambient air sampled through the inlet reaches a bipolar charger or neutralizer, which is usually a radioactive source such as Kr85. The aerosol is then classified according to its electrical mobility in the DMA (Knutson and Whitby 1975b, Chen et al. 1998), and the number concentration for each specific size range is determined in the CPC (Figure 3.6).

![Figure 3.6 NanoScan SMPS simplified schematic operational principle. Source: modified from TSI, NanoScan SMPS manual.](image)

The portable NanoScan SMPS provides time and size-resolved particle number concentration by using a non-radioactive unipolar diffusion charger (corona jet type) (Medved et al. 2000), a radial differential mobility analyser (rDMA, Zhang et al. 1995) and an isopropanol-based CPC.
- Diffusion Size Classifier Miniature (DiSCmini)

The DiSCmini principle is based on particles positive unipolar charging by using a corona charger. Following particle charge, excess of ions is removed in an ion trap, and particles are detected in two stages by electrometers (diffusion and filter), allowing for particle sizing and counting (Figure 3.7). In the first detector stage small particles are deposited on a pile of steel grids by diffusion and detected as an electrical current. The remaining particles end up in the filter stage, where particles are also detected as an electrical current. The ratio of these two currents is a measure of the average particle size determined during the instrument calibration. Total current is calculated as a function of particle diameter, and together with the flow rate the particle concentration is computed.

DiSCmini has high-time resolution of up to 1 second, but lower precision than the SMPS and CPC, with deviations of up to 30%. DiSCmini calibration is made with monodisperse aerosol, and the instrument’s response for polydisperse aerosols with a lognormal size distribution with a geometric standard deviation $\sigma = 1.9$ is then calculated (Fierz et al. 2010, 2011). When aerosols show a wide size distribution the DiSCmini will overestimate particle diameter and underestimate particle number. In addition, its performance in environments with high coarse particle concentrations was seen to be unreliable (Fonseca 2016).

![Diagram of DiSCmini](image)

**Figure 3.7** DiSCmini schematic operational principle. Source: modified from Testo, DiSCmini manual.

- Mini Wide Range Aerosol Spectrometer (Mini-LAS)

The Mini-LAS instrument combines the optical light scattering (single particle counter) and the electrical mobility principles in order to allow simultaneous measurement of micro- and nano-particles. Mass distribution is then calculated considering spherical particles. The optical particle counter measures the size distribution from 250 nm up to 32 $\mu$m and the electrical sensor, measures size distribution from 10 nm up to 250nm. The electrical sensor is composed by a unipolar electrical diffusion charger, a time multiplexed electrode (for particles deposition an extraction from the aerosol) and a
Faraday cup electrometer which measures only particles with an electrical mobility less than a certain limit value.

3.3.2. Offline instrumentation

Additionally to the online instruments, several offline instruments and techniques were used to fully characterize airborne particles and provide personal mass concentration exposures.

Personal exposure to respirable airborne particle mass concentration was gravimetrically determined by pre- and post-weighing of samples collected using a Dorr-Oliver Nylon Cyclone Assembly with Mixed Cellulose Ester Membranes (Figure 3.8 (a) and (b)), 0.80 µm pore size, 25 mm Ø (EDM Millipore™ MF-Millipore™) connected to a pump (Apex, Casella) operating at a 1.7 l min⁻¹ flow. Respirable mass concentration was also gravimetrically analyzed using the CIP I0-I (Areco ARC) sampler operating at a flow rate of 10 l min⁻¹ and air filtration by a rotating porous foam filter (Görner et al. 2009, Görner et al. 2010) (Figure 3.8 (c)).

![Figure 3.8](image-url) (a) and (b) Personal mass exposure samplers, Dorr-Oliver Nylon Cyclone Assembly and (c) CIP I0-I. Source: zefon international, Casella, España (Iván Ruiz, 2016).

From particles collected onto the filters, respirable crystalline silica was quantified by X-ray diffraction, using a BRUKER theta-theta model D8 Advance diffractometer with copper radiation (Kα λ = 1.54183Å) and VÄntec solid-state detector. Data were recorded from 2θ of 26° to 28°, with a step size of 0.07° and acquisition time of 3 s. Certified reference materials were used for quantification and validation (BCR-66, SRM 1878a y SRM 2950-2957). In order to quantify by X-ray diffraction, filters were baked, and then samples were re-suspended, and redeposited onto PVC filters (25 mm Ø) following the
Spanish National Occupational Health and Safety Institute's (INSHT) method based on membrane filter/ X-ray diffraction (MTA/MA -056/A06). Filters were left for at least 2 h in a dryer prior to quantification.

Airborne particles were also collected onto Au grids (Quantifolil ® with 1 µm diameter holes – 4 µm separation of 200 mesh) by using 3-piece conductive polypropylene air sampling cassettes (SKC Inc., USA, 1/8 in. inlet diameter and 25 mm filter Ø). The grids were attached to polycarbonate filters placed in the cassette. The cassette was connected to a Leland pump with an operating flow rate of 3-5 l min⁻¹ (Figure 3.9 (a) and (b)).

Particles collected were later chemically and morphologically analyzed by using two techniques, transmission electron microscopy (TEM J2100 coupled with an energy-dispersive X-ray (EDX) spectrometer; Figure 3.9 (c)) and by using a field emission scanning electron microscope (FESEM) FEI CUANTA 200F.

![Figure 3.9](image)

**Figure 3.9** (a) Leland pump (b) Particle collection using the 3-piece conductive polypropylene air sampling cassettes SKC Inc., and (c) analysis in the TEM J2100.

### 3.4. Measurement strategy

#### 3.4.1. Discrimination of background particles

To accurately characterize worker exposure to airborne particles emitted by a given industrial activity it is essential to discriminate them from background particles (see section 1.2.3.2). In order to achieve this, a non-activity time series approach was used (Brouwer et al. 2009). This approach is based on the idea that worker exposure during the activity is due to the sum of background particles plus particle concentration and particles generated during the activity. Thus, particle concentration was monitored in the worker area before and/or after each activity under study. The main limitation of
using this approach is that it does not consider temporal and spatial changes of background concentrations. In order to tackle this limitation, indoor measurements were carried out at different locations. Particles were monitored near the activity. In addition, particle were monitored in other indoor locations which were sufficiently far from the studied source, so that particles emitted by the activity would not impact indoor measurements, allowing for monitoring of any potential temporal changes in the background.

3.4.2. Sampling locations

In each workplace assessed, particle concentration and characteristics were monitored simultaneously in at least three locations 1) next to the emission source; 2) in the worker area, where devices were placed at a distance from the emission source similar to where the worker is standing and with instruments inlets being at a similar height as worker mouth (1.5 m height) (the location is representative of the breathing zone, even if it may not be considered strictly as such; Asbach et al. (2012); and 3) in indoor air to detect temporal changes. Additionally, when possible, instruments were also deployed to monitor personal breathing zone and outdoor air to detect and characterize outdoor particle influences.

3.4.3. Decision making based on statistical significance

For decision making, the evaluation of the statistical significance of increases in particle concentrations and the comparison of exposure concentrations to legal and/or reference limits is paramount. To determine the statistical significance of particle number and mass concentrations, the approach designed in Asbach et al. (2012) for particle number concentrations was used in this work.

Mean concentration during activity \( > BG ± 3 \cdot (\sigma BG) \)  

where BG is the mean temporal background (or pre-activity) concentration and \( \sigma BG \) is the standard deviation of the background concentration. This is the most widely used approach in the particle exposure literature (Kaminski et al. 2015, Fonseca et al. 2016).

Other techniques also used to assess statistical significance of exposure are conventional statistical tests (t-test and Mann-Whitney “U” test, both for independent samples) and the ARIMA (Autoregressive Integrated Moving Average) time series approach.
To apply the conventional tests, log-normality and variance homogeneity were assessed by using the Kolmogorov-Smirnov and Levene's (absolute) tests respectively, and by histogram plotting. When data did not fully fulfil normality assumptions, the non-parametric Mann-Whitney “U” Test (Wilcoxon rank-sum test) was used, whereas when normality assumptions where fulfilled, the two-sample t test was applied (unequal variances).

Finally, the ARIMA approach was used by Klein Entink et al. (2011) for particle number concentration, and it was later proposed in EN 17058:2018 (standard for workplace exposure- assessment of exposure by inhalation of nano-objects and their aggregates and agglomerates) as the golden standard method for number concentration and other metrics. To analyze an exposure concentration time series using ARIMA, the time series, the sample autocorrelation function and the sample partial autocorrelation function were plotted, in order to select the ARIMA model which best fit with the data. Afterwards, the selected model was applied using a differentiation factor for background and activity time series. When the statistic factor was > 1.95, concentrations were considered statistically significantly higher during the activity than during the background, whereas when the statistic factor was < 1.95 no statistically significant differences were considered. An example of this model can be found in Publication II, specifically in Supplementary materials (Annex B, section 2).

3.4.4. Regulatory compliance

In order to compare regulatory limits with monitored exposure concentrations, time-standardization is necessary. Usually, exposure limits are given as 8h TWA (time weighted averages) corresponding to a full-shift. To transpose monitored concentrations to 8h TWA the following equation was used:

\[ TWA = \frac{t_1 C_1 + t_2 C_2 + \ldots + t_n C_n}{t_1 + t_2 + \ldots + t_n} \]

Eq. (3.2)

where \(C_n\) is the mean concentration during a specific operation and \(t_n\) is the time of the specific activity.

3.4.5. Instrument intercomparison

Because of the need to monitor particle metrics simultaneously at different locations, the comparability of instruments needs to be ensured by means of intercomparison exercises. In this PhD Thesis, instruments were deployed at an air quality monitoring
station in Barcelona where they were challenged with ambient air aerosols. Intercomparison exercises were carried out on several occasions, usually before and/or after the monitoring campaigns. Instruments were placed during 24 to 72h side by side but with sufficient space between them to avoid interferences. Instruments were compared between each other as well as with internal references such as a stationary CPC and SMPS system, and mass concentrations were gravimetrically determined.

3.5. Mass-balance models

The one- and two-box mass-balance models were used and tested for two different industrial scenarios. Both models, are based on a set of mass balance equations including information of the source (contaminant generation), transport and particle losses. Main difference between them is that the two-box model considers that the limits of the model are two boxes one inside the other: near-field “NF” (where the source is) and far-field “FF”, and air flows between boxes (Figure 3.10). The performance of mass-balance models depends on their parametrization, as is discusses in Publications III and IV. The main considerations and types of models used in this Thesis are discussed below.

3.5.1. One-box model

In the one-box model, the mass balance concentration inside the model volume is described as a function of time:

\[
V \frac{dC}{dt} = S + Q \cdot C_o - Q \cdot C
\]

Eq. (3.3)

\[
Q = ACH \cdot V
\]

Eq. (3.4)

![Figure 3.10 One- and two-box models layout.](image-url)
where $S$ (mass/particles min$^{-1}$) is the emission source, $Q$ (m$^3$ h$^{-1}$) the air flow, $ACH$ (h$^{-1}$) air changes per hour, $V$ (m$^3$) the box volume, $C$ the concentration (inside de box and outgoing) and $C_o$ initial and incoming concentration.

3.5.2. Two-box model

In the two-box model, mass balance concentration inside the model volume (NF and FF volume) is described as a function of the time:

- Mass balance in the NF:

$$V_{NF} \frac{dC_{NF}}{dt} = S + \beta \cdot C_{FF} - \beta \cdot C_{NF}$$

Eq. (3.5)

- Mass balance in the FF:

$$V_{FF} \frac{dC_{FF}}{dt} = Q \cdot C_o + \beta \cdot C_{NF} - \beta \cdot C_{FF} - Q \cdot C_{FF}$$

Eq. (3.6)

$$Q = ACH \cdot (V_{NF} + V_{FF})$$

Eq. (3.7)

where $S_M$ or $S_N$ (mass/particles min$^{-1}$, respectively) is the emission source in the NF, $C_{NF}$ and $C_{FF}$ are NF and FF concentrations, $V_{NF}$ and $V_{FF}$ (m$^3$) the volume in NF and FF, and $\beta$ air flow between NF and FF. $C_o$, $Q$ and $ACH$ were described in Eq. (3.3 and 3.4).

3.5.3. Emission rate

The particle emission rate ($S_M$ or $S_N$) can be calculated using different approaches, depending on the type of process (mechanic, thermal...) and on the information available (Figure 3.11).

1) Powdered materials: dustiness index

For dust emissions from powder materials handling, the particle emission rate can be estimated by means of the dustiness index as:

$$S(t) = DI \cdot H \cdot \frac{dM(t)}{dt} \cdot LC$$

Eq. (3.8)

where DI (mg kg$^{-1}$ or particles kg$^{-1}$) is the respirable dustiness index of the material, H (dimensionless) is the handling energy factor for the process under study, $dM(t)/dt$ (kg min$^{-1}$) is the mass flow of the powder (e.g. inorganic fertilizer), and LC (dimensionless) is the protection factor of localized controls. H needs to be assumed (Lidén 2006,
Methodology

Schneider and Jensen 2007, Koivisto et al. 2015), and LC can be experimentally determined, theoretically calculated or extracted from the literature (Fransman et al. 2008, Hewett and Ganser 2017, Goede et al. 2018).

2) Experimental exposure concentrations

When estimation of the emission rates from the dustiness index is not possible (e.g. no powders involved in the process or during a thermal process), two different methods can be used, which estimate emission rates by means of measured particle/mass concentrations.

Figure 3.11 One- and two-box models application working flow. N (cm⁻³): particle number concentration as a function of time (t). M (µg m⁻³): particle mass concentration as a function of time (t). ACH (h⁻¹): air changes per hour. LC: local controls efficiency. NF: near-field. FF: far-field. H: handling energy factor.
i) Convolution theorem

Assuming that concentrations are fully mixed, particle concentrations can be described with a mass balance of aerosol particles in a single compartment (Hewett and Ganser 2017):

\[ \frac{dN(t)}{dt} = \lambda N_{BG}(t) + \frac{S_N(t)}{V} - \lambda N(t) \]  

Eq. (3.9)

where \( N \) (cm\(^{-3}\)) is the particle concentration, \( \lambda \) (min\(^{-1}\)) is the ventilation rate, \( N_{BG} \) (cm\(^{-3}\)) is the background particle concentration coming from outdoors and surrounding compartments, \( S_N \) (min\(^{-1}\)) is the particle emission rate of the source, and \( V \) (m\(^3\)) is the volume of the room. Particle losses were considered only due to ventilation.

When particle emissions from ventilation and indoor sources are negligible (i.e. \( S_{tot}(t) \approx 0 \) min\(^{-1}\), e.g. during background measurements) the particle concentration decay curve may be described as follows:

\[ N(t) = N_{t=0} \cdot e^{-\gamma \cdot t} \]  

Eq. (3.10)

where \( \gamma \) (min\(^{-1}\)) is the total particle decay rate.

According to the convolution theorem, particle concentrations during the activity are a convolution of the particle sources and particle losses as follows (Schripp et al. 2008):

\[ S_{tot}(t) \cdot N(t) = V \int_0^t (Q \cdot N_{BG}(t) + \varepsilon_C S_N(t)) \cdot N(t - \tau) d\tau \]  

Eq. (3.11)

where \( Q \) (m\(^3\) h\(^{-1}\)) is the air flow and \( \varepsilon_C \) (dimensionless) is the protection factor due to enclosure or LEV.

Particle emission term can be solved with a numerical deconvolution as:

\[ S_{tot}(t) = V \frac{N(t) - N(t - \Delta t) \cdot e^{-\gamma \cdot \Delta t}}{\Delta t} \]  

Eq. (3.12)

ii) Steady state equation for cyclic process

In addition, \( S \) (cm\(^{-3}\)) was calculated using the actual particle concentrations monitored, by applying the modified steady state equation for cyclic process (Hewett and Ganser 2017):

\[ S_N = \frac{\bar{C} \cdot V}{t_{ESD}} \]  

Eq. (3.13)

where \( \bar{C} \) (cm\(^{-3}\)) is the mean concentration during the activity (in this case thermal spraying), \( V \) (cm\(^3\)) is the room volume and \( t_{ESD} \) (min) is the spray duration. Assumptions
when using this equation are that particle concentration before the process starts is lower than during spraying, particle removal processes are negligible, and concentrations are fully mixed.

3.6. Risk assessment

3.6.1. ICRP inhalation deposition model

The simplification of the ICRP model described by Hinds (1999) was used to calculate particle regional deposition due to inhalation in the three main regions of the respiratory tract: head-airways, tracheobronchial and alveolar. The model was applied in terms of particle number, surface area and particle mass. Regional deposition refers to the mean probability of an inhaled particle to be deposited in a certain region of the respiratory tract (head airways, trachea bronchi and alveolar) by collection onto airway surfaces (Heyder et al. 1986).

The input for the model is the particle size distribution in terms of particle number; subsequently particle surface area and mass concentration were calculated through the equations described below.

Particle active surface area was calculated by applying particle size distribution to the equation (3.14) described in Heitbrink et al. (2009) as in Koivisto et al. (2012b):

\[
S = \frac{3\lambda D_b}{C_c(D_b)\delta}
\]

where \(\lambda_{\text{air}}\) (0.066 \(\mu\)m) is the mean free path for air, and \(\delta\) (0.905) is the scattering parameter for air. \(D_b\) is the mobility diameter and \(C_c\) the slip correction factor for the corresponding aerodynamic or mobility particle size.

The particle mass was additionally calculated by using mobility particle diameter and effective density as in Koivisto et al. (2012b):

\[
m = \rho_{\text{eff}} \frac{\pi}{6} D_b^3
\]

where \(\rho_{\text{eff}}\) (g cm\(^{-3}\)) is the effective density. When particle density was unknown, 1 g cm\(^{-3}\) was assumed for simplicity.
The regional inhalation dose rate was obtained by multiplying particle size concentrations by the ICRP human respiratory tract model deposition probability (ICRP, 2011) (see figure 1.9). The respiratory volume most widely used is 25 l min\(^{-1}\), corresponding to male respiration during light exercise (Koivisto et al. 2012b). However, other respiratory volumes can also be used according to what best fits in each specific case study. In the model, particles were assumed to be spherical and to preserve their size during inhalation.

### 3.6.2. Risk assessment tools

As previously described there are multiple empirical models and control banding tools currently in use for exposure assessment purposes. In this PhD Thesis, three of them were used and tested for different industrial scenarios assessed. ART and Stoffenmanager were selected as examples of empirical risk assessment models, given that they are recommended by the ECHA (ECHA 2016b) as higher tier 1, they are mostly complete in terms of specifications, and they are widely used (Landberg et al. 2015, 2017, Riedmann et al. 2015, Bekker et al. 2016, Savic et al. 2018). In addition, NanoSafer v1.1beta was used as it is a recently launched control banding tool with focus on NP (Kristensen et al. 2010; Jensen et al. under preparation).

- **Stoffenmanager® v.7.1**: is a risk priorisation web-based tool which consists of a control banding tool (inhalation and dermal), and general and REACH specific quantitative inhalation exposure models (Van Tongeren et al. 2017). It is considered between a tier 1 and tier 2 tool (ECHA, 2016; Landberg et al., 2017; Spinazzè et al., 2017; Van Tongeren et al., 2017), and its general assumptions are based on Marquart et al. (2008) while the rationale of the algorithm is based on Cherrie and Schneider (1999) and adapted as described in Tielemans et al. (2008b). To assess inhalation exposure to engineered NPs, Stoffenmanager has a specific nano-module.

- **The Advanced REACH tool (ART v.1.5)**: is a tier 2 mechanistic exposure modelling tool with a higher level of detail than Stoffenmanager. It also follows a Bayesian approach that combines the mechanistic model with measurements of exposure (Landberg et al. 2017). Similarly to Stoffenmanager, ART is also based on Cherrie and Schneider (1999) with Tielemans et al. (2011) modifications. It is described and explained in detail in Fransman et al. (2011), and it has been tested and calibrated in Schinkel et al. (2011). Stoffenmanager and ART dimensionless total exposure score equations can be found in Riedmann et al. (2015).
- The NanoSafer v.1.1beta: is a control-banding and risk management tool (Kristensen et al. 2010; Jensen et al. in preparation) specifically designed for manufactured nanomaterials and NP release activities (e.g. powder handling and fugitive/point-source emissions), which is currently being refined and further developed under caLIBRAt e Project (http://www.nanocalibrate.eu/home). Hazard assessment and case-specific exposure potentials are combined into an integrated assessment of risk levels (control bands) with associated risk management recommendations. NanoSafer scores can be translated to concentrations by using simple equations (Jensen et al. 2014):

\[
C_{\text{acute}} = 2 \cdot OEL \cdot NS_{\text{acute}}, \quad \text{Eq. (3.16)}
\]

\[
C_{8h \text{ TWA}} = OEL \cdot NS_{8h \text{ TWA}}, \quad \text{Eq. (3.17)}
\]

where \(C_{\text{acute}}\) and \(C_{8h \text{ TWA}}\) are estimated acute and 8h TWA concentrations, \(NS_{\text{acute}}\) and \(NS_{8h \text{ TWA}}\) are NanoSafer scores for acute and 8h TWA. OEL value use will be the OEL for bulk material stablised when:

\[
\text{Volume specific surface area (VSSA)} < 30 \text{ m}^2\text{cm}^{-3}, \quad \text{Eq. (3.18)}
\]

and \(OEL_{\text{nano}}\) when:

\[
\text{VSSA} > 30 \text{ m}^2\text{cm}^{-3}, \quad \text{Eq. (3.19)}
\]

\(OEL_{\text{nano}}\) is estimated from bulk OEL as:

\[
OEL_{\text{nano}} = OEL \cdot \frac{30^{\delta_{\text{nano}}}}{SSA_{\text{nano}}}, \quad \text{Eq. (3.20)}
\]

where OEL is the stablished OEL for the bulk material, \(\delta\) (g cm\(^{-3}\)) is the specific density of the nanomaterial and SSA (m\(^2\) g\(^{-1}\)) is the specific surface area of the nanomaterial.

The three tools consider different input parameters (Table 3.3), and therefore provide different output results as well Table 3.4. For material-related inputs, ART has higher specifications regarding the type of material, dustiness and humidity, whereas NanoSafer focuses more on the type of particle and their physical-chemical characteristics. The other main difference is that Stoffenmanager and NanoSafer consider material health and safety, whereas ART leaves this part out if its scope, and focuses only in exposure concentrations.
Table 3.3 Comparison of input parameters for the three risk assessment models applied.

<table>
<thead>
<tr>
<th>INPUT</th>
<th>ART</th>
<th>Stoffenmanager</th>
<th>NanoSafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS</td>
<td>YES</td>
<td>For components</td>
<td>YES</td>
</tr>
<tr>
<td>Type substance (Physical properties)</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>Dustiness</td>
<td>Enter value or Drop-down level</td>
<td>Chose type of material</td>
<td>Enter value or Drop-down level</td>
</tr>
<tr>
<td>Humidity</td>
<td>Drop-down levels</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>% of product</td>
<td>YES</td>
<td>% For components</td>
<td>NO</td>
</tr>
<tr>
<td>Health and Safety</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Nano Specifications</td>
<td>NO</td>
<td>NO (specific nano-module)</td>
<td>Modified surface, nano, fullerene...</td>
</tr>
<tr>
<td>Primary particle</td>
<td>NO</td>
<td>NO</td>
<td>Shape, Size, SA</td>
</tr>
<tr>
<td>Density</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>Solubility</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>Source position</td>
<td>BZ/FF</td>
<td>BZ/FF</td>
<td>NF/FF</td>
</tr>
<tr>
<td>Type of process</td>
<td>Only mechanical process</td>
<td>Mechanical, thermal...</td>
<td>Only mechanical process</td>
</tr>
<tr>
<td>Type of handling</td>
<td>YES</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>Energy</td>
<td>Drop height</td>
<td>NO</td>
<td>Energy level</td>
</tr>
<tr>
<td>Emission controls</td>
<td>Containment, LEV, glove box, segregation/enclosure</td>
<td>PPE, LEV, segregation/enclosure</td>
<td>Recommended emission controls (in the Output)</td>
</tr>
<tr>
<td>Maintenance</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>Duration</td>
<td>YES</td>
<td>YES</td>
<td>YES (cycle timing)</td>
</tr>
<tr>
<td>Background</td>
<td>YES (with specific processes)</td>
<td>NO (non-activity period)</td>
<td>NO</td>
</tr>
<tr>
<td>Frequency</td>
<td>NO</td>
<td>N° days and n° workers</td>
<td>NO</td>
</tr>
<tr>
<td>Amount of material</td>
<td>NO</td>
<td>NO</td>
<td>YES (enter value)</td>
</tr>
<tr>
<td>Volume</td>
<td>Drop-down values or description</td>
<td>Drop-down values</td>
<td>Enter value</td>
</tr>
<tr>
<td>ACH</td>
<td>Drop-down values or description</td>
<td>Type of ventilation (description)</td>
<td>Enter value or drop-down values</td>
</tr>
</tbody>
</table>

Regarding process characterization, main differences between the tools are that 1) ART and Stoffenmanager allow to assess whether emissions take place in the breathing zone...
or not, whereas in NanoSafer NF-FF values are provided; 2) ART and Stoffenmanager are designed only for mechanical processes, whereas Stoffenmanager considers thermal processes as well; 3) type of handling and energy levels are not considered in Stoffenmanager; and 4) in NanoSafer no emission controls are considered as one of the purposes of the tool is to provide recommendations regarding type of control measures to be applied in a specific scenario. Further developments of the tool are expected to include control measures in the risk assessment evaluation. For the case scenarios of this Thesis, local controls reductions were included considering factors applied in the ART tool. Finally, room characteristics can be better detailed in NanoSafer as it requires specific values as input, whereas ART and Stoffenmanager have only drop-down default values.

The ART tool output is a full-shift predicted concentration in terms of mass. Conversely, the NanoSafer does not provide concentration but instead produces a hazard level, exposure potential (very high, high, moderate, low...) and protection recommendations with an efficiency percentage. Finally, Stoffenmanager's output is an in-between result, providing task and full-shift concentration (for material and components) and a risk level.

Table 3.4 Comparison of output parameters for the three risk assessment models applied.

<table>
<thead>
<tr>
<th>Output</th>
<th>ART</th>
<th>Stoffenmanager</th>
<th>NanoSafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task and full-shift mass concentrations</td>
<td>Task and Full-shift concentrations for material and components, and risk level of exposure</td>
<td>Hazard level, risk level of exposure and recommendations</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4

Results
4. RESULTS

This chapter presents the results of this PhD Thesis in the form of four research publications (papers), which discuss the objectives presented in chapter 2 (Objectives and Structure). While all four publications address the first objective (Worker exposure assessment and particle emissions), the rest of the objectives are dealt with in the different papers. Publication I tackles objective 3 (Dustiness as an exposure prediction tool) on the basis of mechanical handling of powders in a pilot plant. In Publication II, handling (packing) of ceramic materials at industrial scale was used as a base to study objectives 2i and ii (related to the use of tools and metrics for exposure assessment), 3 (Dustiness as tool for exposure prediction), and 5 (Evaluation of risk assessment and control banding tools). Publication III expands on the research presented in Publication II by assessing the performance of mass-balance models when challenged with low concentrations of micron-sized particles, in an industrial scenario during mechanical handling (packing) of a fertilizer. Finally, in Publication IV mass-balance models are tested in the framework of high number concentrations of NPs (unintentionally released), sourcing from thermal spraying of ceramic coatings at industrial scale.

Figure 4.1 Objectives addressed in each research publication.
4.1. Publication I: On the relationship between exposure to particles and dustiness during handling of powders in industrial settings

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Published in:

Annals of Work Exposures and Health, 63(1): 107-123, 2019
doi: 10.1093/annweh/wxy092


Accepted date: 16 October 2018

Journal Impact Factor / 5-Year Impact Factor: 1.615 / 2.101
On the relationship between exposure to particles and dustiness during handling of powders in industrial settings

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Abstract

Exposure to ceramic powders, which is frequent during handling operations, is known to cause adverse health effects. Finding proxy parameters to quantify exposure is useful for efficient and timely exposure assessments. Worker exposure during handling of five materials (a silica sand (S1), three quartzes (Q1, Q2 and Q3) and a kaolin (K1)) with different particle shape (prismatic and platy) and sizes (3.4 - 120 μm) was assessed. Materials handling was simulated using a dry pendular mill under two different energy settings (low and high). Three repetitions of two kilos of material were carried out per material and energy conditions with a flow rate of 8 - 11 kg/h. The performance of the dustiness index as a predictor of worker exposure was evaluated correlating material’s dustiness indexes (with rotating drum and continuous drop) with exposure concentrations. Significant impacts on worker exposure in terms of inhalable and respirable mass fractions were detected for all materials. Mean inhalable mass concentrations during background were always lower than 40 μg/m³ whereas during material handling under high energy settings mean concentrations were 187, 373, 243, 156 and 430 μg/m³ for S1, Q1, Q2, Q3 and K1 respectively. Impacts were not significant with regard to particle number concentration: background particle number concentrations ranged between 10620 – 46421 /cm³ while during handling under high energy settings they were 20880 - 40498 /cm³. Mean lung deposited surface area during background ranged between 27 - 101 μm²/cm³ whereas it ranged between 22 - 42 μm²/cm³ during materials handling. TEM images evidenced the presence of nanoparticles (≤ 100 nm) in the form of aggregates (300 nm - 1 μm) in the worker area, and a slight reduction on mean particle size during handling was detected. Dustiness and exposure concentrations showed a high degree of correlation (R² = 0.77 - 0.97) for the materials and operating conditions assessed, suggesting that dustiness could be considered a relevant predictor for workplace exposure. Nevertheless, the relationship between dustiness and exposure is complex and should be assessed for each process, taking into account not only material behaviour but also energy settings and workplace characteristics.

Keywords: indoor air, prediction of exposure, airborne dust, exposure assessment, particulate matter, industrial settings, nanoparticles
Introduction

Exposure to airborne particles is a growing field of research due to its complexity and intrinsic difficulty with regard to standardization. This is linked to the large variety of sources, processes and hazardous materials involved. The ceramic industry is a relevant case study, as it results in personal exposures in ambient and indoor air to a wide range of potentially hazardous raw materials and because during the manufacturing cycle a wide variety of bulk materials is used. In most cases, these materials are dry micro-sized (or even nano-sized) powders. As described by Brouwer et al. (2004), the aerosolization of submicrometer particles in workplaces is not limited to nanotechnology facilities. New technologies such as laser ablation, laser thermal treatment or inkjet printing, and green materials developments such as bactericidal and easy-clean surfaces, are currently being introduced in the traditional ceramic sectors (Gabaldón-Esteve et al., 2014; Llop et al., 2014; Monfort, 2012). The use of these new technologies as well as the growing and emerging markets represent new challenges in terms of occupational health (Fonseca et al., 2016; Fonseca et al., 2015; Viana et al., 2017; Voliotis et al., 2014).

Particulate matter (PM) as well as ultrafine particles (UFP) can penetrate deep in the human respiratory tract, the finest fractions reaching the alveolar region (Brunekreef & Forsberg, 2005; Pope & Dockery, 2006). Respiratory-related disease in the ceramic industry due to inhalable dust has already been reported (Alim et al., 2015; Dehghan et al., 2009; Neghab et al., 2009). In Spain, concentration limit values have been established for particulate matter exposure (not otherwise specified) as 10000 μg/m³ and 3000 μg/m³ for inhalable and respirable mass fractions, respectively (INSH, 2017).

The number of studies dealing with exposure is relatively low when compared with the wide variety of possible exposure scenarios in industrial settings (Brouwer et al., 2009). However, exposure assessment is a key component of risk assessment, which is generally combined with toxicological studies (Kuhlbusch et al., 2011). Thus, it is essential to determine exposure under different real world industrial scenarios as well as to predict exposure and establish efficient risk management strategies. In recent years many efforts were carried out to control and reduce exposure, although less attention was paid to the production processes and material handling (Lidén, 2006). In this framework, dustiness has risen as a valuable tool for occupational safety (Hamelmann & Schmidt, 2003), as it is a measure of a material’s tendency to generate airborne dust during handling. However, discussions are ongoing about the use of the dustiness index as a direct predictor for worker exposure (Dubey et al., 2017; Fonseca et al., 2018) because dust emissions are known to depend on powder properties, the amount of material handled, the process, and local controls (Fransman et al., 2011). Certain authors (Brouwer, 2006; Class et al., 2001; Fonseca et al., 2018; Heitbrink et al., 1990) found no clear or limited relationship between exposure and dustiness, although they pointed out the importance of this parameter for risk assessment. On the other hand, Breum et al. (2003) despite finding a clear positive relation between dustiness and exposure, did not use their results for exposure prediction. Finally, some factors should be taken into account when establishing the relation between dustiness and exposure: 1) two standard methods are described in (EN 15051); 2) dustiness depends mainly on material particle size distribution, humidity, density, morphology and specific surface area (SSA) (Hamelmann & Schmidt, 2003; Lidén, 2006; López-Lilao et al., 2016, 2015); and 3) dustiness tests should mimic as closely as possible the actual process energy applied (Evans et al., 2013). As a result, dustiness is currently used as an input for exposure modelling (Levin et al., 2014; Schneider and Jensen, 2007) and by materials producers to
modify products in order to reduce dust generation (Lidén, 2006), rather than as a direct exposure predictor.

In this context, the present work aims to 1) assess exposure to airborne particles during handling of five highly used ceramic materials, paying special attention to material characteristics (size and particle shape) as well as to the influence of operating conditions (energy input); 2) assess dustiness indexes of the output materials to understand their emission mechanisms; and 3) correlate actual exposure concentrations with dustiness indexes, with the final goal to contribute on the understanding of the potential use of dustiness as a predictor of worker exposure.

**Methodology**

**Experimental setup and instrumentation**

The experiments took place in the pilot plant of the Institute of Ceramic Technology (ITC), Castellón, Spain during 4 days in October 2016. The pilot plant is divided into two connected rooms of 406 m² and 182 m² partly separated by a wall, which allows for air exchange at two different points (Figure 1). The plant is operated on a regular basis by 5 or more workers carrying out different activities. Material handling took place in room 1. The exterior door leading outdoors was kept open, as this is the plant’s normal procedure.

Worker exposure to airborne particles was monitored during handling of powder materials during a process which included feeding of the materials to a dry pendular mill and extracting the powders from it. In order to study only handling (and not milling) emissions, a mill not altering the primary particle size but instead only modifying the size of the aggregates was selected, so that the process resembled the one that would occur during the handling operations. To verify this, the primary particle diameters of the input and output materials were determined by laser diffraction (wet method, see section 2.3) and no significant differences were observed. Modifying the primary particle size would have required additional mechanical action (Evans et al., 2013), which was not applied in this case. The mill selected for this purpose was a pilot-plant scale Pottemill PM-LB, with a nominal output capacity around 20 kg/h.

Particle mass, number concentration and alveolar lung deposited surface area (LDSA) were monitored as well as particle size distribution and morphological/chemical characterization. Three sampling locations were selected (Figure 1):

- Worker area: the devices were placed at a distance from the emission source similar to where the worker is standing (1 m from the floor and 50 cm from the emission source). The location is representative of the breathing zone, even if it may not be considered strictly as such. Devices used were: a butanol Condensation Particle Counter (CPC, TSI Model 3775; sample flow rate 1.5 l/min) to measure particle number concentration (4 - 1500 nm, 1 minute time resolution); an electrical mobility spectrometer (NanoScan SMPS, TSI Model 3910; sample flow rate 0.7 l/min) to measure particle size distribution in 13 channels (10 - 420 nm, 1 minute time resolution); a miniature diffusion size classifier (DiSCmini Matter Aerosol, Testo; sample flow rate 1 l/min) to measure particle number concentration, mean particle size and lung deposited surface area (LDSA) (10 - 700 nm, 1 minute time resolution); and a Mini Laser Aerosol Spectrometer (Grimm, Mini-LAS 11R; sample flow rate 1.2 l/min) to measure particle mass concentration (0.25 - 32 μm, 31 channels, 1 minute time resolution). In addition, TEM grids (Quanatofolil * Au grids with 1 μm diameter holes - 4 μm separation of 200 mesh) were placed in a sampling cassette (SKC INC., USA, inlet diameter 1/8 in. and filter diameter 25 mm) following the sampling setup described by Tsai et al., (2008). The Cassette was connected to a Leland pump (3 l/min). Sampling was performed in the worker area and indoor locations during handling for each material and for two energy
settings of the pendular mill (low and high; see 2.2). Chemical and morphological analysis was later carried out by TEM J2100 coupled with an energy-dispersive X-ray (EDX) spectrometer.

- Indoor: a monitoring location inside the plant far from the processes of study but still connected by air flows. It was representative of the pilot plant’s background concentrations. Devices used were a DiSCmini (see above) and a Mini Wide Range Aerosol Spectrometer (Mini-WRAS 1371; Grimm; sample flow rate 1.2 l/min) to measure particle mass concentration, particle number concentration and particle size distribution from mainly to discuss about indoor and outdoor influence over the worker area measurements.

All online instruments were time-synchronized and inter-compared overnight. Calibration of the Grimm laser spectrometers (Mini-LAS and Mini-WRAS) followed the procedures recommended by the manufacturer and are occasionally calibrated with regard to gravimetric reference samples. It should be noted that this kind of calibration is not carried out with the same aerosol as monitored in the present work, which would be the advisable procedure for any workplace exposure assessment (PD CEN/TR 16013 - 2:2010).

10 nm to 35 μm in 41 channels with a 1 minute time resolution. Additionally, TEM particle collection was carried out (see above).

- Outdoor: an outside monitoring location was set close to the main entrance of the plant. Devices used were a DiSCmini and a Grimm Mini-LAS (see above).

Indoor and outdoor monitoring points are not going to be extensively discussed. They are used Devices started monitoring between 30 and 60 minutes before the start of the process (pre-activity), and the average results in this period before the process were used as a background particle concentration (Brouwer et al., 2009; Demou et al., 2008).

Worker area exposures were considered statistically significant when the following

![Diagram](image-url)

**Figure 1.** ITC pilot plant layout. Monitoring locations as well as devices used during the handling process are indicated.
approach, described by Asbach et al. (2012) and Kaminski et al. (2015), was fulfilled:

Mean value during operation > BG + 3*(σBG)

where BG is the mean temporal background concentration (pre-activity) and σBG is the standard deviation of the background concentration.

Target materials, operations and conditions

Five different micronized materials, widely used in the ceramic industry, were selected (Table 1 and Table S1, Supporting information): Silica sand, S1 (d_{50} = 120 μm; CAS: 14940-68-2), three types of quartz, Quartz Q1, Quartz Q2 and Quartz Q3 (d_{50} 3.4 - 12.1 μm; CAS: 14808-60-7), and kaolin, K1 (d_{50} = 5.7 μm; CAS: 1332-58-7) sieved through a 5 mm mesh. Materials particle size distribution (d_{50}) determination was carried out by using laser diffraction; methodology described in more detail in section 2.3. According to the aspect ratio (AR) silica sand and quartz particles were considered to be prismatic (ca. spherical), while kaolin was platy (plate-like) shaped (micrographs of Q2 and K1, Figure S1, Supporting information). Because the moisture content of powders can affect material dustiness and exposure (Levin et al., 2015; Lidén, 2006) and also, due to pendular mill working requirements, all materials were previously dried using an oven at 105 - 110 °C during at least 24h.

High energy (HE) (frequently used) and low energy (LE) operating conditions were tested, being representative for this industrial sector. Operating conditions are determined by air and material flow rate, aspiration intensity, milling speed and particle separation (Table 2).

Three repetitions were carried out for each material and condition. Approximately 2 kg of material were manually fed by the pilot plant worker into the mill grinding chamber for each repetition. All the materials were processed for 12 - 15 minutes (material flow 8 - 11 kg/h; Table 2), the exact time depending on how long it took for the material to be introduced in the mill’s chamber due to its flowability. At the end of each repetition the output material was manually collected and stored for subsequent chemical and dustiness analysis.

Finally, cleaning operations were also monitored.

Materials characterisation

Input and output materials were characterized:

- Specific surface area (SSA) was assessed according to the BET method by nitrogen absorption (Brunauer et al., 1928).

- Materials flowability was assessed by using the Hausner ratio (HR); the quotient of the bulk density of the packed particle bed (by tapping) and the aerated bulk density of the particle bed, obtained by dropping powder into a container without stirring or vibration. In this regard, where the bigger the HR the lower the followability (Mallol et al., 2008).

- Particle Size Distribution (PSD) was determined by laser diffraction (d_{laser}) wet method (ISO 13320-1, 2009) using the Mastersizer 2000 that analyse the sample by the theory of Fraunhofer and Mie with a size resolution of 0.02 - 2000 μm and by and X-ray gravitational sedimentation using the Sedigraph method from Micrometrics (d_{sedigraph}).

- The aspect ratio (AR), a particle shape factor defined as the ratio of the particle’s major dimension and minor dimension, was determined by the Parslow-Jennings method for oblate spheroids (Jennings & Parslow, 1988; Otterstedt & Brandreth, 2013). This method is based on the fact that d_{laser} and d_{sedigraph} (previously described) have different dependence on aspect ratio and, therefore, we can only obtain the same diameter in the case of spherical particles.
where $AR$ is the aspect ratio, $d_{\text{stokes}}$ the diameter of a sphere with the same density and setting velocity as the particle of interest ($\mu m$), and $d_{\text{laser}}$ is the diameter of the sphere of same diameter as the cross-sectional projection of the particle ($\mu m$).

\[ d_{\text{stokes}} = \frac{d_{\text{laser}}}{\sqrt{2 \cdot AR \cdot \arctan \sqrt{AR^2 - 1}} + \ln[AR + \sqrt{AR^2 - 1}]} \]

\(1\)

Table 1. Material type, material code, particle shape and most common uses in the ceramic industry are given. Particle size distribution: PSD in terms of di: diameter below which lies $\%$ by volume of total particles, specific surface area: SSA, Hasner ratio: HR and aspect ratio: AR are described for each material. Inhalable mass fraction and classification level are shown for the two dustiness methods (continuous drop and rotating drum). Moisture of all the samples before the start of the manipulation process was $<0.5\%$.

<table>
<thead>
<tr>
<th>Material type</th>
<th>Code</th>
<th>Shape</th>
<th>Uses</th>
<th>$d_{50}$ ($\mu m$)</th>
<th>$d_{10}$ ($\mu m$)</th>
<th>$d_{90}$ ($\mu m$)</th>
<th>SSA (m$^2$/g)</th>
<th>HR</th>
<th>AR</th>
<th>$w_i$ (mg/kg) C/D</th>
<th>$w_i$ (mg/kg) R.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium silica sand</td>
<td>S1</td>
<td>Prismatic</td>
<td>Ceramics production</td>
<td>120</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>1.12</td>
<td>4.3</td>
<td>463 (Very Low)</td>
<td>NDA</td>
</tr>
<tr>
<td>Quartz</td>
<td>Q1</td>
<td>Prismatic</td>
<td>Materials preparation, forming, glazing or firing</td>
<td>12.1</td>
<td>1.4</td>
<td>37.0</td>
<td>1.4</td>
<td>1.64</td>
<td>3.3</td>
<td>4593 (Moderate)</td>
<td>202 (Very Low)</td>
</tr>
<tr>
<td>Quartz</td>
<td>Q2</td>
<td>Prismatic</td>
<td>Pigment production for the colouration of glazes</td>
<td>5.8</td>
<td>1.1</td>
<td>18.8</td>
<td>2.7</td>
<td>1.52</td>
<td>5.7</td>
<td>3855 (Low)</td>
<td>164 (Very Low)</td>
</tr>
<tr>
<td>Quartz</td>
<td>Q3</td>
<td>Prismatic</td>
<td>Used in rubber compounds</td>
<td>3.4</td>
<td>1.0</td>
<td>8.4</td>
<td>4.4</td>
<td>1.57</td>
<td>3.8</td>
<td>3029 (Low)</td>
<td>64  (Very Low)</td>
</tr>
<tr>
<td>Kaolin caobar</td>
<td>K1</td>
<td>Plate (plate-like) or ribbon-like</td>
<td>Traditional ceramics production. Cement and metallurgical industries</td>
<td>5.7</td>
<td>1.4</td>
<td>15.7</td>
<td>9.6</td>
<td>1.83</td>
<td>20</td>
<td>10012 (Moderate)</td>
<td>410 (Low)</td>
</tr>
</tbody>
</table>

This factor is a measure of the irregularity of particle shape, i.e. deviation from a spherical shape. For prismatic, platy, and ribbon-like particles the aspect ratios were 1 - 5, 4 - 15, and 5 - 100, respectively (Otterstedt & Brandreth, 2013). Therefore, the selected quartzes and sands can be considered prismatic particles and the kaolin can be classified as platy or ribbon-like particle.

In addition, airborne particles collected on Au Quantifoil* grids during handling were morphologically and chemically characterised by TEM-EDX (Markowicz & Grieken, 2001; Williams & Carter, 2009).

**Dustiness tests**

Dustiness tests were performed for all materials and conditions (high and low energy) tested, before and after the handling process (input and output materials). The two dustiness tests described by the EN 15051 (2013) (Continuous drop method; López-Lilao et al., 2016), and

Log-normality and homogeneity were assessed with the Shapiro-Wilk and Levene’s test, respectively and, as data did not fulfill normality assumptions, the non-parametric Mann-Whitney “U” Test was performed in order to determine statistically significant differences between mean
airborne particle diameters measured with the NanoScan.

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Air flow rate (m³/h)</th>
<th>Material flow rate (kg/h)</th>
<th>Milling speed (rpm)</th>
<th>Particle separation (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Energy</td>
<td>1600</td>
<td>8-11</td>
<td>1200</td>
<td>600</td>
</tr>
<tr>
<td>High Energy</td>
<td>1800</td>
<td>8-11</td>
<td>2250</td>
<td>1800</td>
</tr>
</tbody>
</table>

Table 2. Milling parameters for low and high energy settings are described, aspiration intensity, mill speed and particle separation. Material process flow rate, for both energy settings, are also described.

Results and Discussion

Exposure assessment

Mean background concentrations (pre-activity) for the inhalable fraction were below 40 µg/m³ for all the materials except for S1 (92.1 µg/m³) and Q1 (58.9 µg/m³) (Table 3). Outdoor, indoor and background concentrations for PM₁₀ were representative of PM₂.₅ outdoor concentrations (20 - 30 µg/m³; Pérez et al., 2008). Outdoor air to indoor micro-sized particle concentration was deemed negligible (Figure S3, Supporting information).

As expected, particle mass concentrations in the worker area, for all the materials, increased during handling (Table 3, Figure 2 and S4, Supporting information). Previous studies have already seen impacts on dust concentrations in both particle number and mass during material handling on paint factories pouring (Koivisto et al., 2015; Koponen et al., 2015), during bag filling of black carbon production (Kühlbusch, et al., 2004), and during weighing bulk CNTs and sanding epoxy containing CNTs (Cena & Peters, 2011). Particle mass concentrations, for all repetitions, showed a marked cycle that consisted on a peak during material feeding and then a decrease, showing a clear impact on coarse particles due to handling for high and low energy settings (Figure 2 and S4, Supporting information). Mean inhalable mass concentrations during low energy settings were 189.5, 80.8, 106.8 and 319.1 µg/m³ for Q1, Q2, Q3 and K1 respectively whereas during high energy settings they were 373.0, 243.6, 156.0 and 429.6 µg/m³ (Table 3). Koponen et al. (2015) also described cyclic behaviour for materials pouring, with a concentration peak at the beginning of the activity. Hence, in some cases the number of repetitions can be more critical than the amount of material processed and thus the repetitions (start and stop) of a process is a factor that should be taken into account for exposure assessment models (Koponen et al., 2015). The time-weighted averages (TWA) for exposure levels are shown in Table S2, Supporting information. The highest value for the inhalable mass fraction was 429.6 µg/m³ during K1 handling. This is well below the inhalable (10000 µg/m³) and respirable (3000 µg/m³) OELs (INSH, 2017). Additional information regarding the calculation of the TWAs is provided in Table S2 (Supporting information).

On the contrary, the impact of handling on fine particles, measured with the CPC, was lower than for micro-sized particles. The trend observed for particle number concentration during handling suggests a more cumulative trend than for mass, especially for high energy conditions (Figure 2 and Figure S4, Supporting information). However, a significant increase in mean number concentration was not observed for any of the materials except for S1. This was probably due to the more frequent coagulation/adsorption processes of ultrafine particles onto coarse particles, which resulted in lower particle number concentrations. Recommended exposure concentrations during handling were not exceeded in any case, again with the exception of S1 which was on the limit of 40000 /cm³ (Van Broekhuizen et al., 2012). Alveolar lung deposited surface area, monitored with DiSCmini (Table 3) was seen to decrease during materials handling when compared with pre-activity values (background). Mean LDSA
during background concentrations ranged between 27.1 - 100.9 µm²/cm³ whereas during materials handling they ranged between 22.1 - 42.3 µm²/cm³.

Concerning mill cleaning operations, the highest 1-min peak concentrations for nano- and micro-sized particles when considering background + handling + cleaning were recorded during the cleaning operation, specifically during vacuuming (Figure 2 and S4, and Table S3, Supporting information). The maximum 1-min peak recorded during the cleaning operation for inhalable mass fraction of material Q1 was 13824 µg/m³. Regarding particle number concentrations, maximum 1-min peak concentrations of 81247, 64443 and 77385 /cm³ were recorded for Q2, Q3 and K1 (materials with lower d₉₀), respectively (Table S3, Supporting information). On the other hand, mean concentrations during cleaning were higher than the corresponding background concentrations for both inhalable and respirable mass fractions and for all materials except S1.

Table 3. Mean particle number, mass concentration and LDSA during handling of the powders at low and high energy settings. NDA: no data available.

<table>
<thead>
<tr>
<th>Material</th>
<th>Measurement point</th>
<th>Particle number (#/cm³)</th>
<th>LDSA (µm²/cm³)</th>
<th>Inhalable fraction (µg/m³)</th>
<th>Respirable fraction (µg/m³)</th>
<th>Particle number (#/cm³)</th>
<th>LDSA (µm²/cm³)</th>
<th>Inhalable fraction (µg/m³)</th>
<th>Respirable fraction (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Background</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>10620</td>
<td>(9179-16431)</td>
<td>NDA</td>
<td>NDA</td>
</tr>
<tr>
<td></td>
<td>Worker area</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>40498</td>
<td>(30713-49155)</td>
<td>NDA</td>
<td>NDA</td>
</tr>
<tr>
<td>Q1</td>
<td>Background</td>
<td>24439</td>
<td>(19249-29660)</td>
<td>46.1 (29.8-156.3)</td>
<td>58.9 (20.3-599.2)</td>
<td>20.9 (16.0-52.6)</td>
<td>42666</td>
<td>(25421-51461)</td>
<td>48.2 (28.8-69.4)</td>
</tr>
<tr>
<td></td>
<td>Worker area</td>
<td>30310</td>
<td>(24624-36399)</td>
<td>30.8 (27.5-40.4)</td>
<td>189.5 (76.0-337.0)</td>
<td>70.7 (40.6-126.9)</td>
<td>28059</td>
<td>(22427-40300)</td>
<td>22.1 (18.4-27.2)</td>
</tr>
<tr>
<td>Q2</td>
<td>Background</td>
<td>29056</td>
<td>(15904-47210)</td>
<td>27.1 (20.7-43.6)</td>
<td>15.2 (3.8-135.1)</td>
<td>5.9 (3.6-15.7)</td>
<td>29056</td>
<td>(15904-47210)</td>
<td>27.1 (20.7-43.6)</td>
</tr>
<tr>
<td></td>
<td>Worker area</td>
<td>15033</td>
<td>(10149-23264)</td>
<td>22.7 (17.0-40.5)</td>
<td>80.8 (11.8-160.5)</td>
<td>16.9 (7.7-122.5)</td>
<td>23091</td>
<td>(16805-30928)</td>
<td>26.9 (20.5-31.1)</td>
</tr>
<tr>
<td>Q3</td>
<td>Background</td>
<td>33064</td>
<td>(24959-43430)</td>
<td>100.9 (68.1-132.6)</td>
<td>34.1 (15.0-343.6)</td>
<td>19.9 (13.1-32.7)</td>
<td>33064</td>
<td>(24959-43430)</td>
<td>100.9 (68.1-132.6)</td>
</tr>
<tr>
<td></td>
<td>Worker area</td>
<td>21756</td>
<td>(17233-35332)</td>
<td>42.3 (29.1-59.7)</td>
<td>106.8 (22.1-1031.7)</td>
<td>22.9 (12.0-68.6)</td>
<td>34214</td>
<td>(24961-48730)</td>
<td>39.1 (28.5-168.0)</td>
</tr>
<tr>
<td>K1</td>
<td>Background</td>
<td>46421</td>
<td>(30470-53894)</td>
<td>72.6 (43.2-104.5)</td>
<td>13.0 (5.8-34.7)</td>
<td>5.5 (4.0-8.0)</td>
<td>46421</td>
<td>(30470-53894)</td>
<td>72.6 (43.2-104.5)</td>
</tr>
<tr>
<td></td>
<td>Worker area</td>
<td>24002</td>
<td>(15419-49458)</td>
<td>22.8 (18.2-35.2)</td>
<td>319.1 (70.6-1705.3)</td>
<td>66.8 (25.6-370.9)</td>
<td>20880</td>
<td>(14149-26659)</td>
<td>27.3 (16.8-39.9)</td>
</tr>
</tbody>
</table>

However, there is no significant increase of mean number concentration for any of the materials when comparing with their respective background concentrations.

Yeganeh et al. (2008) observed an increase of PM₉₅ during a similar sweeping operation of a fullerene production reactor, while an increase in number concentration was also not observed, which is consistent with our results. On the other hand,
Demou et al. (2008) detected increases in particle number concentration during reactor cleaning operations, especially when vacuuming (maxim of 50000 /cm³), identifying the vacuuming operation as an important short-term source of particles during cleaning. Other authors such as Fujitani et al. (2008) and Maynard et al. (2004) also reported the influence of vacuuming on particle number concentration and although the particle source is not clear, two main hypotheses were established by Maynard et al. (2004): (1) particle increase is due to materials aerosolization or (2) particles are generated on the unit’s carbon brush motor, which seems to be the most probable reason in this case. In the present study, the maximum 1-min peaks recorded during the cleaning operation coincided with vacuuming, supporting the results of the previous studies despite differences in materials, processes and devices used.

Additionally, a case study regarding the use of a general ventilation system as a potential mitigation strategy in the pilot plant has been assessed and it is described in the Supporting information (Figure S5, Supporting information).

**Material differences and influence of operating conditions**

Generally particle mass concentrations increased when energy setting was set from low to high except for material Q1 (which decreased from 70.7 μg/m³ under low energy settings to 48.0 μg/m³ under high energy settings) (Figure 3, Table 3). For the inhalable mass fraction, significant increases with respect to the background concentrations were found during handling with high energy conditions (Figure 3b) for all materials, except for S1, ranging from 4.6 to 33.1 times the background concentrations. Contrarily, for low energy settings (Figure 3a), a significant increase was only seen for K1 (24.6 times higher than the background concentration), and in general, increases when comparing with the background values were lower than when using high energy conditions. When using high energy, increases between 25.7 to 66.8%
in inhalable mass concentrations were found comparing with low energy concentrations. Jensen et al. (2015) tested two different working styles (careful and careless) for sanding of glass- and carbon fibre-reinforced composites, and found increases in particle concentrations between 1.1 and 14.1% when working in the careless style compared with careful working style. Results from Jensen et al. (2015) and the ones herein suggest that operating conditions play an important role shaped; mean particle diameters of 5.7 μm and highest SSA) followed by Q1 and Q2 (both prismatic, c.a. spherical) with mean particle diameter of 12.1 and 5.8 μm, respectively and with the lowest SSA values. Thus, no clear relationship between exposure concentrations and particle size, SSA or shape could be identified with the samples monitored. Regarding the respirable mass fraction, significant increases were found when using high energy conditions for Q2, Q3, K1 and S1 (Figure

**Figure 4.** Vertical box plot for respirable and inhalable concentrations of the five materials during handling with high energy settings and each respective background concentration (pre-activity). The boundary of the box closest to zero indicates the 25th percentile and the farthest from zero the 75th percentile. Solid line within the box indicates the median value. Dotted line within the box indicates the mean value. Errors bars above and below indicates the 10th and 90th percentiles. Coloured box indicate significant differences when comparing with each background concentration. Values on the top of each box indicate the increase comparing with its corresponding background concentration (only when statistically significant differences were detected).

on worker exposure concentrations and therefore should be always considered when implementing corrective measures as well as for exposure prediction. On the other hand, the material with the highest inhalable mass exposure was K1 (platy 3d). On the other hand, when using low energy conditions, the respirable mass fraction only showed a significant increase for Q2 and K1 (Figure 3c). Again, also for respirable mass concentrations, higher exposure values were
observed under high energy settings. The two materials with higher exposure concentrations for low and high energy settings were K1 and Q2, respectively, both with material particle $d_{50}$ around 5 $\mu$m (Table 1), but K1 with platy shape and Q2 prismatic. Various authors (López-Lilao et al., 2016, 2015; Pensis et al., 2009; Upton et al., 1990) reported that materials emission patterns do not follow a linear correlation with particle size, and that the assumption that finer materials have higher emissions is not always true. Materials with high content of ultrafine particles and comparably narrow size distribution have high cohesive forces and as a consequence material dustiness is lower than that of materials with a relatively larger mean particle diameter but with low ultrafine particles content. These materials show higher dustiness given that cohesive forces are less strong and ultrafine particles are easily released.

In general, particle number concentrations did not show an increase with respect to the background (pre-activity), except for S1, which was the only material showing a significant increase probably due to sources other than handling (Figure 2, 4 and S4, Supporting information). The presence of ultrafine particles from various sources is frequent in industrial settings (Vititanen et al., 2017). On the other hand, when comparing low and high energy settings, particle number concentration for all the prismatic (c.a. spherical) materials increased with the energy settings while it decreased for the platy (plate-like) shaped material K1 (from 24002 to 20880 /cm$^3$) (Figure 4, Table 3). Contrarily to what happened with the mass fractions, K1 is the material showing the lowest particle number concentration (Figures 3 and 4). Thus, for the materials and conditions assessed, handling of powder materials did not generate statistically significant emissions in terms of particle number concentrations.

This is supported by the TEM images in Figure 7 (see section 3.2.3). According to Figure 5, for S1, Q2, Q3 and K1, when using high energy conditions, mean particle size underwent a statistically significant reduction compared to background mean particle sizes (reductions in diameter in the order of 12 - 43%). However, interferences from other processes may have influenced this decrease for the S1 material (43% decrease). Under low energy conditions this influence was lower, as the reduction was only statistically significant for 2 materials. It may be hypothesised that handling allowed the release of the smaller particles contained in the materials due to aggregates breaking. Further work would be necessary to confirm this hypothesis.

![Figure 4](https://via.placeholder.com/150)

**Figure 4.** Vertical box plot for particle number concentrations of the five materials during handling with high energy settings and each respective background concentration (pre-activity). The boundary of the box closest to zero indicates the 25th percentile and the farthest from zero the 75th percentile. Solid line within the box indicates the median value. Dotted line within the box indicates the mean value. Errors bars above and below indicates the 10th and 90th percentiles. Coloured box indicate significant differences when comparing with each background concentration. Values on the top of each box indicate the increase comparing with its corresponding background concentration (only when statistically significant differences were detected).

However, results presented in Figures 5 and 6 indicate that handling may have had an impact on the mean size of the emitted ultrafine particles. When assessing the particle size distribution (Figure 6, instead of the mean diameter in Figure 5), results show only slight differences during
Figure 5. Mean particle diameter, as measured with the NanoScan in the worker area for the background period and during handling under low and high energy settings and for the five study materials. Letters in italics on the top of the bars indicate (a) significant differences between handling conditions (low and high energy settings) with respect to its background mean particle size and (b) significant differences between low and high energy settings mean particle size. The non-parametric Mann-Whitney “U” test was used to test statistically significant differences. Mean particle size differences between materials were not tested.

Figure 6. Particle number size distribution in the worker area (monitored with NanoScan) during handling under low and high energy settings, and during background conditions.
background (pre-activity), and handling (low and high energy conditions). For Q1, Q3 and K1 materials, a slight dominance of finer particles was seen compared to during background, where the size distribution was dominated by coarser particles. Only during S1 a clear increase of particles under 30 nm was observed (probably due to interferences from other processes, as stated above).

**Exposure characterization – TEM and EDX analysis**

TEM images of the sampled particles during handling were analysed in order to characterise the emitted particles (Figure 7; the EDX analyses are shown in Figure S6, Supporting Information). Particles during handling under high energy
conditions of S1 were mainly formed by Si, Al, and Fe showing a compact structure (Figure 7a and S6a, Supporting information). Aside from this, large nanoparticle aggregates (main element C) were also detected suggesting the contamination by another process (a furnace being switched on or even diesel soot from outdoor air, e.g., Figure 7b, 7c and Figure S6b, Supporting information). This was also the case for materials Q2, Q3 and K1 (Figures 7i, 7j, 7o and Figure S6h, S6k and S6n, Supporting information). Particles observed in Q1, Q2 and Q3 samples were mainly SiO₂ particles (0.5 - 2 μm, < 1 μm and 200 nm respectively) (Figures 7d, 7e, 7f, 7g, 7h and 7k, and S6c, S6d, S6e, S6f, S6g and S6j, Supporting information). However, smaller particles (< 100 nm) were also observed in form of aggregates (Figure 7g, 7j, 7k, 7n and S6f, S6i, S6j, Supporting information). For K1, aggregates of particles < 500 nm (main elements: Si, Fe, O and Ca) presenting a platy shape were observed (Figure 7m, 7n, S6l and S6m, Supporting information). This analysis supports the conclusion extracted above whereby it was observed that, while micron-scale particles dominated emissions during handling, nanoscaled particles forming aggregates were also emitted and may potentially impact worker exposure.

**Comparison between dustiness and exposure concentrations**

Materials dustiness index was assessed for Q1, Q2, Q3 and K1 materials after being handled under low and high energy settings (Table 1). In addition, for high energy conditions the material S1 was also included using the continuous drop method. Dustiness concentrations are usually provided in terms of inhalable and/or respirable mass fraction using mg/kg as units. Inhalable dustiness results were then correlated with inhalable mass fraction exposure concentrations during handling (Figure 8) aiming to assess the potential ability of the dustiness index to predict exposure concentrations. Inhalable dustiness indexes obtained ranged between 463 and 10012 mg/kg for the continuous drop method, and 64 and 410 mg/kg for the rotating drum. K1 and Q1 were the materials showing higher dustiness indexes followed by Q2 and Q3, (Table 1, Figure 8). The lowest dustiness value was found for S1. Pensis et al. (2009) reported that dustiness is dependent on material nature as well as d₅₀. Moreover, López-Lilao et al. (2016) concluded, after examining quartz dustiness, that for quartzes with d₅₀ < 25 μm an increase of mean particle size corresponds to an increase of dustiness while for quartzes with d₅₀ > 25 μm the opposite effect takes place. Taking this into account, the results in Table 1 and Figure 8 seem to agree with those findings, with Q1 having the highest dustiness of the three analysed quartzes. According to the literature, significant correlations may be observed between particle SSA and dustiness when comparing different quartzes (López-Lilao et al., 2016) and different kaolin samples (López-Lilao et al., 2015). Previous works (López Lilao et al., 2017) have shown that, for approximately spherical and dry materials, coarser mean diameters present a higher potential for release of fine particles. Thus, dustiness depends on the amount of fine particles and the material’s ability to release such fine particles. However, dustiness does not only depend on particle SSA and establishing a relationship between these parameters is complex (Pensis et al., 2009; Plinke et al., 1995, 1992). In addition, in Evans et al. (2013), where dustiness of different fine and nanoscale powders was analysed, no correlation between SSA and dustiness was found, suggesting that primary particle size, in their specific case, was not the key factor when determining material dustiness. Thus, it is evident that the current literature presents contradicting results. The present study shows that the highest exposure concentrations and dustiness indexes were measured for materials with very different SSA values (e.g., kaolin (K1) and quartz (Q1), 9.6 and 1.4 m²/g respectively) and different particle shapes (e.g., platy kaolin and prismatic quartz). These results confirm the difficulty to establish a general
Figure 8. Correlation between exposure concentrations during handling and dustiness (inhalable mass fraction) using Q1, Q2, Q3 and K1. SI1 was only used for high energy settings and with the continuous drop method due to availability issues. a) Continuous drop dustiness test b) Rotating drum dustiness test. Dustiness index classification values according to EN 15051 for each method is shown (dotted bars).

The relationship between dustiness and materials physical-chemical characteristics. As shown in Figure 8, $R^2$ correlation values dustiness – exposure ranged between 0.77 and 0.97 when using the inhalable fraction for both energy settings and dustiness methods. The best correlation was obtained for the continuous drop method with the low energy settings ($R^2 = 0.97$); contrarily, the worst correlation was obtained for the rotating drum method with low energy settings ($R^2 = 0.77$). For high energy settings, correlations obtained were $R^2 = 0.83$ and 0.88 for continuous drop and rotating drum method, respectively. The results indicate that continuous drop can reproduce slightly better what happened under low energy handling settings and rotating drum can reproduce better the processes taking place under high energy handling settings given that materials suffer a similar process inside the rotating drum than inside the mill. The continuous drop method uses fresh material continuously whereas the rotating drum method does not, and the material in the continuous drop is just falling and being resuspended with air flow while in the rotating drum method the material suffers rotating forces. Thus, it can be expected that both methods provide different results. Pensis et al. (2009) evaluated both EN dustiness methods and studied the correlation between them when using the inhalable and respirable fractions, and found weak correlations between methods for both mass fractions. However, here a strong correlation between methods (continuous drop and rotating drum) was found when considering the inhalable fraction ($R^2 = 0.78$; data not shown). Results obtained herein regarding dustiness – exposure correlations suggest that dustiness could be considered a predictor of exposure for the materials and particle sizes tested. Other authors have previously reported good exposure – dustiness correlations. Heitbrink et al. (1989) found significant correlations between two dustiness testers and worker exposure during bag packing. Breum et al. (2003) also found good correlation between exposure during installation of cellulose fibres and rotating drum dustiness results. Contrarily, Class et al. (2001) found limited correlation of exposure during manufacturing of insulation wools and ceramic fibres with the dustiness shaking box test, as well as Brouwer et al. (2006), who found a correlation of 0.70 between rotating drum dustiness values and worker exposure during sweeping/cleaning and scooping/weighting/adding. Finally, some other authors did not find a clear correlation as it the case of Heitbrink et al. (1990) who reported very limited correlation, and only good correlation after some adjustments during bag dumping and filling. Recently, Fonseca et al. (2018) did also not find a clear correlation during laboratory spilling of nano-scaled materials with mini-rotating drum dustiness results. To come to the point, no clear
relationship dustiness – exposure has yet been clearly established so that dustiness could be used as a direct predictor of worker exposure. However, dustiness is one of the parameters frequently included in equations for exposure prediction (Levin et al., 2014; Schneider et al., 2011) although prediction modelling for particulate matter is not always as precise as expected (Fonseca et al., 2017; Koivisto et al., 2015). Thus, it is important to continue working on modelling, dustiness test performance as well as to understand which are the key factors to predict worker exposure.

**Conclusions**

Personal exposure during handling of 5 different powder materials, as well as material dustiness, were assessed and compared in a real-world industrial setting in the ceramic industry. Particles between 4 nm and 32 μm were monitored in terms of number and mass concentration. Results evidence that handling of powder materials had a significant impact on exposure in terms of particle mass, and that this impact was larger under high energy settings: the mean inhalable mass fraction under low energy settings 80.8 - 319.1 μg/m³, and 156.0 - 429.6 μg/m³ under high energy settings. Therefore, the modification of the energy settings can be an effective mitigation strategy for this kind of process. On the contrary, emissions in terms of particle number concentrations (mean particle number concentration during handling 15033 – 40498 /cm³) were not significant (pre-activity concentrations = 10620 – 46421 /cm³). However, the assessment of the particle diameter plus the analysis of TEM images evidenced the release of nanoparticles to workplace air and that these nanoparticles may have a potential impact on worker exposure. Dustiness indexes were calculated for all the materials assessed with the two standard methods (continuous drop and rotating drum). A high degree of correlation between dustiness and exposure concentrations was found during handling ($R^2 = 0.77 - 0.97$), for inhalable mass fraction and for low ($R^2 = 0.77 - 0.97$) and high ($R^2 = 0.83 - 0.88$) energy settings. These results suggest that dustiness may be considered a relevant predictor of workplace exposure for the materials, particle sizes, energy settings and dustiness methods evaluated. Proxy parameters such as dustiness for exposure characterisation may be useful tools to deliver timely and efficient exposure assessments. However, due to this parameter’s complexity, the relationship between dustiness and exposure should be assessed for each industrial processes taking into account operational settings as well as materials physical-chemical properties and workplace characteristics.

**Acknowledgements**

This research was founded by the Spanish MINECO (CGL2015-66777-C2-1-R, 2-R), Generalitat de Catalunya AGAUR 2014 SGR33, the Spanish Ministry of the Environment (13CAES006) and FEDER (European Regional Development Fund) “Una manera de hacer Europa”. M.C. Minguillón acknowledges the Ramón y Cajal Fellowship awarded by the Spanish Ministry of Economy, Industry and Competitiveness. The authors also acknowledge the company MOLARIS for their support with technical information on the mill used. The authors declare no conflict of interest relating to the material presented in this article.

**References**


Fransman, W., Van Tongeren, M., Cherrie, J. W.,


http://repositori.uj.edu/xmlui/handle/10234/12301


4.1.1. Additional Results Publication I: On the relationship between exposure to particles and dustiness during handling of powders in industrial settings

After publication, the work presented in Publication I was completed by adding data for two types of clays, with plate-like primary particle shape. This was carried out because, of the materials studied in Publication I, the one presenting highest inhalable and respirable exposure mass concentration during handling was the Kaolin, with plate-like primary particles. Thus, two plate-like clays (white (C1) and red (C2) clay), with similar particle diameter as the other materials, were added to the study at a later stage (Figure 4.2). The two clays were subjected to the same process as the rest of the materials.

![Materials particle diameter](image)

**Figure 4.2** Particle size for all materials

Particle mass concentrations during handling (under low and high energy settings) of C1 material ranged between 727 and 1061 µg m\(^{-3}\), for the inhalable fraction, and 161 and 240 µg m\(^{-3}\) for the respirable one, with increases between 51 and 86 times the background concentration (Figure 4.3). For C2, monitored particle mass concentrations during material handling at low and high energy settings ranged between 1059-1319 µg m\(^{-3}\) and 280-300 µg m\(^{-3}\), with increases 17-27 and 16-19 times the background concentration for the inhalable and respirable fractions, respectively (Figure 4.3). From all 7 studied materials the three presenting higher mass concentration exposure were the three plate-like shaped, even though primary particle size was similar to the rest of materials. Therefore, it seems that exposure could be related to primary particle shape. Further research is necessary to understand this pattern and confirm this hypothesis.
The exposure results from the two clays were also added and used for dustiness-exposure correlations (Figure 4.4). When including C1 and C2 to the high energy settings correlation, exposure correlation with dustiness was 0.97 and 0.99 for the C.D and the R.D methods, respectively. Conversely, for the low energy correlation, exposure-dustiness correlation with the C.D and R.D methods was 0.83 and 0.80, respectively. In these new correlations, especially for the low energy settings, the two clays appear as outliers. These results agree with those found by Evans et al. (2017), where dustiness of several materials was assessed by using the R.D and the Venturi methods, and the two nano-clay materials were seen as clear outliers. Also in Evans et al. (2017), a certain correlation between the two dustiness methods used was found. In this work, good correlation between methods was also found (R^2 = 0.78) (Figure 4.5).
Figure 4.4 Figure 8 from Publication I where the two clays are included.

Figure 4.5 Correlation between R.D and C.D dustiness indexes. R.D: rotating drum. C.D: continuous drop.
4.2. Publication II: Health risk assessment from exposure to particles during packing in working environments

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Published in:

Science of the Total Environment, 671: 474-487, 2019
doi: 10.1016/j.scitotenv.2019.03.347


Accepted date: 22 March 2019

Journal Impact Factor / 5-Year Impact Factor: 4.610 / 4.984
Health risk assessment from exposure to particles during packing in working environments

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HIGHLIGHTS

• Worker exposure to particles during packing of 7 ceramic materials was assessed.
• ICRP modelling revealed that particle deposition occurred mainly in the head airways.
• Risk assessment models generally overestimated measured exposure concentrations.
• Source enclosure effectively reduced exposure and health risk.
• Dustiness correlated with exposure when emissions were driven by material properties.

GRAPHICAL ABSTRACT

Packing of ceramic materials in workplaces Health Impacts

ARTICLE INFO

Article history:
Received 14 January 2019
Received in revised form 22 February 2019
Accepted 22 March 2019
Available online 26 March 2019

Editor: Pavlos Kassomenos

Keywords:
Exposure
Non-communicable disease
Workplace
Human health impacts
Modelling
Ventilation

ABSTRACT

Packing of raw materials in work environments is a known source of potential health impacts (respiratory, cardiovascular) due to exposure to airborne particles. This activity was selected to test different exposure and risk assessment tools, aiming to understand the effectiveness of source enclosure as a strategy to mitigate particle release. Worker exposure to particle mass and number concentrations was monitored during packing of 7 ceramic materials in 3 packing lines in different settings, with low (L), medium (M) and high (H) degrees of source enclosure. Results showed that packing lines L and M significantly increased exposure concentrations (119–609 μg m⁻³ respirable, 1150–4705 μg m⁻³ inhalable, 24,755–51,645 cm⁻³ particle number), while non-significant increases were detected in line H. These results evidence the effectiveness of source enclosure as a mitigation strategy, in the case of packing of ceramic materials. Total deposited particle surface area during packing ranged between 5.4 and 11.8 × 10⁵ μm² min⁻¹, with particles depositing mainly in the alveoli (51–64%) followed by head airways (27–41%) and trachea bronchi (7–10%). The comparison between the results from different risk assessment tools (Stoffenmanager, ART, NanoSafer) and the actual measured exposure concentrations evidenced that all of the tools overestimated exposure concentrations, by factors of 1.5–8. Further research is necessary to bridge the current gap between measured and modelled health risk assessments.

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https://doi.org/10.1016/j.scitotenv.2019.03.347
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1. Introduction

Exposure to particulate matter (PM) is known to cause adverse health effects such as respiratory and cardiovascular non-communicable diseases (Landrigan et al., 2017). The finest fractions (with aerodynamic particle diameter Dp ≤ 2.5 μm) are considered the most harmful for human health (Gakidou et al., 2017; Landrigan et al., 2017; World Health Organization, 2016). In workplace settings, ceramic industry workers are known to suffer from work-related asthma due to airborne dust inhalation (Kurt et al., 2018). Elements such as Cr, Cd or Pb were detected in ceramic workers blood and urine samples in higher amounts than in control workers, causing a diminution of lung function and oxidative stress (Hormozi et al., 2018; Shouroki et al., 2015). Workers in the ceramic sector can also be exposed to respirable crystalline silica (RCS) dust which was found to cause silicosis and oxidative damage in workers (Anlar et al., 2017; Nardi et al., 2018). Moreover, RCS has been recently classified as carcinogenic for humans (Directive 2017/2398/EC). Reducing worker exposure to RCS is paramount and efforts are being carried out to reduce not only exposure but also toxicity (e.g., by using organosilane coatings; Ziemann et al., 2017).

Industrial bag filling, packing and pouring processes are high exposure risk activities in the ceramic sector. Studies in different industrial sectors report from very low to high levels of worker exposure to particles, e.g., during pouring and packing of fertilizers, paint pigments, TiO₂, carbon black, fullerenes and carbon nanofibers (Ding et al., 2017; Evans et al., 2013, 2010; Fujitani et al., 2008; Koivistio et al., 2012a, 2012b; Koivistio et al., 2015; Koponen et al., 2015; Kulhbusch et al., 2004; Ribalta et al., 2019a, 2019b), as well as packing and pouring of cement materials (Nota et al., 2018; Peters et al., 2008). The literature is increasing at a steady rate and more exposure concentrations to particles during packing of different materials in a ceramic industry plant; (2) report inhalation doses in terms of particle number, mass and surface area to link exposure to health outcomes; (3) explore the applicability of different methods to determine the statistical significance of coarse particle emissions, and (4) contribute to reducing the gap between measured and modelled exposure concentrations, with the aim to improve the performance of human risk assessment models in real world scenarios.

2. Methodology

2.1. Work environment

The measurements were carried out during packing of 7 ceramic materials (2 clays, 2 feldspars, 2 kaolin and 1 quartz) in 3 different packing lines, between the 14th and 28th of February 2018 at 2 industrial settings, named as #1 and #2 (for confidentiality reasons) and located in the vicinity of Valencia, Spain (Fig. 1). All materials are highly used in the ceramic industry, and thus representative of this sector. The 3 packing lines are representative of 3 different levels of source containment, with low, medium and high mitigation strategies and referred to as L, M and H respectively.

- Industrial plant #1 (Fig. 1(a)): Packing lines L and M were located in plant #1 which has a total volume (total surface area x height) of 2100 m³ (Fig. 1). Packing of big bags (1200 kg) was carried out through a cylindrical opening at a 400–800 kg min⁻¹ flow depending on the material being packed. Packing line L was not enclosed and had no closing system to attach the bag to the feed funnel whereas packing line M was not enclosed but had a partially closing system to attach the bag to the feed funnel preventing release of airborne dust; (Supplemental Fig. S1(a) and (b)). Both packing lines were equipped with a local exhaust ventilation system (LEV), with a flow rate of 18,000 m³ h⁻¹ (value provided by the company), and a subsequent bag filter. Additionally, plant #1 was naturally ventilated with air coming from outdoors via doors (flow rate 187–725 m³ h⁻¹, experimentally measured) which were always open. Experimentally determined total air exchange per hour (ACH) was 9 h⁻¹. Packing lines L and M were not operated at the same time.

- Industrial plant #2 (Fig. 1(b)): with a total volume (total surface area x height) of 420 m³ (Fig. 1), it contained packing line H where packing of small bags (20–25 kg) was carried out through a lateral cylindrical opening at 75 kg min⁻¹ flow. The packing line was not enclosed but the bag was completely attached to the feed funnel during the bag filling process (Supplemental Fig. S1(d)), and was equipped with a LEV system (flow rate of 2400 m³ h⁻¹, value provided by the company) and a subsequent bag filter, meaning that particle emissions were much more mitigated than in lines L and M in industrial plant #1. In addition, the plant #2 was naturally ventilated through a pair of doors (flow rate 386–437 m³ h⁻¹, experimentally measured) with a total experimentally determined ACH of 7 h⁻¹.

During packing, worker’s tasks were to (1) manually place a pallet and an empty bag in the packing area (Supplemental Fig. S1(a) and (b)); (2) control and guarantee the correct functioning of the line during the packing process, with the worker standing at approximately 2 m from the emission source, and (3) manually close the bag except in packing line H (Supplemental Fig. S1(c)). Diesel-powered forklifts were used to move the filled bags to the storage area; this task was usually carried out by another worker.

A summary of the packing lines operated each day, the materials used and the number of repetitions monitored, is described in Table 1.

2.2. Materials

Clay 1 and clay 2 consist of ~90% of clay (CAS: 999999–99–4). The main components of Feldspar 1 and 2 (>90%) is feldspar (CAS: 68476–25–5) with a RCS content between 1 and 10%, determined using the SWeRF method. The main component of Quartz 1 is quartz >95% (CAS: 014808–60–7). Kaolin 1 and 2 are composed by >90% kaolinite (CAS: 1332-58-7) and < 1% quartz. The true and bulk density of all materials is between 2.5 and 2.6 and 0.9–1.5 g cm⁻³, respectively. Materials characteristics and chemical composition are shown in Table 1 and Supplemental Table S1.
2.3. Dustiness

Material dustiness was assessed by using the continuous drop (C.D) standard method (EN 15051) (CEN, 2013) (Supplemental Fig. S2).

The C.D device, made of stainless steel, consists of a cylindrical pipe through which air circulates in an upward direction with a volume flow rate of 53 l min\(^{-1}\) (López-Lilao et al., 2015). Sampling heads for inhalable (designed by Institut für Gefahrstoff-Forschung-IGF) and respirable (FSP-2, BGIA) fractions are located slightly above the discharge position of the material. Samples for gravimetric measurements of inhalable and respirable fractions were collected on cellulose thimbles, single thickness, 10 × 50 mm and PVC filters of 37 mm and 5 μm of porosity respectively.

The experiments were repeated 2 times to ensure results repeatability and total duration of each test was 10 min.

2.4. Real time measurements

Particle number and mass concentrations were monitored in real time by using mobility and optical particle sizers, aerosol photometers, diffusion chargers and a condensation particle counter (Table 2). Air flows in the plant (WA) were experimentally measured with a Weather Transmitter WXT536, WXT530 Series, Vaisala, Helsinki, Finland. The uncertainties of the portable instruments are reported in Viana et al. (2015). Calibration of the Grimm laser spectrometers (Mini-LAS and Mini-WRAS) followed the procedures recommended by the manufacturer and were also

---

**Table 1**


<table>
<thead>
<tr>
<th>Material</th>
<th>Activity description</th>
<th>Packing Line</th>
<th>Batch Rep.</th>
<th>Day (02/2018)</th>
<th>Process time (min)</th>
<th>C.D (mg kg(^{-1}))</th>
<th>(d_{50}) (μm)</th>
<th>Moisture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay 1</td>
<td>#1</td>
<td>L</td>
<td>3</td>
<td>14th</td>
<td>174</td>
<td>1733 ± 880/6 ± 1</td>
<td>13</td>
<td>11</td>
</tr>
<tr>
<td>Feldspar 1</td>
<td>#1</td>
<td>M</td>
<td>3</td>
<td>20th</td>
<td>342 (243*)</td>
<td>10,266 ± 253/59 ± 2</td>
<td>31–39</td>
<td>0.2</td>
</tr>
<tr>
<td>Quartz 1</td>
<td>#1</td>
<td>M</td>
<td>2</td>
<td>21th</td>
<td>264</td>
<td>8891 ± 1002/43 ± 17</td>
<td>30–38</td>
<td>0.1</td>
</tr>
<tr>
<td>Clay 2</td>
<td>#1</td>
<td>L</td>
<td>2</td>
<td>22th</td>
<td>287</td>
<td>5,170,918 ± 70 ± 1</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>Kaolin 1</td>
<td>#1</td>
<td>L</td>
<td>2</td>
<td>23th</td>
<td>162</td>
<td>18,886 ± 174 ± 44 ± 5</td>
<td>13</td>
<td>11</td>
</tr>
<tr>
<td>Feldspar 2</td>
<td>#2</td>
<td>H</td>
<td>2</td>
<td>26th</td>
<td>350</td>
<td>9651 ± 215/77 ± 0</td>
<td>22</td>
<td>0.3</td>
</tr>
<tr>
<td>Kaolin 2</td>
<td>#2</td>
<td>H</td>
<td>2</td>
<td>28th</td>
<td>309</td>
<td>12,325 ± 235/104 ± 1</td>
<td>8</td>
<td>0.7</td>
</tr>
</tbody>
</table>
calibrated with regard to gravimetric reference samples collecting ambient aerosols. It should be noted that this kind of calibration was therefore not carried out with the same aerosol as monitored in the present work, which would be the advisable procedure for any workplace exposure assessment (PD CEN/TR 16013-2:2010). Monitoring was conducted in the worker area (WA), indoors, and outdoors (Fig. 1). The instruments were placed on a portable table at approximately 1 m height (instrument inlets being at 1.5 m above the ground level and at 1.5–2 m from the emission source), and were used without connecting any tubing to the inlets. Thus, measurements were considered representative of exposure but not strictly breathing zone (Asbach et al., 2012). All instruments were synchronized prior to the measurements and intercompared (Supplementary Table S2).

In the industrial plant #1, particle concentrations were measured for 2/3 batch repetitions of 20 bags each (each batch was between 1 and 2 h). Conversely, in the industrial plant #2, concentrations were measured for 4 to 5 h of continuous activity (packing). Total packing for all materials lasted between 3 and 5 h (162–200 mesh). The grids were attached to polycarbonate filters placed in a sampling cassette (SKC INC., USA, 1/8 in. inlet diameter and 25 mm filter Ø). The cassette was connected to a Leland pump with an operating flow rate of 3 l min⁻¹ and air filtration by a rotating porous foam filter (Görner et al., 2010; Görner et al., 2009). Respirable mass fraction in the worker breathing zone (BZ) was determined by pre- and post- weighing using a Dorr-Oliver Nylon Cyclone Assembly with a Mixed Cellulose Ester Membranes, 0.80 μm pore size, 25 mm Ø (EDM Millipore™ MF-Millipore™) connected to a pump (Apex, Casella) operating at 1.7 l min⁻¹ flow (Supplemental Fig. S1(c)). BZ filters were baked in an oven, re-suspended in ultrapure water and traganth, and redeposited onto PVC filters (25 mm Ø) following the national occupational health and safety institute’s (INSHT) method based on membrane filter/X-ray diffraction (MTA/MA –056/006). Filters were left for at least 2 h in a dryer prior to quantification. Exposure to RCS was quantified by the X-ray diffraction technique, using a BRUKER theta-theta model D8 Advance diffractometer with copper radiation (Kx λ = 1.54183 Å) and VAntec solid-state detector. Data were recorded from 2θ of 26° to 28°, with a step size of 0.07° and acquisition time of 3 s. Certified reference materials were used for quantification and validation (BCR-66, SRM 1878a y SRM 2950-2957).

2.6. Data processing

8-Hour time weighted average (8 h TWA) WA concentrations for online mass measurements were calculated as follows:

\[
TWA = \frac{\sum t_i C_i}{\sum t_i} \quad (1)
\]

where \(C_i\) is the mean concentration during a specific operation and \(t_i\) is the time of the specific operation, and compared to 8 h TWA limit values for unspecified dusts (respirable mass concentration, 3000 μg m⁻³ and inhalable mass concentration, 10,000 μg m⁻³) and RCS (50 μg m⁻³) (INSHT, 2018). Note that sampling periods were different for each material thus; temporal background concentrations were used to complete the 8 h TWA. 8 h TWA RCS was calculated by applying the content of RCS in percentage obtained with the gravimetical analysis, to calculated 8 h TWA respirable mass concentration.

Table 2

<table>
<thead>
<tr>
<th>Instrument Description</th>
<th>Location</th>
<th>Manufacturer</th>
<th>Sample flow rate (l min⁻¹)</th>
<th>Information</th>
<th>Particle size range</th>
<th>Concentration range</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butanol Condensation Particle Counter (CPC TSI Model 3775)</td>
<td>Worker Area</td>
<td>TSI Inc., Shoreview, MN, USA</td>
<td>3.9</td>
<td>Particle number concentration</td>
<td>4–1500 nm</td>
<td>0–10⁷ cm⁻³</td>
<td>6-s</td>
</tr>
<tr>
<td>Mini Wide Range Aerosol Spectrometer (Mini-WRAS 1371)</td>
<td>Worker Area</td>
<td>Grimm Aerosol Technik, Ainring, Germany</td>
<td>5.0</td>
<td>Particle mass and number concentration and PSD</td>
<td>10 nm–35 μm</td>
<td>0.1–10⁻⁴ μg m⁻³</td>
<td>1-min</td>
</tr>
<tr>
<td>Mini Laser Aerosol Spectrometer (Grimm Mini-LAS)</td>
<td>Worker Area, Indoor and Outdoor</td>
<td>Grimm Aerosol Technik, Ainring, Germany</td>
<td>1.2</td>
<td>Particle number concentration, mean particle size and alveolar lung deposited surface area</td>
<td>10–700 nm</td>
<td>10⁻³–10⁻⁶ cm⁻³</td>
<td>1-s</td>
</tr>
<tr>
<td>Optical Particle Sizer (OPS, TSI Model 3330)</td>
<td>Indoor</td>
<td>TSI Inc., Shoreview, MN, USA</td>
<td>1.2</td>
<td>Particle mass concentration</td>
<td>0.25–32 μm</td>
<td>0.1–10⁻⁴ μg m⁻³</td>
<td>6-s</td>
</tr>
<tr>
<td>*Electrical Mobility spectrometer (NanoScan SMP TSI Model 3910)</td>
<td>Worker Area</td>
<td>TSI Inc., Shoreview, MN, USA</td>
<td>0.7</td>
<td>Particle number concentration and PSD</td>
<td>10–420 nm</td>
<td>0–10⁻³ cm⁻³</td>
<td>1-min</td>
</tr>
<tr>
<td>Light scattering laser photometer (DustTrak™ DRX aerosol monitor TSI Model 8533)</td>
<td>Outdoor</td>
<td>TSI Inc., Shoreview, MN, USA</td>
<td>3.9</td>
<td>Particle mass concentration</td>
<td>PM₁₀, PM₄, PM₂.₅, and PM₁</td>
<td>0.001–150 mg m⁻³</td>
<td>1-min</td>
</tr>
</tbody>
</table>

* NanoScan was only used during Clay 1 monitoring due to technical problems. PSD: particle size distribution.
Conversely to particle number concentration for which a specific approach has been designed (Asbach et al., 2012), for particle mass there is no specific method to determine statistically significant increases other than conventional statistical tests. Therefore, the need was identified to test the performance of different methods which could be useful to establish guidelines in occupational exposure assessment studies. Here, 3 methods to determine statistically significant increases in exposure during packing, compared to pre-activity periods, were tested:

1) The approach described by Asbach et al. (2012) and Kaminski et al. (2015) for particle number, from now on referred to as nanoGEM approach:

\[ \text{Mean concentration during packing} = \text{BG} \pm 3 \times (\text{sd of BG}) \]  

2) Conventional statistical methods; two-sample t-test and Mann-Whitney “U” test, parametric and non-parametric tests for independent samples.

Log-normality and variance homogeneity were assessed by using the Kolmogorov-Smirnov and Levene’s (absolute) test respectively, and by histogram plotting. In general, data did not fully fulfill normality assumptions. However, for datasets >30–40 samples, the violation of normality assumptions should not be a major problem (Chasemi and Zahediasl, 2012; Pallant, 2007). Therefore, in order to determine statistically significant differences between measured concentrations during background and packing the two-sample t-test (from now on referred to as t-test) was performed (unequal variances) as well as the non-parametric Mann-Whitney “U” Test (Wilcoxon rank-sum test) (from now on referred to as MW “U” test), both for independent samples and typically used as in e.g. (Fonseca et al., 2018; Ribatala et al., 2019).

3) Autoregressive Integrated Moving Average (ARIMA) time series approach. ARIMA models are used for nanoparticle exposure assessment in Klein Entink et al. (2011) and proposed in the EN 17058, 2018 (standard for workplace exposure assessment of exposure by inhalation of nano-objects and their aggregates and agglomerates) as the golden standard method for number concentration and other metrics analyses. The ARIMA models are the most general type of models used for analyzing time series while considering the autocorrelation between samples. Examples of the ARIMA analysis performed are shown in Annex A (Supplemental Material).

2.7. Particle inhalation dose

The inhalation dose of deposited particles in the respiratory tract during inspiration and expiration was quantified in terms of particle number concentration, particle active surface area and mass. Particle active surface area was calculated for particles up to 750 nm (cut-off diameter at 679 nm) by using particle size distribution (PSD) (Heitbrink et al., 2009; Keller et al., 2001) as in Koivisto et al. (2012a). Particle mass was calculated by using mobility particle diameter and effective density as in Koivisto et al. (2012a). Particle density during packing was assumed to be 2.55 g cm\(^{-3}\) as it is the materials’ mean density (López Lilao et al., 2017) described by the provider, and 1.5 g cm\(^{-3}\) during background (Martins et al., 2015). The regional inhalation dose rate, calculated for head airways, tracheobronchial and alveolar regions, was obtained by applying WA particle size concentrations to simplified deposition fraction probability equations for the ICRP human respiratory tract model (Cousins et al., 2011) as described by Hinds (1999). The respiratory volume used was 25 l min\(^{-1}\), corresponding to male respiration during light exercise (Koivisto et al., 2012b). In the model, particles were assumed to be spherical and to preserve their size during inhalation.

2.8. Risk assessment using online tools (Stoffenmanager, ART and NanoSafer)

Stoffenmanager® v.7.1, is a risk prioritisation web-based tool which consists of a control banding tool (inhalation and dermal), with a part designed for exposure to engineered nanoparticles (inhalation) and general and REACH specific quantitative inhalation exposure parts (van Tongeren et al., 2017). It is between tier 1 and 2 tool as recommended by ECHA (ECHA, 2016; Landberg et al., 2017; Spinazzé et al., 2017; van Tongeren et al., 2017), and its general assumptions are based on Marquart et al. (2008) whereas the rationale of the algorithm is based on Cherrie and Schneider (1999) and adapted as described in Tielemans et al. (2008a). The Advanced REACH tool (ART), is a tier 2 mechanistic exposure modelling tool with a higher level of detail than the Stoffenmanager and recommended by the ECHA (ECHA, 2016). It also has a Bayesian approach that combines the mechanistic model with measurements of exposure (Landberg et al., 2017). Similarly to Stoffenmanager, ART is also based on Cherrie and Schneider (1999) approach with Tielemans et al. (2008b) modifications. It is described and explained in detail in Fransman et al. (2011) and has been tested and calibrated in Schinkel et al. (2011).

Stoffenmanager and ART dimensionless total exposure score equations can be found in Riedmann et al. (2015).

The NanoSafer v1.1 is a control-banding and risk management tool (Kristensen et al., 2010; Jensen et al., in preparation) for manufactured nanomaterials. In addition to manufactured nanomaterials, the tool can also be used to assess and manage emissions from nanoparticle-forming processes such as powder handling and fugitive/source emissions. Hazard assessment and case-specific exposure potentials are currently combined into an integrated assessment of risk levels expressed in control bands with associated risk management recommendations and e-learning on how to reduce exposure or risk thereof. The tool is currently intended for small and medium-size companies and laboratories with no or limited experience in working with nanomaterials and/or insufficient resources to perform a full precautionary risk assessment. Further developments in future aim to expand the application domains and include assessment with risk management measures as part of calibrate project (http://www.nanocalibrate.eu/home).

3. Results and discussion

3.1. Worker exposure monitoring

Worker exposure is here analyzed considering the packing line type and the material being packed. In the following sections, results are discussed considering statistical significance obtained only when using the nanoGEM approach. Discussion regarding differences when using different statistical tests will be done in a separate section 3.6. The results for Clay 2 from line L, Feldspar 1 from line M and Feldspar 2 from line H are discussed in detail in this section, while the results from the rest of the materials are shown in Supplemental Material-Fig. S3, S4, S5 and S6. The case studies in this section were selected due to their representativeness and due to the fact that statistically significant exposure concentrations were recorded. Measured concentrations for all materials are shown in Table 3.

3.1.1. Packing line L (low mitigation strategies)

In packing line L, located in the industrial plant #1, packing of Clay 1, Clay 2 and Kaolin 1 was monitored (Table 1). For Clay 1 and Kaolin 1, 2 batches of 20 bags of 1200 kg each were monitored whereas for the Clay
2, 20 pallets consisting of 3 bags (400 kg each; total 1200 kg) were monitored.

Packaging of Clay 2 in line L (Fig. 2 and Table 3) increased total particle number concentrations significantly (34806-36253 cm⁻³) compared to background concentrations (18,348 ± 3412 cm⁻³). However, these increases seem to be related to outdoor influence (Supplemental Table S3). In addition, statistically significant increases of inhalable (1524–1998 μg m⁻³) and respirable (135–139 μg m⁻³) mass concentrations were monitored, with increases from pre-activity concentrations of 1317–1791 μg m⁻³ for inhalable and 117–121 μg m⁻³ for respirable fractions. BZ and WA respirable dust concentrations gravimetrically analyzed were 226 μg m⁻³ and 230 μg m⁻³, respectively, which are slightly higher than online respirable concentrations measured by the mini-LAS. RCS exposure was 7.3 μg m⁻³ (32.7% of total respirable dust) (Table 3). Arithmetic mean particle diameter (10 nm-35 μm, Mini-WRAS particle count) during packing was 82.2–82.7 nm whereas during pre-activity it was 79.2 ± 4.2 nm. Clear peaks for particulate matter (Fig. 2(b) and (c)) can be identified coinciding with the start of a new pallet (of 1200 kg) being packed which will contain 3 bags of 400 kg. Therefore, peaks are not related to the start of pouring but to the start of the next bag of 400 kg. Cyclic process in which the start of packing in line M, the concentration of particles increased, Quartz 1 presented lower mass concentrations than Feldspar 1 (Fig. 4(c)) whereas the concentration of particles (d)) with in-duction was lower than pre-activity (BG) concentrations using the nanoGEM approach. BZ: breathing zone. DL: detection limit. NaN: Not available number. *The pump stopped during the sampling. Mini-WRAS arithmetic mean particle size is calculated by using particle count distribution.

In general, Clay 1 (Supplemental Fig. S3) differs from the other 2 materials as no significant increases were detected. This is in agreement with the dustiness indexes, Clay 1 presenting the lowest value of the 3 materials (1733 ± 880 mg kg⁻¹). Table 1 shows the C/D dustiness results in terms of inhalable (Wi) and respirable (Wr) mass fractions (mg kg⁻¹). In sum, line L (with low mitigation strategies) generated statistically significant impacts on exposure in terms of particle number and mass (respirable and inhalable) for 2 of 3 materials (Clay 2 and Kaolin 1).

3.1.2. Packing line M (medium mitigation strategies)

Packing of Feldspar 1 (3 batches of 20 bags of 1200 kg each) (Fig. 4) and Quartz 1 (2 batches of 20 bags of 1200 kg each) (Supplemental Fig. S5) in line M (industrial plant #1) was monitored.

During packing of Feldspar 1 (Fig. 4), total particle number concentration measured with the CPC (26777–51,645 cm⁻³) was similar to pre-activity (42,038 ± 5595 cm⁻³). The same was true for the respirable mass fraction (119–577 μg m⁻³ during packing vs. 212 ± 70 μg m⁻³ during background) but with a significant increase during batch 1 (Table 3). Contrarily, the inhalable mass fraction was found to be significantly higher during all packing repetitions (1412–3416 μg m⁻³) when compared to pre-activity concentrations (643 ± 224 μg m⁻³) with increases between 770 and 2773 μg m⁻³. As occurred during packing in line L, peaks can be identified at the beginning of each bag being packed (Fig. 4(b) and (c)) especially from 16:00 to 18:00 of particles 1–5 μm (Fig. 4(b)). Peaks were less marked during the morning shift due to another indoor process which was slightly covering up packing emissions. Particle mean diameter (10 nm-35 μm) during packing was 80.2–84.9 nm whereas during pre-activity was 80.9 ± 2.4 nm. During packing in line M, the concentration of particles >2 μm increased when packing Feldspar 1 (Fig. 3(c)) whereas the concentration of particles between 0.01 and 0.5 μm increased when packing Quartz 1 (Fig. 3(d)). SEM images for Feldspar 1 show high concentrations of feldspar particles (>1 μm diameter) and diesel agglomerates (Supplemental Fig. S7(c) and (d)). Conversely, for Quartz 1, quartz particles observed were >1 μm diameter (Supplemental Fig. S7(g) and (h)). During packing, Quartz 1 presented lower mass concentrations than Feldspar 1.

### Table 3

<table>
<thead>
<tr>
<th>Sampling</th>
<th>CPC (cm⁻³)</th>
<th>MiniWras (nm)</th>
<th>Mini-LAS (μg m⁻³)</th>
<th>Gravimetric Respirable Mass (μg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nₜ₉₀</td>
<td>Size</td>
<td>Inhalable</td>
<td>Respirable</td>
</tr>
<tr>
<td>Clay 1_L</td>
<td>Batch 1</td>
<td>42,410 ± 32,660</td>
<td>50 ± 9</td>
<td>986 ± 1000</td>
</tr>
<tr>
<td>Day 1</td>
<td>Batch 2</td>
<td>37,896 ± 12,825</td>
<td>51 ± 7</td>
<td>1847 ± 2571</td>
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<tr>
<td></td>
<td>Batch 3</td>
<td>34,535 ± 6339</td>
<td>56 ± 6</td>
<td>1697 ± 2390</td>
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<td>42,038 ± 5595</td>
<td>81 ± 2</td>
<td>1370 ± 1434</td>
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<tr>
<td>Feldspar 1_M</td>
<td>Batch 1</td>
<td>51,645 ± 15,528</td>
<td>80 ± 5</td>
<td>3416 ± 4688</td>
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<tr>
<td>Day 2</td>
<td>Batch 2</td>
<td>39,989 ± 68,776</td>
<td>84 ± 27</td>
<td>2180 ± 4965</td>
</tr>
<tr>
<td></td>
<td>Batch 3</td>
<td>26,777 ± 11,431</td>
<td>85 ± 19</td>
<td>1412 ± 1564</td>
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<tr>
<td></td>
<td>Batch NaN</td>
<td>23,291 ± 6988</td>
<td>94 ± 21</td>
<td>3529 ± 3324</td>
</tr>
<tr>
<td>Quartz 1_M</td>
<td>Batch 1</td>
<td>24,755 ± 4862</td>
<td>83 ± 9</td>
<td>1714 ± 2094</td>
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<tr>
<td>Day 3</td>
<td>Batch 2</td>
<td>46,670 ± 17,666</td>
<td>74 ± 5</td>
<td>1150 ± 620</td>
</tr>
<tr>
<td>Clay 2_L</td>
<td>Batch 1</td>
<td>36,253 ± 7074</td>
<td>79 ± 4</td>
<td>1998 ± 3403</td>
</tr>
<tr>
<td>Day 4</td>
<td>Batch 2</td>
<td>34,806 ± 4002</td>
<td>83 ± 5</td>
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</tr>
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<td></td>
<td>Batch BG</td>
<td>15,721 ± 2185</td>
<td>86 ± 3</td>
<td>92 ± 114</td>
</tr>
<tr>
<td>Kaolin 1_L</td>
<td>Batch 1</td>
<td>40,565 ± 10,218</td>
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<td>Day 5</td>
<td>Batch 2</td>
<td>42,331 ± 3358</td>
<td>87 ± 7</td>
<td>4705 ± 4224</td>
</tr>
<tr>
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<td>Batch BG</td>
<td>69,673 ± 29,030</td>
<td>76 ± 5</td>
<td>1824 ± 1270</td>
</tr>
<tr>
<td>Feldspar 2_H</td>
<td>Batch 6</td>
<td>43,049 ± 10,829</td>
<td>87 ± 25</td>
<td>4264 ± 17,531</td>
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<td></td>
<td>Batch BG</td>
<td>19,476 ± 10,503</td>
<td>97 ± 11</td>
<td>1573 ± 1628</td>
</tr>
<tr>
<td>Kaolin 2_H</td>
<td>Batch 1</td>
<td>12,484 ± 6143</td>
<td>90 ± 19</td>
<td>898 ± 806</td>
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<tr>
<td>Day 7</td>
<td>Batch 2</td>
<td>71,996 ± 127,876</td>
<td>74 ± 10</td>
<td>830 ± 762</td>
</tr>
<tr>
<td></td>
<td>Batch BG</td>
<td>50,504 ± 28,475</td>
<td>69 ± 7</td>
<td>283 ± 193</td>
</tr>
</tbody>
</table>

*Worker wearing the cyclone was carrying out other activities not related to packing which may have influenced in the low concentrations registered on the BE that day.
which is in agreement with dustiness indexes Quartz 1 < Feldspar 1. In general Quartz 1 (Supplemental Fig. S5) behaved differently than Feldspar 1, showing only a significant increase in particle number during one batch (Table 3). When comparing WA with indoor measures during packing, WA was seen to have slightly lower particle number concentration than the indoor location but higher mass concentrations.

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Fig. 2. Particle concentration at the worker area during packing of Clay 2: (a) particle number concentration time series (CPC and DM; DiSCmini); (b) particle size distribution time series measured with the MiniWras, solid black line shows MiniWras d50; (c) mass concentration time series measured by Grimm mini-LAS. Black vertical lines indicate start (solid line) and stop (dashed line) of each batch. Vertical top black lines mark the start of each bag being packed. Horizontal grey line shows the background period.

Fig. 3. Particle size distribution in the worker area during pre-activity and packing in packing line L for Clay 2 (a) and Kaolin 1 (b) and packing line M for Feldspar 1 (c) and Quartz 1 (d).
(Supplemental Table S3). Before Quartz 1 pre-activity period, maintenance tasks were carried out in the plant, which probably influenced pre-activity and indoor concentrations.

BZ and WA respirable dust concentrations for Feldspar 1 and Quartz 1 gravimetrically analyzed were 1065 µg m⁻³ and 313 µg m⁻³, and 468 µg m⁻³ and 186 µg m⁻³ respectively (Table 3). Conversely, in line L respirable dust in BZ and WA were approximately in the same range (see 3.1.1). Near field online measurements were seen to underestimate worker exposure when compared with personal exposure (Koivisto et al., 2015; Koponen et al., 2015) although this is not always the case as found by (Janssen et al., 1998). Here, BZ mass concentrations were seen to be higher than WA concentrations only for Feldspar 1 and Quartz 1, both materials packed in line M. The difference between line L and M results could be explained by the fact that materials packed in packing line M were the ones with a higher dustiness index and during pouring the level of mitigation strategies is "medium", additionally main exposure of the worker to the material was when the worker manually closed the bag and not during material pouring into the bag (when closing there was no extraction system and the worker was directly on the emission source).

RCS exposure in the BZ was 74.6 (7% of total respirable mass concentration) and 160.5 (34.3% total respirable mass concentration) µg m⁻³ for Feldspar 1 and Quartz 1 respectively (Table 3). RCS content during Quartz 1 packing was lower than expected as during dustiness tests respirable silica content represented 97–100% of the total respirable dust collected (Supplemental Table S4), which shows that worker exposure measurement was not only due to Quartz 1 packing.

3.1.3. Packing line H (high mitigation strategies)

In packing line H (industrial plant #2), packing of Feldspar 2 (Fig. 5) and Kaolin 2 (Supplemental Fig. S6) in bags of 20–25 kg was monitored during 5 to 6 h. This line had the most stringent mitigation measures of all three lines, with the opening of the bag fully enclosed and automated system.

Packing of Feldspar 2 did not significantly increase particle number or mass concentrations (Fig. 5 and Table 3). Particle number concentrations measured with the CPC during pre-activity was 69,673 ± 29,930 cm⁻³ whereas during packing they ranged between 19,476–43,049 cm⁻³. Mean inhalable and respirable mass concentrations during pre-activity were 1824 ± 1270 and 333 ± 179 µg m⁻³ and, although during batch 1 mass concentrations increased (4264 ± 17,531 and 701 ± 2607 µg m⁻³ for inhalable and respirable fractions), those were not statistically significant, most likely due to the fact that they were related to unexpected events during packing e.g. broken bags during pouring (Fig. 5 (c)). If only the period between 12:00 and 14:00 is considered (where no events occurred), then inhalable and respirable concentrations were 1127 ± 617 µg m⁻³ and 187 ± 93 µg m⁻³ respectively. WA respirable dust concentration was 437 µg m⁻³. Particle mean diameter (10 nm–35 nm) during packing and pre-activity was 87.2–97.3 nm and 76.2 ± 4.6 nm, respectively. Conversely, Kaolin 2 did not behave the same way, showing significant increases for particle number, although this was due to outdoor and indoor influence (Supplemental Table S3), and mass concentration remained the same during packing than during pre-activity.

In packing line H, the 2 materials did not behave exactly the same, but no significant increases were detected for particle mass concentration for any of them. Kaolin 2 had higher dustiness index than Feldspar 2 but conversely showed lowest concentrations during packing. This is in line with the fact that line H is the one with the strongest mitigation strategies. However, it is important to highlight that high respirable mass concentrations (up to 20,000 µg m⁻³) were detected during specific events such as bags breaking, which may impact worker exposure but would not be detected if only 8 h TWA was considered. This highlights the relevance of real-world and time-resolved particle monitoring in occupational risk assessment.

3.2. 8 h time-weighted average (8 h TWA)

Particle number concentrations increased significantly only during Clay 2, Kaolin 1 and during 1 repetition of the Quartz 1. However, those increases were always below 40,000 cm⁻³, the nano-reference value used as precautionary approach in this specific case (non-biodegradable granular nanomaterials in the range of 1–100 nm and density ~ 6 kg l⁻¹) (Van Broekhuizen et al., 2012).

Increases of inhalable and respirable mass concentrations were found during packing for Feldspar 1, Clay 2 and Kaolin 1. However, 8 h
TWA concentrations (Table 4) did not exceed in any case the limit values for particles not otherwise specified of inhalable (8 to 28 times $\leq 10,000 \, \mu g \, m^{-3}$) and respirable (4 to 14 times $\leq 3000 \, \mu g \, m^{-3}$) mass fractions (INSH, 2018). RCS exposure limit value ($50 \, \mu g \, m^{-3}$) was also not exceeded. RCS exposure in the WA for Feldspar 1, Quartz 1 and Clay 2 was 16, 43 and 35 $\mu g \, m^{-3}$ (3, 1.2 and 1.4 times lower than the occupational limit, respectively). Thus, although RCS 8 h TWA was not exceeded and considering that values correspond to a 5 to 6 h packing shift, it is important to mention that a 7 or 8 h packing could lead to exceed the RCS exposure limit values.

### 3.3. Inhalation dose

Inhalation dose rates were estimated for each day using size distribution data from the MiniWras with the exception of Clay 1, for which PSD was obtained using the NanoScan SMPS. Thus, it should be noted that results for Clay 1 are not directly comparable with the rest.

Total deposited particle surface area during packing ranged between $5.4 \times 10^5$ and $11.8 \times 10^5 \, \mu m^2 \, min^{-1}$. The main deposition region during packing was the alveoli ($50.8$–$63.7\%$) followed by head airways ($26.6$–$41.3\%$).

![Fig. 5. Particle concentration at the worker area during packing of Feldspar 2: (a) particle number concentration time series (CPC and DM; DISCmini); (b) particle size distribution time series measured with the MiniWras, solid black line shows MiniWras $d_{50}$; (c) mass concentration time series measured by Grimm mini-LAS. Black vertical lines indicate start (solid line) and stop (dashed line) of each batch. Vertical top black lines mark specific events (bags being broken or other accidents). Horizontal grey line shows the background period.](image-url)

### Table 4

<table>
<thead>
<tr>
<th>Sampling time “min”</th>
<th>WA Respirable 8 h TWA (μg m$^{-3}$)</th>
<th>WA Inhalable 8 h TWA (μg m$^{-3}$)</th>
<th>ART (inhalable μg m$^{-3}$)</th>
<th>Stoffenmanager (inhalable μg m$^{-3}$)</th>
<th>NanoSafer v1.1 (respirable (NF/FF, 8 h TWA) μg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C.D based Mechanistic Bayesian</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay 1_L</td>
<td>174 min C.D Wt = 1733 C.D Wt = 6</td>
<td>129</td>
<td>1454</td>
<td>300 (160–570)</td>
<td>2200 (1500–3300)</td>
</tr>
<tr>
<td></td>
<td>C.D Wt = 59</td>
<td></td>
<td></td>
<td>[−4.9]</td>
<td>[1.5]</td>
</tr>
<tr>
<td></td>
<td>342 min C.D Wt = 10,246</td>
<td>227</td>
<td>1679</td>
<td>1600 (860–3100)</td>
<td>4000 (2900–5500)</td>
</tr>
<tr>
<td></td>
<td>C.D Wt = 59</td>
<td></td>
<td></td>
<td>[−1.1]</td>
<td>[2.4]</td>
</tr>
<tr>
<td></td>
<td>264 min C.D Wt = 8891</td>
<td>126</td>
<td>1317</td>
<td>900 (480–1700)</td>
<td>3400 (2500–4700)</td>
</tr>
<tr>
<td></td>
<td>C.D Wt = 43</td>
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<td></td>
<td>[−1.5]</td>
<td>[2.6]</td>
</tr>
<tr>
<td></td>
<td>Clay 2_L</td>
<td>287 min C.D Wt = 5170</td>
<td>108</td>
<td>3300 (1700–6200)</td>
<td>4700 (3500–6400)</td>
</tr>
<tr>
<td></td>
<td>Kaolin 1_L</td>
<td>162 min C.D Wt = 18,888</td>
<td>166</td>
<td>1800 (980–3500)</td>
<td>4100 (3000–5500)</td>
</tr>
<tr>
<td></td>
<td>C.D Wt = 44</td>
<td></td>
<td></td>
<td>[1.2]</td>
<td>[2.7]</td>
</tr>
</tbody>
</table>

* 8 h TWA RCS was calculated by applying the content of RCS in percentage obtained with the gravimetric analysis, to calculated 8 h TWA respirable mass concentration.
and trachea bronchi (7.3–9.6%) [Fig. 6]. However, deposition in the trachea bronchi and alveolar regions during packing was reduced when compared to pre-activity, whereas it increased in the head airways (between 1.2 and 23%). The same occurred with particle number and mass, which showed increases in particles deposited in the head airways during packing (0.8–4.9% and 0.1–5.4%, respectively) and reductions in the trachea bronchi and alveolar regions. These results are in agreement with the mean PSD of packing emissions which are mainly coarse.

It is important to point out that surface dose analysis as estimated here can only be applied for particles up to 750 nm (Heitbrink et al., 2009; Keller et al., 2001), but PSD for some of the materials (Feldspar 1, Clay 2 and Kaolin 1) was >1 μm. This should be considered as a limitation. Hygroscopicity was not considered, which can lead to over- or under-estimations of particle deposition in the respiratory tract depending on the dry and humid size of the particles (Martonen and Clark, 1983; Asgharian, 2004; Winkler-Heil et al., 2014; Ching and Kajino, 2018; Salamtonidis et al., under review, JAS).

In this model, the 3 metrics (number, mass and surface area) were included based on Wang et al. (2010) and Koivisto et al. (2012a, 2012b). Even though percentages of deposited particles in the different regions were different, similar results were obtained indicating that airborne emitted particles during packing increased deposition in the head airways.

### 3.4. Risk Assessment Modelling

Different web-based tools have been developed in order to provide risk assessment of chemical hazards (Fransman et al., 2011; Kristensen et al., 2010; Tieleman et al., 2008a; Jensen et al., in preparation), Tier 1–2 risk assessment tools Stoffenmanager and ART have been tested in different scenarios including dust emissions (Bekker et al., 2016; Landberg et al., 2017, 2015; Riedmann et al., 2015; Savic et al., 2018) and they are recommended by ECHA (ECHA, 2016). However, there is controversy regarding whether or not web-based tools results are sufficiently robust to be used with decision-making regulatory purposes (Raul and Dwyer, 2003; Koivisto et al., 2019). In general, models are seen to overestimate actual exposures (van Tongeren et al., 2017, Savic et al., 2018) although underestimations have been reported (Landberg et al., 2017). In addition, prediction accuracy depends on many factors such as the type of process or the concentration ranges, and further studies are required to fully understand the performance of online modelling tools.

![Fig. 6. Percentage of surface deposited area in the respiratory tract per region during packing and pre-activity for of all materials. Abbreviations codes are: BG, background (pre-activity period); C1, Clay 1; F1, Feldspar 1; Q1, Quartz 1; C2, Clay 2; K1, Kaolin 1; F2, Feldspar 2; K2, Kaolin 2.](image)
were associated with general recommendations for risk management such as:

**RL4:** High toxicity suspected and/or high exposure potential. Use highly efficient local exhaust ventilation, fume-hood, glove-box etc. Make sure to have the personal respiratory protection equipment (PP3 or higher quality) available in case of accidents.

**RL5:** Very high toxicity suspected and/or moderate to very high exposure. The work should be conducted under strict dust release control, such as in a fume-hood, separate enclosure etc. Air-supplied respirators or highly efficient filter masks (PP3 or higher quality) may be used as a supplement and must be readily available in case of accidents. Expert advice is recommended.

In overall, NanoSafer overestimated WA measured concentrations for all materials with a factor between 13 and 97 when near-field (NF) output concentrations were considered, and between 1 and 8 when far-field (FF) output concentrations were considered. WA was located between 1.5 and 2 m from the emission source which is in the limit of the NF defined by NanoSafer (2 m). This explains why the ratios of mass predicted and mass measured are closer to 1 if FF concentrations are considered.

### 3.5. Dustiness-exposure concentration correlation

The use of the dustiness index as an exposure predictor metric has been explored by several authors (Brouwer et al., 2006; Evans et al., 2013; Levin et al., 2014; Ribalta et al., 2019b). Following the EN 15051 dustiness classification with the C.D method, the material showing the highest exposure to inhalable mass concentration (Kaolin 1) was also the material with highest inhalable dustiness index (18,886 ± 174 mg kg\(^{-1}\)), which was followed by Kaolin 2, Feldspar 1, Feldspar 2, Quartz 1 and Clay 2.

Correlation between exposure during materials being packed in line L (low mitigation strategy) and their dustiness index (using inhalable fraction) was relatively high (\(R^2 = 0.80\)) (Fig. 7(a)). However, this correlation was low for packing lines M and H, which have moderate to high mitigation strategies (\(R^2 = 0.27\)) (Fig. 7(b)). Thus, results seem to suggest that a clear correlation dustiness exposure exists when materials characteristics (e.g. dustiness) dominate over process characteristics (e.g. degree of source enclosure). Conversely, when emissions depend more on process characteristics correlation is not straightforward.

The respirable mass-based dustiness indices varied over 1 order of magnitude with Kaolin 2 and Feldspar 2 having the highest (104 ± 1 mg kg\(^{-1}\) and 77 ± 0 mg kg\(^{-1}\)) (Table 1). According to the EN 15051, the respirable dustiness tests reveal that 4 powders are categorized as very low (Clay 1) and low (Clay 2, Quartz 1, and Kaolin 1) and 3 (Feldspar 1, Feldspar 2, and Kaolin 2) are in the category of powders with moderate dustiness. When considering correlations for the respirable fraction, these were similar but less robust than for the inhalable fraction (\(R^2 = 0.55\) for packing line L and \(R^2 = 0.02\) for packing lines M and H, data not shown).

Current discussions are ongoing regarding this topic (Dubey et al., 2017; Fonseca et al., 2018; Ribalta et al., 2019b) as yet no clear direct relationship dustiness-exposure has been established. In Fonseca et al. (2018) no clear correlation during laboratory spilling of nano-scaled materials under a fume hood with the small-rotating drum dustiness results was found, whereas in Ribalta et al. (2019b) good correlations between dustiness (measured with the continuous drop and rotating drum) were found during handling of different coarse ceramic materials. Earlier studies also found correlation (Breum et al., 2003; Brouwer et al., 2006; Heitbrink et al., 1989) although, some others did not (Class et al., 2001; Heitbrink et al., 1990).

### 3.6. Statistical significance variations depending on the statistical method used

The nanoGEM approach, a specific user-friendly approach, was designed in order to assess the statistical significance of exposure impacts for particle number. However, no specific approach is available, other than statistical tests, for particle mass concentration. Thus, different approaches were tested for the current dataset, in terms of particle number and mass.

Results (Table 5) showed that with respect to currently available and frequently used nanoGEM method, the t-test and the MW "U" test provided slightly more conservative results. The t-test differs only in 1 case for inhalable mass and 1 case for respirable mass out of 21 cases. Similarly, the MW "U" test differs in 1 and 2 cases for inhalable and respirable mass fractions, respectively. Conversely, for particle number, all 3 methods provided the same results. Therefore, using the t-test or the MW "U" test for mass could provide slightly more conservative results to the point of view of exposure assessment. However, this could come as the cost of using a less friendly-user approach.

With regard to the method proposed as “golden standard by the EN 17058:2018” (ARIMA), in 6 cases results were less conservative (no significant exposures were identified in contrast to the other tests) than results obtained when using the other tests. Considering the obtained results, ARIMA models are complex to apply and require expert knowledge, and they did not identify exposures to mass in the case studies.

**Fig. 7.** Continuous drop dustiness index correlated with exposure for materials packed in line L (a), and M and H (b). Inhalable fraction is used.
Finally, it was observed that using the nanoGEM approach could lead to a slight underestimation of the statistical significance when the pre-
activity dataset is characterized by a high variability, which is frequent
in industrial monitoring, especially for particle mass concentration.
This is not usually the case in laboratory experiments. However, it
should be noted that the nanoGEM methodology was not designed to be
applied to particle mass concentrations. As a result, the nanoGEM cri-
terion may be applicable to assess the significance of particle emissions in terms of mass concentrations taking into account the above limita-
tions. The design of a method tailored to particle mass concentrations
would be advisable.

4. Conclusions

Exposure and health impacts were assessed during industrial pack-
ing of 7 materials in 3 lines with different levels of mitigation (low, me-
dium and high). The main conclusions extracted are summarized below:

4.1. Impact of enclosure strategies on exposure

It may be concluded that packing in packing line L and M had a sig-
nificant impact on worker exposure with regard to particles in the 11.5 nm – 35 μm size range, significantly increasing worker exposure and reaching high respirable (135–609 μg m⁻³) for packing line L and 119–577 μg m⁻³ for packing line M) and inhalable (1370–4705 μg m⁻³ for packing line L and 1150–3416 μg m⁻³ for packing line M) mass concentrations. However, 8 h TWA limits were not exceeded in any case. RCS exposure limits were also not exceeded but values were close to the limit, indicating a potential risk of exposure. Con-
versely, packing in line H, which had the highest mitigation strategies,
was seen to have an impact, only during accidental spills e.g. bags being broken, with respirable mass concentration reaching 20,000 μg m⁻³. Therefore, the degree of source enclosure showed a clear in-
verse relationship with the exposure concentrations monitored evidencing the effectiveness of mitigation strategies in place. In addi-
tion, results highlight the relevance of real-world and time-resolved ex-
posure assessments in occupational exposure, as 8 h TWA is unable to
detect time-resolved high exposures which may significantly impact
workers’ health. In this case study, where micro-sized materials (d₅₀
8–40 μm) where packed, airborne particles emitted were seen to
deposit mainly in the head airways of the human respiratory tract, indi-
cating that risk of penetration to the alveolar region is low.

4.2. Exposure assessment tools

the dustiness index (inhalable fraction) of the materials tested cor-
related with exposure concentrations during packing in packing line L
(R² 0.80), but no correlation was found for packing in lines M and H
(R² 0.27). Thus, it may be concluded that dustiness can be a useful met-
ric for exposure prediction when materials properties are the main de-
terminant of worker exposure. However, when process properties (e.g.
degree of enclosure) play a more important role, correlation is not straightfor-
ward and parametrization is needed.

In addition, 4 different approaches were tested to assess the statisti-
cal significance of exposure concentrations (in terms of particle number and mass): t-test, Mann-Whitney (MW) test, the ARIMA models (re-
ferred to as the golden standard in EN 17058:2018), and the frequently
used nanoGEM approach. The comparison between methods evidenced
that (a) the ARIMA method is the least conservative of the 4; (b) the t-
test, MW test and nanoGEM approach provided the same results for 18
out of 21 cases analyzed; (c) for the 3 remaining cases, the differences
obtained referred to exposures in terms of particle mass, and never to
particle number concentrations, which is expected considering that
nanoGEM was designed to be used for particle number and not mass
concentrations, (d) the nanoGEM approach may lead to underestima-
tions when assessing scenarios with highly variable background con-
centrations (in terms of particle mass). From the point of view of
usability, the nanoGEM method was seen to be the most practical and
the least time and resource consuming.

4.3. Risk assessment modelling

3 models were tested: ART, Stoffenmanager and NanoSafer. Only in 3
cases out of 5 cases, ART estimated the measured exposure within a factor ± 2
and for the 5 cases it was within the inter-quartile confidence interval.
The Stoffenmanager web-based tool overestimated all predictions, and
only in three cases it was by a factor < 2. NanoSafer overestimated mea-
sured exposure respirable mass concentrations in all case scenarios
within a factor between 13 and 97, and 1 and 8 when NF and FF concen-
trations were considered, respectively.

Acknowledgments

This research was founded by the Spanish MINECO (CGL2015-
66777-C2–1-R, 2-R), Generalitat de Catalunya AGAUR 2017 SGR41, the
Spanish Ministry of the Environment (13CAES006), and FEDER
(European Regional Development Fund) “Una manera de hacer Eu-
ropa”. Additional support was provided by calIBRate project funded by
the European Union’s Horizon 2020 research and innovation pro-
gramme under grant agreement No 686239. M.C. Minguillón acknowl-
edges the Ramón y Cajal Fellowship awarded by the Spanish Ministry
of Economy, Industry and Competitiveness.

The authors also acknowledge the company in which the measure-
ments were carried out for their support. The authors declare no conflict
of interest relating to the material presented in this article.

Appendix A Supplementary data

Supplementary data to this article can be found online at https://doi.
org/10.1016/j.scitotenv.2019.03.347.

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Determinación de célula libre cristalina (cuarzo, cristobalita, tridimita) en aire -Método del filtro de membrana / Difracción de rayos X MTA/MA –056/A06, n.d.


4.2.1. Additional Results Publication II: Health risk assessment from exposure to particles during packing in working environments

The work presented in this paper was expanded for this PhD Thesis by performing the risk assessment for the materials packed in packing line H (high mitigation strategies applied) with the ART, Stoffenmanager and the NanoSafer tools.

Table 4.1 Calculated 8h TWA (including pre-activity concentrations) for inhalable and respirable mass fractions based on exposure measurements conducted in the worker area (WA). Risk assessment results conducted with the ART (Mechanistic and Bayesian), Stoffenmanager and NanoSafer v1.1 using Continuous drop (C.D) index. NF: near-field. FF: far-field.

<table>
<thead>
<tr>
<th>WA Respirable (µg m⁻³)</th>
<th>WA Inhalable (µg m⁻³)</th>
<th>ART (inhalable µg m⁻³)</th>
<th>Stoffenmanager (inhalable µg m⁻³)</th>
<th>NanoSafer (respirable (NF-FF) µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mechanistic</td>
<td>Bayesian</td>
<td></td>
</tr>
<tr>
<td>Feldspar 2</td>
<td>386</td>
<td>2512</td>
<td>1400 (740-2600)</td>
<td>3800 (2800-5100)</td>
</tr>
<tr>
<td>Kaolin 2</td>
<td>149</td>
<td>709</td>
<td>1200 (650-2300)</td>
<td>3700 (2700-5100)</td>
</tr>
</tbody>
</table>

The ART mechanistic model underestimated measured exposure inhalable mass concentrations for Feldspar 2 and overestimated exposure for Kaolin 2, but within a ratio range of 0.6-1.7. Conversely, ART Bayesian overestimated exposure for both materials, with a ratio < 2 only for Feldspar 2. Stoffenmanager underestimated exposure for both materials with ratios 0.3 and 0.8 for Feldspar 2 and Kaolin 2, respectively. Conversely, NanoSafer, as with the other materials of this study, highly overestimated exposures for both materials. It should be noted, as discussed in chapter 3 (Methodology), that NanoSafer was developed to model mainly risks due to NP exposures, although it should be able to assess and manage emissions from powder handling and point source emissions. NanoSafer is at present undergoing test and calibration phases. Therefore, the results provided by this model should not be considered as final and are fully directly applicable to this case study.

Additionally, the ART tool was applied by using R.D dustiness index instead of the C.D index. The same was not conducted with Stoffenmanager (as the tool do not have the option to introduce a dustiness index or level categorization), or NanoSafer (as the input required is respirable dustiness index and difference between C.D W_R and R.D W_R is very small, 6-104 vs. 13-80 mg Kg⁻¹, respectively). The ART mechanistic model underestimated...
exposure in all cases with ratios modelled/measured < 0.2. Conversely, ART Bayesian predicted concentrations within a ratio range 0.5-2.0 in 5 out of 11 cases, with underestimations for 9 out of 11 cases.

**Table 4.2** Calculated 8h TWA (including pre-activity concentrations) for inhalable mass fraction in the worker area. Risk assessment results conducted with the ART (Mechanistic and Bayesian using Rotating drum (R.D) index. WA Inhalable: exposure concentrations measured in the worker area (WA).

<table>
<thead>
<tr>
<th>Packing Line</th>
<th>Material</th>
<th>WA Inhalable (µg m⁻³)</th>
<th>ART (inhalable µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mechanistic</td>
</tr>
<tr>
<td>Low</td>
<td>Clay 1</td>
<td>1454</td>
<td>39 (20-74)</td>
</tr>
<tr>
<td></td>
<td>Clay 2</td>
<td>780</td>
<td>97 (52-190)</td>
</tr>
<tr>
<td></td>
<td>Kaolin 1</td>
<td>1538</td>
<td>55 (29-110)</td>
</tr>
<tr>
<td>Medium</td>
<td>Feldspar 1</td>
<td>1679</td>
<td>25 (13-48)</td>
</tr>
<tr>
<td></td>
<td>Quartz 1</td>
<td>1317</td>
<td>27 (14-52)</td>
</tr>
<tr>
<td>High</td>
<td>Feldspar 2</td>
<td>2512</td>
<td>140 (73-270)</td>
</tr>
<tr>
<td></td>
<td>Kaolin 2</td>
<td>709</td>
<td>120 (65-240)</td>
</tr>
</tbody>
</table>
4.3. Publication III: Testing the performance of one and two box models as tools for risk assessment of particle exposure during packing of inorganic fertilizer

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Published in:

\textit{Science of the Total Environment, 650: 2423–2436, 2019}


Accepted date: 28 September 2018

Journal Impact Factor / 5-Year Impact Factor: 4.610 / 4.984
Testing the performance of one and two box models as tools for risk assessment of particle exposure during packing of inorganic fertilizer

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HIGHLIGHTS
• Occupational exposure to particles during industrial packing was assessed.
• No significant increases were found during packing of a granulate fertilizer.
• One and two box models predicted adequately actual worker exposure.
• Including outdoor concentrations in models was seen to improve their performance.
• Models parametrization was seen to be a key issue to adequately predict exposure.

ABSTRACT
Modelling of particle exposure is a useful tool for preliminary exposure assessment in workplaces with low and high exposure concentrations. However, actual exposure measurements are needed to assess models reliability. Worker exposure was monitored during packing of an inorganic granulate fertilizer at industrial scale using small and big bags. Particle concentrations were modelled with one and two box models, where the emission source was estimated with the fertilizer’s dustiness index. The exposure levels were used to calculate inhaled dose rates and test accuracy of the exposure modellings. The particle number concentrations were measured from worker area by using a mobility and optical particle sizer which were used to calculate surface area and mass concentrations. The concentrations in the worker area during pre-activity ranged 63,797–81,073 cm−3, 4.6×106 to 7.5×106 μm2 cm−3, and 354 to 634 μgm−3 (respirable mass fraction) and during packing 50,300 to 85,949 cm−3, 4.3×106 to 7.6×106 μm2 cm−3, and 279 to 668 μgm−3 (respirable mass fraction). Thus, the packing process did not significantly increase the exposure levels. Chemical exposure was also under control based on REACH standards. The particle surface area deposition rate in respiratory tract was up to 7.6×106 μm2 min−1 during packing, with 52%–61% of deposition occurring in the alveolar region. Ratios of the modelled and measured concentrations were 0.98 ± 0.19 and 0.84 ± 0.12 for small and big bags, respectively, when using the one box model, and 0.88 ± 0.25 and 0.82 ± 0.12, when using the two box model. The modelling precision improved for both models when outdoor particle concentrations were included. This study shows that exposure concentrations in a low emission industrial scenario, e.g.
1. Introduction

Industrial bag filling, packing and pouring processes have been pointed out as activities with high potential to emit airborne particles. Studies in different industrial sectors had reported from very low to high levels of worker exposure to particles, e.g.; during pouring and packing of paint pigments, packing of TiO₂, carbon black, fullerences and carbon nanofibers (Ding et al., 2017; Fujitani et al., 2008; Koivisto et al., 2015, 2012a; Koponen et al., 2015; Kuhlbusch et al., 2004; Evans et al., 2010) as well as packing and pouring of cement materials (Noto et al., 2018; Peters et al., 2008). Additionally, differences in particle release have been observed when pouring different materials, different amounts, and using different types of mixing tanks (Koponen et al., 2015). Thus, every case is specific and further research is needed in order to understand emission patterns during packing and pouring.

Exposure to particulate matter (PM) is known to cause various adverse health effects, such as respiratory and cardiovascular diseases (Landrigan et al., 2017). Current epidemiological and toxicological studies consider PM2.5 (with aerodynamic particle diameter Dₚ ≤ 2.5 μm) as the most harmful component for human health (Gakidou et al., 2017; Landrigan et al., 2017; World Health Organization, 2016). Inhalation by humans of dust from inorganic complex fertilizers, which are the object of the present study, results in health effects which might be detected especially after long-term exposures. Inorganic complex fertilizers generally contain basic nutrients (nitrogen, phosphorus, potassium) as well as secondary and micronutrients (calcium, magnesium, boron, manganese) (Roy et al., 2006). Specifically, the fertilizer under study in this work is composed of ammonium nitrate, potassium nitrate and calcium fluoride. Ammonium nitrate, when inhaled, was seen to cause possibly meaningful pulmonary function changes (Kleinman et al., 1980) and to be irritating, cause coughing, bronchospasms, laryngospasm and laryngeal edema even at low concentrations (Gorguner and Akgun, 2003). Additionally, the clinical examination of workers of the ammonium nitrate production showed frequent cases of chronic bronchitis and radiculoneuropathy (Tsimakuridze et al., 2005). On the other hand, ammonium nitrate is known to be potentially explosive when confined. Potassium nitrate, has been seen to be irritating for the respiratory tract (INCHEM, 2001). Therefore, the study of packing of an inorganic fertilizer is of interest as workers can be exposed to relatively high concentrations of airborne fertilizer particles, which might cause respiratory health effects.

Exposure prediction models have been proposed as valuable risk assessment tools, since the initial application of exposure prediction models, several research papers have been published regarding their theoretical aspects (Ganser and Hewett, 2017; Hewett and Ganser, 2017; Hussein and Kulmala, 2008; Nazaroff, 2004; Nazaroff and Cass, 1989). The two box model is a well-accepted exposure assessment tool in the risk assessment field as, even with its simplified assumptions, it is able to adequately simulate actual conditions for various processes including volatile compounds and PM emissions (Arnold et al., 2017; Jayjock et al., 2011). In the chemical industry, models have been tested in a variety of cases (Nicás, 2016; Sahmel et al., 2009 and references therein). However, when testing the models for PM in actual industrial environments, the number of studies decreases (Boelter et al., 2009; Johnson et al., 2011; Jones et al., 2011; Koivisto et al., 2015; Lopez et al., 2015). Recently, Arnold et al. (2017) conducted a study where the one and two box models were evaluated under highly controlled conditions. Predicted exposure results for three industrial solvents when using near and far field models was categorized excellent and good to excellent under the ASTM Standard 5157 criteria (Arnold et al., 2017). However, in order to implement prediction models as trustable tools for worker risk assessment, additional real-world cases (including low and high exposure concentration scenarios) need to be evaluated, in order to validate model performance under real-world settings. Especially, performance of models on low concentration scenarios is relevant since real industrial exposure concentrations (especially for nanomaterials) are frequently low (Fonseca et al., 2018; Koivisto et al., 2012a; Koponen et al., 2015; Kuhlbusch et al., 2004). Thus, if models are to be used as tools for risk assessment, testing their performance in low emission and concentration scenarios is paramount. This, will favour understanding of the uncertainties related to critical parameters, such as the source characterization, local controls, and air mixing (Jayjock et al., 2011; Sahmel et al., 2009).

The objectives of the present study were 1) to perform a worker exposure and risk assessment study of packing of an inorganic complex fertilizer in an industrial plant, and 2) to test the one box and two box models performance in a real-world setting in order to contribute to the better understanding and validation of exposure prediction models. A real industrial case scenario, characterized by low particle emissions and subsequently low exposure concentrations, was selected for this purpose with the aim to test the applicability of models at the lower end of the particle concentration range. In this way, results are expected to be extrapolable to industrial settings dealing with nanomaterial exposures, which are typically low (e.g., Koivisto et al., 2012a; Kuhlbusch et al., 2004).

2. Methodology

2.1. Fertilizer chemical composition

The main chemical components of the fertilizer under study (commercial complex inorganic fertilizer) were ammonium nitrate; NH₄NO₃ (15–20%), potassium nitrate; KNO₃ (12.5–15%) and calcium fluoride; CaF₂ (2–3%), according to the material’s safety data sheet. The fertilizer was granulated in 2.5 to 5 mm diameter spherical pellets. The product is not classified as hazardous according to regulation EC 1272/2008. However, it may intensify fire (oxidizer) it causes serious eye irritation, the inhalation of its degradation products may cause health hazards, and serious effects may be derived following exposure (material’s safety data sheet). According to the European Chemicals Association (ECHA), Derived No Effect Level (DNEL) for long term inhalation are 37.6 mg m⁻³ for ammonium nitrate, 36.7 mg m⁻³ for potassium nitrate and 5 mg m⁻³ for calcium fluoride. For calcium fluoride, the EU occupational exposures limit (OEL) time-weighted average (TWA) is 2.5 mg m⁻³. Recommended controls are good general ventilation, the use of safety glasses with side-shields, chemical resistant gloves and respiratory protection in case of inadequate ventilation (material’s safety data sheet).

2.2. Work environment and packing process

The measurements were carried out during packing of a fertilizer in two different packing lines between the 23th and 26th of January 2017 at an industrial facility located in Castellón, Spain.

The packing hall was only naturally ventilated and the replacement air came from outdoors and from adjacent industrial hall via doors, which were always open (Fig. 1). The packing lines were for small bags (25 kg) and big bags (600 kg) where the studied fertilizer was...
poured into the bags from a silo by using a feed funnel. Fig. S1 in the Supporting information shows photos from the packing lines. The two packing lines were not operated at the same time. Two-day measurements were conducted at both packing lines, small bags day 1 (SB1), small bags day 2 (SB2), big bags day 1 (BB1) and big bags day 2 (BB2). In small bags, packing was carried out through an opening fitting the bag width (33–35 cm) and subsequently mechanically sealed. The fertilizer was poured at a flow of 250 kg min⁻¹ and the drop height was 5 cm from the feed funnel to the bag opening. Total material drop height was approximately 0.6 m. The packing process was fully automated and took place 2.3 m from the feed funnel to the bag opening. Total material drop height was 1.3 m. In that case, the bag was manually closed by the worker, who was standing in front of the bag at approximately 0.5 m distance.

During small and big bags filling, workers tasks were to control and guarantee the correct functioning of the lines as well as to move the filled bags to the storage area using an electric forklift. Occasionally, diesel-powered forklifts were performing truck loading and unloading operations in the hall.

2.3. Aerosol measurements and sampling

Particle number and mass concentrations were monitored in real time in the worker area (WA), indoors, and outdoors (Fig. 1). All online instruments were synchronized prior to the measurements and intercompared overnight between experiments. Particle concentrations during packing were measured for approximately 2 h. Additionally, 30 min of pre-activity concentrations were measured for each day except for BB2.

In the worker area, the instruments were placed on a portable table at approximately 1 m height (instrument inlets being at 1.5 m above the ground level), at 0.5 m from the emission source and 1 m from the worker (Figs. 1 and S1, Supporting information). The monitoring instruments were:

- An electrical mobility spectrometer (NanoScan, SMPS TSI Model 3910; sample flow rate 0.7 l min⁻¹) to measure particle number concentration and particle size distribution in 13 channels from 10 to 420 nm with a 1 minute time resolution
- A Mini Wide Range Aerosol Spectrometer (Mini-WRAS 1371; sample flow rate 1.2 l min⁻¹) to measure particle mass concentration, particle number concentration and particle size distribution from 10 nm to 35 μm in 41 channels with a 1 minute time resolution
- A Mini Laser Aerosol Spectrometer (Grimm, Mini-LAS 11R; sample flow rate 1.2 l min⁻¹) to measure particle mass concentration from 0.25 to 32 μm in 31 channels with a 1 minute time resolution.

The indoor and outdoor concentrations were monitored by using a DISCmini and a Grimm Mini-LAS, with the same settings as described above.

During the packing process, particles emitted were collected onto Au grids (Quantifoil® with 1 μm diameter holes – 4 μm separation of 200 mesh). The grids were attached to polycarbonate filters that were placed in a sampling cassette (SKC INC., USA, inlet diameter 1/8 in. and filter diameter 25 mm). The cassette was connected to a Leland pump with an operating flow rate of 3 l min⁻¹. The morphology and primary particle size of the particles collected were determined using a transmission electron microscope (TEM, Jeol, JEM 1220, Tokyo, Japan) coupled with an energy-dispersive X-ray (EDX) spectrometer. Particle samples for subsequent chemical characterization were not collected due to the short sampling times (3–4 h), as the samples would not have been representative of full 8-hour shifts. This should be considered a limitation of the study.

The worker area particle number size distributions measured by the NanoScan and MiniWras were combined according to Koivisto et al. (2012a) to obtain a wide range for particle size distribution from 10 nm to 35 μm. NanoScan size channels between 11.5 and 86.6 μm were used while channels ranging from 139 nm to 35 μm were taken from the MiniWras. Between 86.6 μm and 139 nm a combined channel (108.6 μm) was created. Upper channels from NanoScan (~<115.5 μm) were not used as it is known to not have a good resolution for particles >200 nm (Fonseca et al., 2016), while MiniWras was seen to not accurately measure particles under 50 nm; therefore, MiniWras lower channels were not used (see Fig. S2, Supporting information) and explanation. Here, due to channels cut, ultrafine particles are defined as Dₚ < 660.0 nm, fine particles as 660.0 nm < Dₚ < 943.0 nm and coarse particles as >943.0 nm.

Increases and reductions in exposure during packing when comparing with pre-activity levels were considered statistically significant when the following approach (Asbach et al., 2012; Kaminski et al., 2015) was fulfilled:

\[
\text{Mean concentration during packing} = \frac{\text{BG} \pm 3 \times (\sigma \text{BG})}{\text{BG}}
\]

where BG is the mean temporal background (pre-activity) concentration and σBG is the standard deviation of the background concentration.

2.4. Dustiness

Material dustiness was assessed by using the continuous drop standard method (EN 15051). The continuous drop device, made of stainless
steel, consisted of a cylindrical pipe through which air circulated in an upward direction with a volume flow rate of 53 l min$^{-1}$. Concentric to the cylindrical pipe there was an inner pipe, slightly shorter than the cylindrical pipe, through which material was dropped at a flow rate of 6 to 10 g min$^{-1}$, so that the powdered material was released into a counter-current airflow (López-Lilao et al., 2015). Total material drop height during the test is approximately 1.2 m. Two sampling heads for inhalable (approximately PST; designed by Institut für Gefahrstoff-Forschung-IGF) and respirable (approximately PM$_2.5$; FSP-2, BGIA) fractions were located slightly above the discharge position of the material. Samples for gravimetric measurements of inhalable and respirable fractions were collected on cellulose thimbles, single thickness, 10 × 50 mm$^2$ and PVC filters of 37 mm and 5 μm of porosity respectively. The experiment, which lasted for 10 min, was repeated two times to ensure results repeatability. Between experiment repetitions, the sampling heads for inhalable and respirable fractions were superficially cleaned while the rest of the device was thoroughly cleaned only at the end of the test.

2.5. Exposure modelling

2.5.1. One- and two-box dispersion models

Exposure modelling was performed by using a one box model (Hewett and Ganser, 2017) and a two box model (Ganser and Hewett, 2017). Fig. 2 shows the models schemes and the mass balance.

![Fig. 2. One box and two box model description and parameters values (table). For small bags, one box model (a) and two box model (c) and for big bags, one box model (b) and two box model (d).](image-url)
2.5.2. Emission source

The emission (S) from the packing process is described based on the dustiness index as:

\[ S(t) = DIH \frac{dM(t)}{dt} LC \]  

(1)

where DI is the respirable dustiness index of the fertilizer expressed in mg kg\(^{-1}\) or particles kg\(^{-1}\), \(H\) is the handling energy factor for the process, \(dM/dt\) (kg min\(^{-1}\)) is the mass flow of the fertilizer, and LC is the protection factor of localized controls. The respirable dustiness index of the fertilizer was obtained using the continuous method, as it is the method that adapts better to the process under study (Pujara, 1997; Ribalta et al., 2018).

2.5.3. Modelling parameterization

The input parameters needed to run the model and experimentally unavailable in this case study are the handling energy factor (H), local control factors (LC), and the air flow rate (\(\beta\)) between near field (NF) and far field (FF) (for two box model only).

By definition, \(H\), links the energy applied during the process with the energy applied during the dustiness test (Schneider and Jensen, 2007) and can range from 0 to 1 (Koivistio et al., 2015; Lidén, 2006). The parameter \(H\) has been defined for the rotating drum dustiness test by Van Tongeren et al. (2011) for the Advanced REACH tool. However, currently the scaling of the source by using handling energy factor is not yet well understood and works are ongoing in order to parameterize the \(H\) factor. Here, taking into account the previous cited works and based on our experimental knowledge of the bagging facility, \(H\) was assumed to be 0.5 for small bags as the drop height during small bags packing was approximately 50% of the drop height in dustiness tests, and 1 for the big bags as the material drop height was similar to the dustiness drop height (see Sections 2.2 and 2.4). With regard to local controls (LC), two main controls were detected. For both small and big bags, the bag itself was estimated in this work to reduce particle release by 40% (applied in the emission rate equation as LCbag = 0.6). In addition, for small bags one box model, the effect of the enclosure was taken into account and applied in the model reducing emission by 50% (LCenclosed = 0.5) (Fransman et al., 2008). Finally, \(\beta\) was estimated after testing the range values reported by Baldwin and Maynard (1998) and Arnold et al. (2017) taking into account the characteristics from our case scenarios. A sensitivity analysis for different \(\beta\) was carried out and is reported in the section below (Table 1). Small bags NF volume was 6 m\(^3\) (2 × 2 × 1.5 m) corresponding to the size of the enclosure and for big bags 25 m\(^3\) (3.5 × 3 × 2.5 m), as this is the volume of the packing area including the bag and the worker. For small bags \(\beta\) was set at 0.75 m\(^3\) min\(^{-1}\) (0.0125 m s\(^{-1}\)) as the air flow rate was considered to be low due to the enclosure of the packing line (enclosure opening of 1 m², free surface area (FSA)). In this case, for the two box model, as the effect of the enclosure was introduced by the NF-FF \(\beta\), the local control regarding the enclosure (LCenclosed) in the emission rate equation was suppressed. Big bags FSA is 28 m² as the top, bottom and one of the four sides are covered. For big bags, the air flow rate was considered to be higher as there was no enclosure or division between NF and FF, so \(\beta\) was set to 30 m\(^3\) min\(^{-1}\) (0.036 m s\(^{-1}\)). The model schemes and parameters are listed in Fig. 2. The air exchange rate (AER) between indoor and outdoor air was experimentally calculated considering outdoor wind speed during the measurement period (obtained from the local air quality monitoring network), the size of the outdoors door, and the size of the industrial unit. This resulted in a mean air exchange rate of around 7 h\(^{-1}\) for the entire period.

2.6. Calculated active surface area and mass concentrations

The particle active surface area was calculated by applying particle size distribution obtained from NanoScan and MiniWras data combination to Eq. (2) described in Heitbrink et al. (2009) as in Koivistio et al. (2012b).

\[ s = \frac{3\pi D_b}{C_f D_b}\lambda \]  

(2)

where \(\lambda\) is the mean free path for air, 0.066 μm, and \(\delta\) is the scattering parameter for air, 0.905. \(D_b\) is the mobility diameter and \(C_f\) the slip correction factor for the corresponding aerodynamic or mobility particle size.

The particle mass was additionally calculated by using mobility particle diameter and effective density as in Koivistio et al. (2012b)

\[ m = \rho_{eff} \frac{\pi}{6} D_b^3 \]  

(3)

where \(\rho_{eff}\) is the effective density. As fertilizer and airborne particles density was unknown, 1 g cm\(^{-3}\) was assumed for simplicity.

2.7. Calculated regional inhalation dose rate

The inhalation dose of deposited particles in the respiratory system during inspiration and expiration was quantified. The regional inhalation dose rate was obtained by multiplying particle size concentrations

<table>
<thead>
<tr>
<th>(\beta) (m(^3) min(^{-1}))</th>
<th>S (m s(^{-1}))</th>
<th>BB1 ratio</th>
<th>BB2 ratio</th>
<th>(\beta) (m(^3) min(^{-1}))</th>
<th>S (m s(^{-1}))</th>
<th>BB1 ratio</th>
<th>BB2 ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>With outdoor</td>
<td>Without outdoor</td>
<td>With outdoor</td>
<td>Without outdoor</td>
<td>With outdoor</td>
<td>Without outdoor</td>
<td>With outdoor</td>
<td>Without outdoor</td>
</tr>
<tr>
<td>0.36</td>
<td>0.006</td>
<td>0.69</td>
<td>0.63</td>
<td>0.68</td>
<td>0.39</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.5</td>
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<td>0.81</td>
<td>0.51</td>
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<td>–</td>
</tr>
<tr>
<td>0.75</td>
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<td>1.11</td>
<td>1.06</td>
<td>0.99</td>
<td>0.70</td>
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<td>0.011</td>
</tr>
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</tr>
<tr>
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<td>0.018</td>
</tr>
<tr>
<td>1.8</td>
<td>0.030</td>
<td>1.66</td>
<td>1.60</td>
<td>1.51</td>
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<td>–</td>
<td>–</td>
</tr>
<tr>
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<td>1.80</td>
<td>1.75</td>
<td>1.67</td>
<td>1.36</td>
<td>30</td>
<td>0.036</td>
</tr>
<tr>
<td>(33.6)</td>
<td>(0.04)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>1.89</td>
<td>1.84</td>
<td>1.79</td>
<td>1.50</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Variation (%)</td>
<td>36.4</td>
<td>34.6</td>
<td>38.0</td>
<td>25.8</td>
<td>Variation (%)</td>
<td>3.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>
on the worker area (NanoScan and MiniWras data combination) by the ICRP human respiratory tract model deposition probability (Eckerman et al., 2011). The respiratory volume used was 25 l min\(^{-1}\), corresponding to male respiration during light exercise (Koivisto et al., 2012b). The regional dose was calculated for head airways, tracheobronchial and alveolar regions by using simplified deposition fraction equations for the ICRP model as described by Hinds (1999). In the model, particles were assumed to be spherical and to preserve their size during inhalation.

2.8. Chemical risk assessment

A chemical risk assessment was conducted by using Stoffenmanager® v.7.1 (hereinafter referred to as Stoffenmanager), which is a risk prioritisation web-based tool consisting of a control banding tool (inhalation and dermal), with a part designed for exposure to engineered nanoparticles (inhalation) and general and REACH specific quantitative inhalation exposure parts (van Tongeren et al., 2017). Stoffenmanager is recommended by ECHA for Tier 2 regulatory exposure assessment (ECHA, 2016a; Spinazzè et al., 2017; van Tongeren et al., 2017). Stoffenmanager background and general assumptions are based on Marquart et al. (2008) whereas the rationale of the algorithm is based on Cherrie and Schneider (1999) but adapted in several ways as described by Tielemans et al. (2008). Stoffenmanager has been validated for different scenarios involving handling of powders, solids, low-volatile and volatile liquids using N6000 measurements (Stoffenmanager®) and in 10 scientific studies (Bekker et al., 2016; Lamb et al., 2015; Landberg et al., 2017, 2015; Riedmann et al., 2015; Savic et al., 2018, 2016; Schinkel et al., 2010; Spinazzè et al., 2017; van Tongeren et al., 2017).

The relative chemical composition of the main components of the fertilizer (ammonium nitrate, 20%; potassium nitrate, 15%; calcium fluoride, 3%) was used to calculate likely inhalable concentrations for each chemical component, based on the total measured inhalable mass concentrations. Subsequently, concentrations were compared with the Derived No Effect Level (DNEL) and risk assessment was applied using the ECHA guidance (ECHA, 2016b) approach which defines risk characterization:

- Controlled risk: [concentration]/DNLE < 1
- Uncontrolled risk: [concentration]/DNLE > 1.

3. Results

3.1. Material morphology and characterization

Samples collected onto Au TEM grids were observed and characterized using TEM-EDX. In the samples collected during SB2 (Fig. 3a, b, c, d and e) and BB1 (Fig. 3f, g, h and i) experiments, particles which main elements were O, Na, K, Ca, Cr and Zn were detected proving the presence of fertilizer particles in the worker area (Fig. 3a, b, c, d, f, g and h). A few differences were observed between both samples. Fertilizer particles size was between 1 \(\mu\)m to \(\approx\) 35 \(\mu\)m in both samples, although in BB1 there was a bigger proportion of bigger particles (Fig. 3f) whereas in SB2 a bigger proportion of smaller ones (Fig. 3c). Additionally, agglomerates of nanoparticles, with particle size \(< 50 \text{ nm}\) and main components O and C, were found on both samples indicating the presence of diesel combustible particles in the worker area, coming from the diesel forklift (Fig. 3d, e, h and i). Those agglomerates were occasionally seen in the BB1 samples (Fig. 3h and i), whereas in the SB2 they were highly abundant (Fig. 3c, d and e) owing to a higher activity of diesel forklifts inside the plant (96.2%; Table 2).

3.2. Dustiness indices

Material dustiness was assessed using the continuous drop method and results were given in terms of inhalable and respirable mass fractions (mg kg\(^{-1}\)) gravimetrically analyzed. Following the EN 15051 dustiness classification for continuous drop, the fertilizer under study was classified as a material with low and very low dustiness indices, with
1026 ± 210 mg kg⁻¹ and 16 ± 3 mg kg⁻¹ for inhalable and respirable fractions, respectively.

3.3. Concentrations

3.3.1. Worker area concentrations

The measurements started 34 to 46 min prior to the packing process. Packing lasted between 1 h 20 min and 2 h 43 min (Table 2). For BB2 no background concentrations could be recorded. During SB1 (Fig. S3), total particle number and inhalable mass concentrations during packing were similar to background concentrations (Table 3 and Fig. S3). Concentrations of fine particles (100 nm–1 μm) and thoracic and respirable mass concentrations were lower during packing compared with pre-activity levels (Table 3, Fig. S3, Supporting information), which resulted from decreasing background concentrations during the pre-activity period (see Fig. S3). Thus, it was concluded that during SB1 experiments no significant impacts on particle exposure were detected. Similarly, during SB2 (Fig. 4) experiments no statistically significant differences were observed in terms of mass concentrations between the pre-activity and activity periods (Table 3, Fig. 4). These results are in agreement with the low dustiness index of the fertilizer material. Conversely, during SB2 total particle number concentration did increase significantly with regard to pre-activity levels (on average for total particle number, 17340 cm⁻³) (Table 3, Fig. 4). This increase may have been linked to diesel emissions from a diesel forklift which operated inside the plant during this period, as will be discussed below. In addition, very few differences were observed in particle size distributions between the pre-activity and activity period size distributions for SB1 and SB2 (Fig. 5a and b). In Koivisto et al. (2012a) measurements during packing of TiO₂ into large and small bags was seen to increase particles >500 nm. Even so, the present results were to be expected as when classifying the fertilizer according to its dustiness index, it was sorted as a material with very low and low capacity to generate airborne dust for inhalable and respirable fractions, respectively.

As described above, particle number concentrations increased significantly only during two of the four experiments, i.e., SB2 and BB1. However, those increases were not clearly related to the packing activity as no specific relation was seen with the start and stop of the process (Figs. 4 and 6). Increases of ultrafine particles in comparison with the background were always below 40,000 cm⁻³, the suggested reference limit value in this specific case (non-biodegradable granular nanomaterials in the range of 1–100 nm and density < 6 kg l⁻¹) (Van Broekhuizen et al., 2012).

Inhalable and respirable mass concentrations did not exceed in any case the limit values for particles not otherwise specified of 10 and 3 mg m⁻³, respectively (INSH, 2018). Thus, it may be concluded that packing activity of the specific fertilizer did not have a significant impact on worker exposure with regard to particles in the 11.5 nm–35 μm size range. It should be pointed out that in this study worker exposure concentrations do not correspond strictly to the worker breathing zone (because instruments were not worn by the workers), which are expected to be higher (Koivisto et al., 2015; Koponen et al., 2015). Additionally,

During BB1 (Fig. 6), particle number and mass concentrations were again similar to pre-activity concentrations, showing slightly higher (non-statistically significant) mean concentrations (Table 3). Total particle number concentrations increased by 4876 cm⁻³ and respirable mass concentration by 314 μg m⁻³ (Table 3, Fig. 6). During the BB2 experiments (Fig. S4) pre-activity concentrations were not available because the activity was initiated before the monitoring instrumentation was ready, and therefore worker exposure can only be discussed comparing indoor background concentrations. As in the case of SB1 and SB2 very few differences were observed in particle size distribution between the pre-activity and BB1 packing periods. Only slight increases in particles <30 nm and >10 μm were observed (Fig. 5c). Contrarily, in Koivisto et al. (2012a), packing of TiO₂ into large bags was seen to increase particles >500 nm. Even so, the present results were to be expected as when classifying the fertilizer according to its dustiness index, it was sorted as a material with very low and low capacity to generate airborne dust for inhalable and respirable fractions, respectively.
the measurements were carried out for a maximum of 2.5 h and therefore not representative of the 8 h necessary to calculate the 8 h time weighted average over a full shift.

Packing processes and similar industrial activities such as material pouring have been previously studied among different types of industries with results indicating that packing, pouring or dumping processes usually lead to slight increases in worker exposure concentrations. Packing of carbon black in bags of 25 kg and 1000 kg was shown to increase airborne particles > 400 nm and mass concentrations (Ding et al., 2017; Kuhlbusch et al., 2004). Fullerenes packing increased particle number > 1000 nm (Fujitani et al., 2008). Evans et al. (2010) also found that dumping of carbon nanofibers into a drum resulted in an increase of respirable mass concentrations. In the case of the cement industry, Notø et al. (2018) found that packing was associated with an increase of worker exposure to the thoracic mass fraction of 12% and 33% when working less than and more than half a shift, respectively. On the contrary, pouring of cement at a construction site was seen to have highly variable and low percentages of inhalable mass exposure, probably because of workers performing pouring operations also carrying out other activities (Peters et al., 2008). In comparison to these studies, the fertilizer packing case presented in this work seemed to have one of the lowest impacts on worker exposure to particle mass and number concentrations.

3.3.2. Outdoor concentrations

The packing hall was connected by two doors (Fig. 1) to outdoors and to another industrial unit. In both sites other processes were occasionally ongoing. Thus, influence of outdoors and other processes taking
place in the adjacent industrial unit were to be expected. Outdoor particle number concentrations as well as PM$_{10}$ mass were usually lower or in a similar range as the worker area and indoor concentrations (thoracic mass fraction) (Tables S1 and S2, Supporting information). Regarding mean particle size, it was usually smaller in the outdoor location than in the indoor and worker area by 10–20 nm (Table S1, Supporting information) due to the influence of outdoor traffic emissions. Mean particle size remained more or less constant between pre-activity and packing periods in the worker area (38–32, 28–37, 33–37, 41–44 nm), indoor (43–37, 38–43 nm) and outdoor (23–20, 31–31, 29–32 nm) measurement points for all days. In general, outdoor concentrations seemed to follow a different pattern from the rest of the locations even if with some exceptions where similar peaks in outdoor, indoor and worker area were observed (e.g., Figs. 4, 11:30; S3, 15:10; S4, 12:15). Numerous studies have reported the infiltration of outdoor particles into diverse indoor environments, especially through windows and doors when they are open (Bennett and Koutrakis, 2006; Hussein et al., 2009; Koponen et al., 2001; Reche et al., 2014; Rivas et al., 2015; Wang et al., 2010). In Wang et al. (2010), outdoor infiltration was detected in a similar packing industrial unit where indoor and outdoor areas were connected by opened doors as in the present study.

3.3.3. Forklifts activity

Electric and diesel forklift activity was recorded and is shown on the top of Figs. 4, 6, S3 and S4 and as a percentage of total recorded time in Table 2. On certain occasions, increases in particle number concentrations in the worker area and indoor seemed to be related to the use of the diesel forklift while in others this relationship was more difficult to establish. For example, the highest statistically significant increase in mean particle number concentration in the worker area was for SB2, also having the highest percentage of diesel forklift activity 96.2% (Table 2). Moreover, when an increase in number concentration linked to the activity of a diesel forklift was seen in the worker area it was also seen in the indoor and outdoor measurement points. This is probably due to the fact that the diesel forklift was used to load and unload trucks, which means that the forklift was moving from outdoor to indoor having to drive by all the measurement points (worker area, indoor and outdoor). Diesel and propane forklifts have been previously identified as a common source of ultrafine particles (20–50 nm) in activities such as warehouse bagging and packing (Ding et al., 2017; Huang et al., 2010; Kuhlbusch et al., 2004; Tsai et al., 2011; Viitanen et al., 2017; Wang et al., 2010).

In terms of particle mass concentration, no increases were detected linked to diesel forklift emissions. However, during the SB2 packing period, two peaks at 10:40 and 11:30 (Fig. 4b) of particles at around 1 μm were identified, which coincided with the start of an electric forklift. This may have resulted from coarse particle resuspension, as observed previously (Huang et al., 2010).

3.4. Regional inhalation dose rates

Inhalation dose rates were estimated for each day using combined data from NanoScan and MiniWras (Tables 3 and S3). Particle number dose rates (n) during packing ranged between 682 × 10$^6$ and 1122 × 10$^6$ min$^{-1}$. Increases (between 87 × 10$^6$ and 240 × 10$^6$ min$^{-1}$) during the packing process were obtained when comparing with pre-activity periods for all days. Surface dose (s) analysis was calculated as well as respiratory tract deposition percentages. From the total surface area of the deposited particles during packing (3.3–7.6 × 10$^6$ μm$^2$ min$^{-1}$), 52–61% was estimated to deposit in the alveolar region, 13–14% in the trachea bronchi and 25–36% in the head airways (Table 3). The percentage for the alveolar region is lower than that found by Wang et al. (2010), who determined the percentage of deposited surface area in the alveolar region to be 80% during packing in a carbon black manufacturing industry. No increases in the total surface deposited area during packing were observed when compared with the pre-activity periods except for SB2. In addition, an increase on the percentage on the alveolar and trachea bronchi regions during packing was observed for SB1, whereas for the rest, percentages remained approximately the same. This increase in number and surface deposited area is most likely due to the diesel forklift activity or another process taking place near the packing area and not due to the packing process itself, which emits coarser particles as described in previous sections. The day with the highest percentage of diesel forklift activity (SB2) showed the highest increase in total surface deposited area (4.6 × 10$^6$ and 6.0 × 10$^6$ μm$^2$ min$^{-1}$ for pre-activity and process respectively). Higher percentages of deposited particles were detected in the alveolar and head airways regions. Particles deposition on the tracheobronchial area is dominated by particles with diameters

![Figure 6](image_url)
under 10 nm. Here, instruments used have a lower limit at around 20 nm. Thus, when analyzing tracheobronchial estimations the previous fact must be considered.

Particle number deposition percentages on the alveolar region ranged between 66 and 69%, similar range as in Wang et al. (2010), who found it to be 64% during packing in a carbon black manufacturing industry. As pointed out in Wang et al. (2010) the use of both metrics, number concentration and surface area, is advisable as, when used separately, different results may be obtained. In Koivisto et al. (2012b) inhalation dose rates as well as percentages of deposited particles in the respiratory tract were calculated for nanoparticle production process in terms of particle number, mass and active surface area. Increases in number concentration and surface area were detected when comparing pre-activity period with process. For that specific case, number concentration was found to be the metric defining better the particles emitted during the process whereas surface area was found to describe process and background particles (Koivisto et al., 2012b).

3.5. Risk assessment: chemical exposure

Chemical risk assessment during fertilizer packing was assessed using Stoffenmanager and by comparing measured inhalable mass concentrations of the different fertilizer components with ECHA (European Chemicals Agency) DNEL values (Table 4). Stoffenmanager results reports can be found in Tables S4 and S5, Supporting information. Stoffenmanager predicted concentrations for the packing task (pre-activity concentrations not considered) and risk assessment ratios are shown in Table 4 together with actual online total inhalable concentrations and likely components concentrations with its calculated risk assessment ratios (see Section 2.8). For small and big bags, predicted and measured concentrations for the chemical components were in all cases below the established DNEL. For small bags, the ammonium nitrate predicted concentration was 360 μg m⁻³ whereas measured were 410 and 260 μg m⁻³ for SB1 and SB2 respectively. Ratios [concentration]/DNLE were 0.011 or <0.01, well below 1 indicating that the chemical risk is controlled (<1) according to the REACH classification (ECHA, 2016b). Similarly, for the big bags, ratios [concentration]/DNLE for ammonium nitrate of 0.022 for predicted and <0.01 for measured (BB1 and BB2) were obtained. For potassium nitrate, predicted concentrations for small and big bags were 270 and 620 μg m⁻³ respectively, whereas measured concentrations ranged between 160 and 300 μg m⁻³ with ratios [concentration]/DNLE ranging between 0.004 and 0.016 (<1). Similarly, calcium fluoride [concentration]/DNLE ratios for small and big bags were <1 (0.006–0.024) with concentrations ranging between 30 and 120 μg m⁻³. Therefore, under the REACH approach for risk assessment, exposure to the chemical components of the fertilizer in the present study should be considered under control.

3.6. Prediction models

Exposure concentrations were modelled using the one and two box models including and excluding outdoor concentrations. Worker area monitored concentrations were compared to one box modelled results, and to FF modelled concentrations when using the two box model, as worker area monitoring instruments were not placed inside the limits of the defined NF area.

As described in Section 2.5.3, a sensitivity analysis was carried out to identify the optimal air flow rate between NF and FF (β) in the two box model for this industrial setting. The range of values tested was obtained from the literature (Baldwin and Maynard, 1998; Arnold et al., 2017), and the results of this analysis are summarized in Tables 1 and 4. For small bags, a range of S = 0.006–0.05 m s⁻¹, where S is wind speed inside the plant, corresponding to β = 0.36–3 m² min⁻¹ was tested. Modelled concentrations were seen to vary between 26 and 38%. On the other hand, for big bags a range of S = 0.0125–0.04 m s⁻¹ corresponding to β = 9.4–30 m² min⁻¹ was tested, and modelled concentrations were seen to vary <5 %. Results evidenced that for small bags, higher β (e.g., 3 m² min⁻¹) resulted in modelled/measured ratios up to 1.89, whereas lower β largely underestimated modelled concentrations (ratios = 0.39–0.69 for β = 0.36 m² min⁻¹). As a result, a β of 0.75 m² min⁻¹ was selected for the small bag scenarios. In a similar analysis, for the big bag scenarios β = 30 m² min⁻¹ (Table 1), although as explained β does not seem to be a critical parameter for this scenario.

With the parametrization selected, for the one box setup including outdoor concentrations, modelled concentrations (325, 404, 759 and 546 μg m⁻³ for SB1, SB2, BB1 and BB2, respectively) (Table 5) were able to reproduce actual exposure measurements (279, 318, 668 and 529 μg m⁻³ for SB1, SB2, BB1 and BB2, respectively) (Table 3). Predicted concentrations were only slightly higher than the measured values (Tables 3 and 4). The ratio (mmodelled/mmeasured) of 1.22 ± 0.07 for the small bags and 1.09 ± 0.08 for big bags (Table 5). For the two box model including outdoors, modelled concentrations (311, 316, 745 and 538 μg m⁻³ for SB1, SB2, BB1 and BB2, respectively) (Table 3) were predicted concentrations were higher than measured concentrations with a ratio (mmodelled/mmeasured) of 1.05 ± 0.08 for small bags and 1.07 ± 0.07 for big bags (Table 5).

Modelled concentrations without adding outdoor concentrations (Table 5) were generally lower than measured concentrations (and only slightly higher in 2 cases; SB1 one and two box model

Table 4
Stoffenmanager tool results for the small and big bags case scenarios (task concentration) in terms of total and component (ammonium nitrate, potassium nitrate and calcium fluoride) inhalable concentrations. Actual online measured inhalable concentrations and likely component concentrations calculated using composition percentages of the fertilizer. DNLE values for each fertilizer component. Risk assessment (Risk ass.) is calculated following the REACH approach: [concentration]/DNLE = 1, controlled risk; [concentration]/DNLE > 1, uncontrolled risk. SB: small bags; BB: big bags.

<table>
<thead>
<tr>
<th></th>
<th>Total inhalable [μg m⁻³]</th>
<th>Ammonium nitrate (20%) [inhaling μg m⁻³]</th>
<th>Potassium nitrate (15%) [inhaling μg m⁻³]</th>
<th>Calcium fluoride (3%) [inhaling μg m⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8 h TWA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stoffenmanager</td>
<td></td>
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</tr>
<tr>
<td>Small bags</td>
<td>1800</td>
<td>37.600</td>
<td>36.700</td>
<td>5000</td>
</tr>
<tr>
<td>Small bags risk ass.</td>
<td>–</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.011</td>
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<tr>
<td>Big bags</td>
<td>4110</td>
<td>820</td>
<td>620</td>
<td>120</td>
</tr>
<tr>
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<td>–</td>
<td>0.022</td>
<td>0.017</td>
<td>0.025</td>
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<td><strong>Small bags actual online measured concentrations</strong></td>
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<td>Small bags 1 (SB1)</td>
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<td>410</td>
<td>300</td>
<td>60</td>
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<tr>
<td>Risk ass. SB1</td>
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<td>&lt;0.01 (0.008)</td>
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<td>&lt;0.01 (0.005)</td>
<td>&lt;0.01 (0.008)</td>
</tr>
<tr>
<td><strong>Big bags actual online measured concentrations</strong></td>
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<td></td>
<td></td>
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<tr>
<td>Big bags 1 (BB1)</td>
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<td>370</td>
<td>280</td>
<td>60</td>
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<tr>
<td>Risk ass. BB1</td>
<td>–</td>
<td>(0.010)</td>
<td>&lt;0.01 (0.008)</td>
<td>0.011</td>
</tr>
<tr>
<td>Big bags 2 (BB2)</td>
<td>1047</td>
<td>210</td>
<td>160</td>
<td>30</td>
</tr>
<tr>
<td>Risk ass. BB2</td>
<td>–</td>
<td>&lt;0.01 (0.006)</td>
<td>&lt;0.01 (0.004)</td>
<td>&lt;0.01 (0.006)</td>
</tr>
</tbody>
</table>
including outdoor). The ratio \( \frac{m_{\text{measured}}}{m_{\text{modelled}}} \) for the one box model was 0.98 ± 0.19 for the small bags and 0.84 ± 0.12 for the big bags. The ratio \( \frac{m_{\text{measured}}}{m_{\text{modelled}}} \) for the two box model was of 0.88 ± 0.25 for the small bags and 0.82 ± 0.12 for big bags. Thus, the model underestimated exposure concentrations when outdoor contributions were not included. Commonly, model testing assumes that the initial concentration is zero and that the supplied air is free of contaminants (Zhang et al., 2009). However, as discussed in Section 3.3.2, the initial concentration is zero and that the supplied air is free of contaminants were not included. Commonly, model testing assumes that the initial concentration is zero and that the supplied air is free of contaminants (Zhang et al., 2009). However, as discussed in Section 3.3.2, the initial concentration is zero and that the supplied air is free of contaminants (Zhang et al., 2009). However, as discussed in Section 3.3.2, the initial concentration is zero and that the supplied air is free of contaminants (Zhang et al., 2009).

4. Discussion: parametrization of exposure models

Evidently, the results obtained regarding modelled concentrations are highly dependent on model parameters (Mølgaard et al., 2014) such as the handling energy factor, local controls, air exchange rate (AER) and NF-FF air flow (\( \beta \)), which are not yet fully parametrized (Cherrie et al., 2011; Jaycock et al., 2011; Sahmel et al., 2009; Baldwin and Maynard, 1998; Keil and Zhao, 2017) and are often challenging to estimate (Zhang et al., 2009). Sensitivity analyses such as the one presented in Table 1 are also valuable.

In the case of the AER and \( \beta \), experimental data were not available for this case study and they were thus obtained from the literature and tested by means of a sensitivity analysis, \( \beta \) was seen to be a key parameter when modelling the small bags case scenario while it was not critical for the big bags case scenario. That may be explained by the fact that the small bags case scenario was a real two box case (with an actual enclosure and with a small surface area for the air flow between NF and FF) whereas for the big bags there was no real separation between NF and FF and consequently the theoretical free surface area used in the model was much higher.

Local controls prevent dispersion of the aerosolized particles in the room air or remove the particles from air, e.g. enclosures or local extraction systems (Fransman et al., 2008). When having to consider extractions systems, local control values associated can be relatively easy to determine, but in cases like enclosures or barriers it is more complex especially without having actual exposure concentrations. Local exhaust ventilation efficiency can be calculated by a relatively simple equation (Hewett and Ganser, 2017) although some unknown parameters are required. For cases such as the present study when there is no possibility to experimentally establish a value, Fransman et al. (2008) conducted a review with values proposed for different local controls. Here, enclosure local control and bag protection was included in the equation by using values reviewed in Fransman et al. (2008). The output modelled concentrations were seen to correctly predict measured concentrations when using the reported values.

Finally, the emission source characterization is one of the main sources of uncertainty in the model, as it is strongly case-specific. This is one of the reasons why studies dealing with real-world scenarios are highly necessary in the literature. As in the present study, emission source characterization can be based on the dustiness index which may be obtained by standard methods (Lidén, 2006). However, the handling energy factor must be considered (Koivisto et al., 2015; Lidén, 2006; Schneider and Jensen, 2007) and it is still not completely parametrized. When the dustiness concept cannot be used, equations to estimate emission rates have been described (Hewett and Ganser, 2017; Sachse et al., 2012) and used on real scenarios by using mass equation balance and a convolution theorem (Koivisto et al., 2018a; Koivisto et al., 2018b). However, unlike the other parameters, literature regarding emission rates is still limited.

Thus, although here good estimations were obtained, it is important to keep in mind that uncertainties can be considerable when some of the parameters (e.g. local controls or \( \beta \)) are unknown and must be literature based or estimated. Therefore, an appropriate selection of the parameters is essential.

Additionally, an important consideration to be discussed at this point is that the models do not consider particle losses due to sedimentation. Cherrie et al. (2011) found that for particles < 10 \( \mu \text{m} \) the impact of deposition might be reasonably ignored, but for particles with a higher aerodynamic diameter the deposition impact may be important. Fig. 5 shows that most of the emitted particles during packing were under 10 \( \mu \text{m} \). However, for BB1, a slight increase of particles > 10 \( \mu \text{m} \) during packing was observed.

Stoffenmanager overestimated total inhalable exposure levels by a factor of 1.4 to 3.9 with the exception of SB1 in which the prediction was accurate. This is in line with findings by Landberg et al. (2017) who showed that Stoffenmanager overestimates low exposures and underestimates high exposures, and Spinazzé et al. (2017) who showed that ca. 50% of the simulations overestimated the exposure levels for solvents. The overestimation may be party related to the error in the general ventilation multipliers that are used to describe dilution of the concentrations (Koivisto et al., 2018c). However, a better explanation is that Stoffenmanager is a non-physical model that does not follow principal laws of physics, such as mass balance and it does not describe the reality well (Koivisto et al., 2018c).

Based on the above considerations, it may be concluded that the use of the one box and two box models in the industrial setting tested can satisfactorily predict low particle concentration exposures, especially when input parameters are sufficiently robust. In Sahmel et al. (2009),

### Table 5

One box and two box modelled respirable concentration results including and without including outdoor concentrations. Ratios between modelled and measured concentrations for each specific case are shown in brackets. Last two columns are mean ratio values (and standard deviation) for small and big bags (SB and BB). Last row shows the measured respirable fraction concentrations in the workers area and the spatial background.

<table>
<thead>
<tr>
<th>Concentration (( \mu\text{g} \text{ m}^{-3} ))</th>
<th>SB1</th>
<th>SB2</th>
<th>BB1</th>
<th>BB2</th>
<th>Ratio mean ± (s.d.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One box with outdoor</td>
<td>325 (1.16)</td>
<td>404 (1.27)</td>
<td>759 (1.14)</td>
<td>546 (1.03)</td>
<td>1.22 (0.07)</td>
</tr>
<tr>
<td>Two box with outdoor (FF)</td>
<td>311 (1.11)</td>
<td>316 (0.99)</td>
<td>745 (1.12)</td>
<td>538 (1.02)</td>
<td>1.05 (0.08)</td>
</tr>
<tr>
<td>One box</td>
<td>310 (1.11)</td>
<td>270 (0.85)</td>
<td>501 (0.75)</td>
<td>488 (0.92)</td>
<td>0.98 (0.19)</td>
</tr>
<tr>
<td>Two box (FF)</td>
<td>296 (1.06)</td>
<td>223 (0.70)</td>
<td>487 (0.73)</td>
<td>480 (0.90)</td>
<td>0.88 (0.25)</td>
</tr>
<tr>
<td>Measured respirable fraction in worker area</td>
<td>279</td>
<td>318</td>
<td>668</td>
<td>528</td>
<td>–</td>
</tr>
</tbody>
</table>

**Note:** Small bags are highly dependent on model parameters (Mølgaard et al., 2014)
the steady state model, similar to the one box model used here, was seen to correctly perform concentration modelling when choosing the appropriate factors. However, in industrial settings many considerations must be taken into account and what is clearly observed in a laboratory scale or controlled settings cannot be directly extrapolated to the industrial world. To this end, the parameters used in this work and the coefficients applied, described in Section 2.5, may be useful as input for future modelling studies.

5. Conclusions

Packing of a fertilizer into small (respirable fraction range 279–318 μg m⁻³) and big bags (respirable fraction range 487–668 μg m⁻³) was not seen to significantly increase worker exposure compared with pre-activity concentrations in terms of inhalable and respirable concentrations. However, increases in particle number concentrations were observed, quite likely related to the diesel forklift activity. A statistically significant increase in ultrafine particles was observed for SB2 (58,646 cm⁻³ during pre-activity; 75,912 cm⁻³ during packing). According to REACH standards, the chemical risk due to exposure to fertilizers in the present study should be considered under control. It should be noted, however, that personal exposure samples were not collected in this work, and that chemical exposures were quantified based on the fertilizer’s chemical composition. This dataset was used to test the performance of one and two box models as tools for risk assessment under real-world industrial settings.

The one and two box models were tested in a real industrial exposure case scenario, where low exposure concentrations were detected, during packing of a fertilizer into small and big bags, with and without enclosure. Both models seemed to be able to predict low exposure concentrations. When outdoor concentrations were not included in the models, modelled concentrations slightly underestimated actual concentrations, with ratios modelled/measured ranging between 0.82 ± 0.12 and 0.98 ± 0.19 for the respirable size fraction. The use of outdoor concentrations as an input for the models was seen to improve model performance, resulting in slight overestimations at measured concentrations what was estimated as preferable from a risk assessment point of view. In addition, higher precision between repetitions was achieved when including outdoor contributions (ratio modelled/measured 1.05 ± 0.08 to 1.22 ± 0.07). Thus, it was concluded that including outdoor concentrations in the model resulted in an improved model performance, which may be considered a step forward in the application of risk assessment models.

With regard to the selection of the one or two box models, similar results for the small and big bags case scenarios were obtained. However, slightly better results were obtained when using the two box model for the small bags scenario (one box model 1.22 ± 0.07; two box model 1.05 ± 0.08), whereas both models provided similar results for the big bags (1.09 ± 0.08 and 1.07 ± 0.07 respectively). Thus, it may be concluded that, even in complex real-world settings where low exposure concentrations are monitored, the simplest approach of the one box model was adequate when predictions were needed for nanoscale aerosol measurements. This dataset was used to test the performance of one and two box models as tools for risk assessment under real-world industrial settings.

Stoffenmanager estimated that the packing process increases exposure levels from 2000 to 4000 μg m⁻³ for small and big bags even though the packing did not elevate the concentrations in detectable amounts (1600–2000 μg m⁻³, measured concentrations). Thus, in this case, using Stoffenmanager for assessing risk management measures would not be recommended.

Acknowledgments

This research was founded by the Spanish MINECO (CGL2015-66777-C2-1-R, 2-R), Generalitat de Catalunya AGAUR 2017 SGR41, the Spanish Ministry of the Environment (13C AES006), FEDER (European Regional Development Fund) “Una manera de hacer Europa” and H2020 project calIBRAtE (Work Package 7). M.C. Mingüillón acknowledges the Ramón y Cajal Fellowship awarded by the Spanish Ministry of Economy, Industry and Competitiveness. The authors also acknowledge the company in which the measurements were carried out for their support. The authors declare no conflict of interest relating to the material presented in this article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.09.379.

References


Ecker, K., Harrison, J., Menzel, H.-G., Clement, C.H., 2011. Annexes. The authors declare no conflict of interest relating to the material presented in this article.


4.3.1. Additional Results Publication III: Testing the performance of one and two box models as tools for risk assessment of particle exposure during packing of inorganic fertilizer

After publication and with the aim to apply risk assessment tools to the highest number of case studies possible in this work, this publication was expanded by performing risk assessment (with 8h TWA concentrations) for the small and big bags scenarios with the ART, NanoSafer and Stoffenmanager models by using the C.D index. ART mechanistic underestimates (< 0.4) inhalable mass exposure for all cases. Conversely, ART Bayesian and Stoffenmanager underestimated exposure for the small bags scenario but overestimated (ratio 1.8-2.1 and 1.2-1.4 ART Bayesian and Stoffenmanager, respectively) the big bags scenarios. The NanoSafer was seen to highly overestimate exposure (ratio 6.7-6.8) for the big bags scenario when considering NF modelled concentrations, but to accurately predict them when considering FF modelled concentrations (ratio 1.1). Conversely, for the small bags case scenario, NanoSafer NF modelled concentrations predicted actual concentrations with a ratio 1.2-1.8, but underestimated actual concentrations when considering FF modelled concentrations.

Table 4.3 Calculated 8h TWA (including pre-activity concentrations) for inhalable and respirable mass fractions in the worker area. Risk assessment results conducted with the ART (Mechanistic and Bayesian), Stoffenmanager and NanoSafer v1.1 using Continuous drop (C.D) index. NF: near-field. FF: far-field.

<table>
<thead>
<tr>
<th>Case</th>
<th>WA Respirable (µg m⁻³)</th>
<th>WA Inhalable (µg m⁻³)</th>
<th>ART (inhalable µg m⁻³)</th>
<th>Stoffenmanager (inhalable µg m⁻³)</th>
<th>NanoSafer (respirable (NF-FF) µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small bags</td>
<td>526 355</td>
<td>1999 1768</td>
<td>6.5 (3.5-12)</td>
<td>220 (120-460)</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>1687 1445</td>
<td></td>
<td></td>
<td></td>
<td>623-10</td>
</tr>
<tr>
<td>Big bags</td>
<td>408 413</td>
<td>1687 1445</td>
<td>590 (310-1100)</td>
<td>3100 (2100-4400)</td>
<td>2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2771-434</td>
</tr>
</tbody>
</table>

Additionally, the ART tool was applied by using R.D dustiness index. The same was not carried out with Stoffenmanager (as the tool does not have the option to introduce a dustiness index or level categorization), or NanoSafer (as the input required is respirable dustiness index and difference between C.D Wₚ and R.D Wₚ is very small, 16 vs. 12 mg Kg⁻¹, respectively). ART mechanistic and Bayesian models underestimated exposure in all scenarios, and only for the big bags the ART Bayesian model underestimated with a ratio modelled/measured > 0.5.
Table 4.4 Calculated 8h TWA (including pre-activity concentrations) for inhalable mass fraction based on exposure measurements conducted in the worker area (WA). Risk assessment results conducted with the ART (Mechanistic and Bayesian using Rotating drum (R.D) index.

<table>
<thead>
<tr>
<th>Case</th>
<th>WA Inhalable (μg m⁻³)</th>
<th>ART (inhalable μg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mechanistic</td>
</tr>
<tr>
<td>Small bags</td>
<td>1999</td>
<td>0.65 (0.34-1.2)</td>
</tr>
<tr>
<td></td>
<td>1768</td>
<td></td>
</tr>
<tr>
<td>Big bags</td>
<td>1687</td>
<td>59 (31-110)</td>
</tr>
<tr>
<td></td>
<td>1445</td>
<td></td>
</tr>
</tbody>
</table>
4.4. Publication IV: Modelling of high nanoparticle exposure in an indoor industrial scenario with a one-box model

Authors:

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Published in:


Accepted date: 11 May 2019

Journal Impact Factor / 5-Year Impact Factor: 2.145 / 2.608
Modeling of High Nanoparticle Exposure in an Indoor Industrial Scenario with a One-Box Model

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Received: 11 April 2019; Accepted: 11 May 2019; Published: 14 May 2019

Abstract: Mass balance models have proved to be effective tools for exposure prediction in occupational settings. However, they are still not extensively tested in real-world scenarios, or for particle number concentrations. An industrial scenario characterized by high emissions of unintentionally-generated nanoparticles (NP) was selected to assess the performance of a one-box model. Worker exposure to NPs due to thermal spraying was monitored, and two methods were used to calculate emission rates: the convolution theorem, and the cyclic steady state equation. Monitored concentrations ranged between 4.2 × 10^4 – 2.5 × 10^5 cm^−3. Estimated emission rates were comparable with both methods: 1.4 × 10^11 – 1.2 × 10^13 min^−1 (convolution) and 1.3 × 10^12 – 1.4 × 10^13 min^−1 (cyclic steady state). Modeled concentrations were 1.4 – 6 × 10^4 cm^−3 (convolution) and 1.7 – 7.1 × 10^4 cm^−3 (cyclic steady state). Results indicated a clear underestimation of measured particle concentrations, with ratios modeled/measured between 0.2–0.7. While both model parametrizations provided similar results on average, using convolution emission rates improved performance on a case-by-case basis. Thus, using cyclic steady state emission rates would be advisable for preliminary risk assessment, while for more precise results, the convolution theorem would be a better option. Results show that one-box models may be useful tools for preliminary risk assessment in occupational settings when room air is well mixed.

Keywords: prediction; emission rates; air exchange rate; ultrafine particles; unintentional nanoparticles; incidental nanoparticles; plasma spraying; worker exposure; particle mass concentration

1. Introduction

Thermal spraying is applied at an industrial scale to produce thermally- and mechanically-resistant coatings. A feedstock material (metal, alloy or ceramic) is projected at high temperature and velocity onto the surface to be coated. Protective coatings are widely used in the ceramic, automotive, naval, aeronautic and metallurgy industries to prevent corrosion and wear, as well as to restore different types of damaged surfaces [1–5]. From a risk assessment perspective, thermal spraying is known to generate unintentional nanoparticle (NP) emissions (with diameters < 100 nm; 10^6 cm^−3) at pilot-plant and industrial scales [6,7]. High particle mass concentrations have also been reported [8,9]. Similar NP emission and formation mechanisms have been identified in a large variety of industrial processes [10–17].
Identifying and modeling exposure to this kind of NPs is relevant due to their potential health impacts. Exposure to particulate matter (PM) may cause respiratory and cardiovascular diseases [18], where respirable particles (those which can penetrate into non-ciliated airways, EN 481, 1995) are considered as a harmful component for human health [18–21]. Oberdörster, (2001) [22] indicated the ability of finer size fractions (<100 nm; NP) to penetrate deeper in the respiratory tract. In vivo studies have revealed that NPs can cross the alveolar barrier and cause pulmonary inflammation, which turns into cardiovascular risk [23] in much higher numbers than coarser particles, as they can reach deeper areas in the respiratory tract and therefore have a longer retention time [21].

Thus, unintentional NP release in workplaces is a key environmental health and safety issue which requires further research to understand the determinants of personal exposure. Mass-balance models are useful tools for this purpose, as they allow understanding of critical factors affecting exposure and could lead to efficient risk mitigation strategies [24]. Theoretical modeling aspects have been extensively discussed [25–29]. Indoor exposure assessment is frequently performed using one- and two-box models, which have been shown to predict exposure levels with relative accuracy when adequately parametrized in several environments (e.g., indoor concentrations of volatile compounds; PM concentrations in controlled and industrial scenarios [30,31]).

Key challenges for model application are source characterization, local controls and air mixing rates [30,32–36]. In addition, there is a need to test model performance under real-world conditions. Because of the large variety of indoor micro-environments and emission sources, libraries compiling model parameters would be highly useful for modeling studies [33,37]. Source characterization requires dedicated attention, as it is the main determinant of exposure. In the case of primary particle emissions, tools such as the dustiness index are available to estimate emission rates. However, as in the case of understanding exposure determinants in thermal spraying [6,7], emission rates must be quantified from measured concentrations using methods such as the convolution theorem or mathematical mass balance [27,38]. The use of estimated emission rates from actual monitored concentrations has been seen to provide good modeling results in laboratory studies [35,36,39]. However, literature related to emission rates of unintentional NP at industrial scale is limited [15,40]. As a result, emission rates for industrial sources of unintentional NP release and its use for real-world scenario modeling is highly valuable in view of the increasing use of prediction models and web-based risk assessment tools.

In this context, the aims of the present study are (1) to quantify NP emission rates for two different industrials scale thermal spraying processes; and (2) to test the performance of a one-box model in a real-world setting where high NP concentrations were monitored.

2. Materials and Methods

2.1. Work environment and Process

NP monitoring was carried out during thermal spraying of ceramic coatings in an industrial workshop (T.M. Comas, Blanes, Barcelona, Spain). Two types of spraying were applied, 1) High Velocity Oxy-Fuel coating spraying (HVOF), using low temperatures (< 3000 °C) and high velocities; and 2) Atmospheric Plasma Spraying (APS), using high temperatures (up to 14000 °C) [1,7,41]. Measurements were conducted over a 4-day period in April 2016. The workshop has three thermal spraying booths in an area of approximately 240 m² (14 m wide and 17 m in length) (Figure 1). Here, only data from booth #1 (APS) and #3 (HVOF) will be considered for the modeling approach (Figure 1 and Table S1, Supplementary material) given that booth #2 was not operated continuously. The central area of the workshop (outside the booths), from now on called the worker area (WA) is equipped with a general ventilation extraction system that consisted of three extractors with 11800 m³ h⁻¹ flow each (value provided by the company, not measured). Booth #3 and #1 were additionally equipped with a localized extraction ventilation system (LEV), but only Booth #3’s LEV air flow rate was provided by the company (6500 m³ h⁻¹). Booth #3’s activity periods had a short duration and high frequency (5–10 min, 7–9 repetitions/half day) whereas in booth #1, periods had a longer duration.
and lower frequency (20–30 min, 2–4 repetitions/half day). The two booths were not operated at the same time. However, certain activities such as the cooling and sanding of pieces were occasionally carried out in parallel. More details on the campaign can be found in Salmatonidis et al. (2019) [7]. In booth #1 the door was usually closed while spraying although not completely, thus allowing air mixing between the booth and the WA. In booth #3, during the activity the worker had to enter and leave the booth more frequently due to technical needs of the process and increased the air mixing between the booth and the WA.

![Booth 1 Model Area; V=465 m³](image1)

![Booth 3 Model Area; V=250 m³](image2)

<table>
<thead>
<tr>
<th>Model Area</th>
<th>V, [m³]</th>
<th>Q, [m³h⁻¹]</th>
<th>ACH, [h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>465</td>
<td>16078</td>
<td>35</td>
</tr>
<tr>
<td>#3</td>
<td>250</td>
<td>6216</td>
<td>25</td>
</tr>
</tbody>
</table>

**Figure 1.** Modeled areas limit, volumes (m³), ventilation air speeds (m s⁻¹), and description of instruments deployed and their location. Green and black arrows indicate incoming air flows and ventilation extraction flows, respectively. Dashed arrow indicates air flow from booth to WA. The table shows parameterization of the one-box model: V (m³) is volume used for modeling, Q (m³ h⁻¹) is ventilation air volume flow through the WA, ACH (h⁻¹) is the air changes per hour calculated from measured air speeds and used for modeling.

2.2. Feedstock Material

In booth #1 (days 1 and 2), two types of commercial products (feedstock) were sprayed: Amdry 6228 (Oerlikon Metco, Pfäffikon, Switzerland) and ANVAL 50/50 (Anval) (Table S1). The Amdry 6228 formula is Al₂O₃ 13TiO₂, and it consists of alumina 84% (CAS: 1344-28-1), 14% titania (CAS: 13463-67-7), and organic binder silicon dioxide (CAS: 7631-86-9). The mean aggregate size is 36.0 μm [7] and particles are considered mainly spheroidal with

![Discrete aerosol sampling](image3)

The feedstock sprayed in booth #3 (days 3 and 4) was a WOKA 3702–1 powder (Oerlikon Metco, Pfäffikon, Switzerland) (Table S1). Its formula is WC 20Cr₃C₂ 7Ni, and it consists of 69.5% tungsten carbide (CAS: 12070–12–1), 14.5% trichromium dicarbide (CAS: 12012-35-0), 9% chromium (CAS: 7440-47-3) and 7% nickel (7440-02-0). An unspecified portion of metallic chromium and nickel may be converted during the thermal spray process to hexavalent chromium and nickel compounds, respectively, which are classified as IARC group 1 carcinogen (Safety data sheet, Supplementary material). The mean aggregate size is 34.3 μm [7] and particles are considered mainly spheroidal with
an apparent density between 3.8–4.9 g cm$^{-3}$. WOKA 3702–1 is classified as hazardous according to Regulation (EC) 1272/2008 [43] and it is suspected to cause cancer.

2.3. Online Measurements and Airborne Particle Collection

Mean particle diameter, and particle number and mass concentrations were monitored inside the booths and in the central WA (Figure 1). Additionally, particle size distribution was monitored in the WA.

The monitoring instruments deployed were:

- A miniature diffusion size classifier (DiSCmini Matter Aerosol, Testo; sample flow rate 1 l min$^{-1}$) to measure particle number concentration, mean particle size and alveolar lung deposition surface area (LDSA) in a range of 10 to 700 nm, with a 1-minute time resolution.
- A Mini Laser Aerosol Spectrometer (Grimm, Mini-LAS 11R; sample flow rate 1.2 L min$^{-1}$) to measure particle mass concentration from 0.25 to 32 µm in 31 channels, with a 1-minute time resolution.

Inside the spraying booths, instruments were located near the cabin extraction system, and at 1.5 m from the plasma spray nozzle.

The WA instruments were located outside the booths, at approximately 4 m from the door (Figure 1). The instruments were located between 0.5 and 1.5 m above ground. Concentrations were monitored by using a DiSCmini and a Grimm Mini-LAS (as described above), as well as:

- An electrical mobility spectrometer (NanoScan, SMPS TSI Model 3910; sample flow rate 0.7 L min$^{-1}$) to measure particle number concentration and size distribution in 13 channels from 10 to 420 nm, with a 1-minute time resolution.
- A Mini Wide Range Aerosol Spectrometer (Mini-WRAS 1371; sample flow rate 1.2 L min$^{-1}$) to measure particle mass concentration, number concentration and size distribution from 10 nm to 35 µm in 41 channels, with a 1-minute time resolution.

Particle metrics were monitored each day between 10:00 and 17:00. During the lunch breaks, from 12:45 to 13:45, processes were switched off and this period was considered to be representative of background (BG) concentrations.

Instrument intercomparison was carried out prior to the industrial measurements at an air quality monitoring station in Barcelona, Spain, using ambient air aerosols [7]. The fact that instruments were intercompared using a different type of aerosol is acknowledged as a limitation of this work.

Increases in particle number and respirable mass concentrations during spraying were considered statistically significant when the following approach, described by Asbach et al. (2012) [44] and Kaminski et al. (2015) [45], was fulfilled:

\[
\text{Mean concentration during spraying} > \text{BG} \pm 3(\sigma\text{BG}), \tag{1}
\]

where BG is the mean temporal background concentration and $\sigma$BG is the standard deviation of the BG concentration.

Finally, in order to complement the air flow data provided by the company, air speeds at booths LEV, central ventilation extraction, and inside the plant were experimentally measured (shown in Figure 1) with an anemometer (VelociCalc® thermal anemometer, TSI Model 9545; TSI Inc., Shoreview, MN, USA; range 0–30 m s$^{-1}$; accuracy ±3% or ±0.015 m s$^{-1}$; resolution 0.01 m s$^{-1}$).
2.4. Exposure Modeling

2.4.1. Air changes per hour (ACH)

The number of air changes per hour (ACH) in the WA was calculated by using the measured air speeds in the central ventilation extraction and also next to the booth doors, as:

\[ \text{ACH} = \frac{Q}{V} = \frac{(\text{m}^3 \cdot \text{h}^{-1})}{\text{m}^3}, \]  

(2)

where \( Q \) (\( \text{m}^3 \cdot \text{h}^{-1} \)) is the total flow rate and \( V \) (\( \text{m}^3 \)) is the total room volume.

2.4.2. Particle Emission Rates

Particle emissions were monitored in close proximity to the source (the spraying nozzle), with the logistical limitations characteristic of operational industrial scenarios, where measurements should be as least invasive as possible. Despite the air extraction systems in place, particle number concentrations measured inside the booths largely exceeded the instrument (DiSCmini) monitoring range (\( 4 \times 10^6 \, \text{cm}^{-3} \); Figure 1 and Figure S1 in Supplementary materials). As a result, particle emissions rates could not be calculated based on data collected inside the booths. To overcome this limitation, emission rates were calculated based on the data collected in the WA, i.e., how much particles are leaking from the booth to the WA (booth is the source). This was based on the assumption that air exchange between both areas was frequent: the booth doors were sometimes wide open (when the operator had to access the inside of the booth), and when they were closed they were not fully airtight, and small holes through which cables were inserted were visible along the booth walls. As a result, particle emissions in the booths impacted concentrations in the WA significantly [7]. Similar results have been reported by other authors [46], indicating impacts on particle number concentrations up to 6 m away from the source.

In the present work, particle emission rates were estimated from concentrations measured in the WA, and thus do not strictly correspond to actual emission rates but are rather considered as transported emission rates from the booths to the WA. These transported emissions were used as input to model particle concentrations in the WA. For the sake of clarity and in the present work, transported emission rates from the booths to the WA, measured in the WA, will be referred to as emission rates.

Emission rates were calculated by using two different approaches:

Convolution Theorem

Assuming that NP concentrations are fully mixed, the WA particle concentrations can be described with a mass balance of aerosol particles in a single compartment [28]:

\[ \frac{dN(t)}{dt} = \lambda N_{BG}(t) + \left( S_N \left( t \right) \right) / V - \lambda N(t), \]  

(3)

where \( N \) (\( \text{cm}^{-3} \)) is the WA particle concentration, \( \lambda \) (min\(^{-1}\)) is the WA total particle loss rate including particle removal processes like ventilation and deposition, \( N_{BG} \) (\( \text{cm}^{-3} \)) is the background particle concentration coming from outdoors and surrounding compartments, \( S_N \) (min\(^{-1}\)) is the particle emission rate of the source, and \( V \) (\( \text{m}^3 \)) is the volume of the WA room.

The one-box model [28] assumes that 1) particles are fully mixed at all times; 2) particles are created by the source and through infiltration; and 3) there are no other particle losses than mechanical ventilation. Particle losses by sedimentation may be considered negligible because of the high air exchange ratio (ACH) measured (25–35 h\(^{-1}\), Figure 1).

When background particle emissions and indoor sources are negligible (i.e., \( S_{tot} \left( t \right) \approx 0 \, \text{min}^{-1} \)), e.g., during the lunch break, the particle number concentration decay curve may be described as follows:

\[ N(t) = N_{t=0} \cdot e^{-\gamma t}, \]  

(4)
The calculated ACH varied from 25 to 35 h\(^{-1}\), which is much higher than particle deposition rates, which are typically below 4 h\(^{-1}\) in indoor environments for particles within the measurement range in this work (10 nm to 35 \(\mu\)m; [47]). Thus, the only particle loss considered is through ventilation, and here it was assumed that \(\lambda \approx\) ACH.

According to the convolution theorem, the particle number concentration during the activity is a convolution of the particle sources and particle losses as follows [38]:

\[
S_{\text{tot}}(t) \cdot N(t) = V_0 \int Q(t) N(t) + \epsilon_C S_N(t) \cdot N(t-\tau) d\tau,
\]

where \(Q\) (m\(^3\) h\(^{-1}\)) is the air flow and \(\epsilon_C\) (-) is the protection factor of the booth.

The particle emission term can be solved with a numerical deconvolution as:

\[
S_{\text{tot}}(t) = V \cdot (N(t) - N(t-\Delta t) \cdot e^{-\gamma \cdot \Delta t}) / \Delta t,
\]

In this work, particle emission rates were calculated for the pre-activity period when \(S_N(t) = 0\) min\(^{-1}\) to estimate background particle generation rate \(S_{BG}(t) = QN_{BG}(t)\) (corresponding mainly to infiltration from outdoor air). Because the booth protection factor \(\epsilon_C\) was not known, the plasma spray emission rate term is a combination of \(\epsilon_C S_N\) where background particle emission rate \(S_{BG}\) is subtracted.

Steady State Equation for Cyclic Processes

In addition, emission rates during the activity were also calculated using particle number concentrations (cm\(^{-3}\)) monitored in the WA with the NanoScan instrument, by applying the modified steady state equation for cyclic processes [7]:

\[
S_N = \hat{C} \cdot V / t_{\text{ESD}},
\]

where \(\hat{C}\) (cm\(^{-3}\)) is the mean concentration of particles (as number concentration) during spraying, \(V\) (cm\(^3\)) is the volume of the room, and \(t_{\text{ESD}}\) (min) is the spraying duration. Assumptions were that particle concentrations before the activity were lower than during the activity, particle removal processes were negligible, and that particle concentrations were fully mixed.

2.4.3. One-box Mass Balance Model

As particle concentrations monitored inside the booths exceeded the instrument’s measurement range, applying a two-box model to estimate particle concentrations inside and outside the booths was not possible. Therefore, a one-box model was applied to calculated particle number concentrations. With the emission rates calculated in the WA, the one-box model was applied to the WA volume considering the influence of two types of ventilation systems: the central one in the WA, and the ventilation driving the air flows from the WA to the booth due to the booth’s LEV (Figure 1). Booth air extraction systems were compensated with air coming from the WA (through the door and through small holes for cables) and from outdoors (through a direct pipeline connecting with outdoor air). Background particle concentrations were included in the model with the incoming air, as this was seen to improve mass-balance model performance and accuracy [33].

3. Results and Discussion

3.1. Exposure Concentrations

Particle number concentrations (Table 1) were monitored during thermal spraying in booth #1 (APS, days 1 and 2) and #3 (HVOF, days 3 and 4). Respirable particle mass concentrations varied from 130 to 709 \(\mu\)g m\(^{-3}\) inside the booths, and 93 to 172 \(\mu\)g m\(^{-3}\) in the WA (Table S2, Supplementary material), which is below the occupational exposure limits (OELs) given in the material safety data sheet (MSDS). A clear impact on particle number concentrations was observed inside the booths and
in the WA, once the spraying activity started (Figure 2 and Figures S2 and S3, Supplementary material). Additionally, chemical analyses of the airborne particles indicated that they had the same composition as the feedstock material being sprayed (more details in Salmatonidis et al., 2019 [7]). Thus, it was concluded that the spraying activities generated high concentrations of unintentionally emitted NPs. Chemical analyses of the airborne particles indicated that their composition in terms of mass was that of the raw feedstock material, and that chromium was present in the form of chromium carbide and nickel in its free form (more details in Salmatonidis et al., 2019 [7]).

Figure 2. Booth #3, Day 3 (a) shows the particle number concentrations measured inside the booth by DiSCmini (DM), from worker area by NanoScan (WA) and particle emission rates solved by convolution from NanoScan WA concentrations. Blue line shows when the DM concentration was >10^5 cm^-3 indicating that the plasma spray was ON and green line when the DM concentration was <10^5 cm^-3 indicating that the plasma spray was OFF. Figure (b) shows the particle size distributions measured by the NanoScan in the WA.

The particle number concentrations, measured with the DiSCmini inside the booths during spraying, ranged between 8.5 × 10^5 and 3.5 × 10^6 cm^-3 in booth #1, and between 1.0 × 10^6 and 1.9 × 10^6 cm^-3 in booth #3 (Table 1), exceeding instruments detection limit (Figure 2 and Figures S1, S2 and S3, Supplementary material). The operators wore personal protective equipment (FPP3, masks in booth #3, and welding helmet with respirator in booth #1) when they entered the booths but in the WA, the operators only wore the masks intermittently. NP concentrations were approximately one order of magnitude lower than inside the booths (6.4 × 10^5-9.6 × 10^4 cm^-3 and 1.1-3.5 × 10^5 cm^-3 for booth #1 and #3, respectively). However, the impact of booth #1 emissions on WA concentrations (especially during day 1) was lower than that of booth #3 emissions (Table 1). Particle concentrations recorded in the WA by the NanoScan monitor were similar to the ones measured by the DiSCmini: 4.2-7.8 × 10^4 cm^-3 and 9.0 × 10^4-2.5 × 10^5 cm^-3, for booth #1 and #3, respectively. Due to the similarity between both datasets, and the fact that the NanoScan provided additional information on particle size distributions, the latter dataset was used as an input for the one-box model.

In booth #3 the worker had to enter the booth between repetitions to exchange the coated surface with a new one (to be coated). As the spraying periods were short (5–10 min), the door of the booth was kept open between repetitions during Day 2/Morning, whereas during Day 2/Afternoon the door was alternatively open and closed. This explains the significantly lower concentrations measured in the WA during Day 2/Afternoon compared to during the Morning (Figure 2).
In all cases (inside the booths, and in the WA except on Day 1), particle concentrations exceeded the 40,000 cm\(^{-3}\) threshold considered the nano-reference value used in the precautionary approach [48], and they were statistically significantly higher than background concentrations [44], Eq. 1).

Table 1. Measured particle number concentration during the thermal spraying activity. Statistically significant increases are marked in bold.

<table>
<thead>
<tr>
<th>Day</th>
<th>Shift</th>
<th>Booth Area (WA)</th>
<th>Inactivity (BG)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DISCmini N (cm(^{-3}))</td>
<td>DISCmini N (cm(^{-3}))</td>
</tr>
<tr>
<td>Booth #1 Model Area (Day 1)</td>
<td>Afternoon</td>
<td>3.5 \times 10^6</td>
<td>6.4 \times 10^3</td>
</tr>
<tr>
<td>Booth #1 Model Area (Day 2)</td>
<td>Morning</td>
<td>1.1 \times 10^6</td>
<td>9.6 \times 10^4</td>
</tr>
<tr>
<td></td>
<td>Afternoon</td>
<td>8.5 \times 10^5</td>
<td>6.7 \times 10^4</td>
</tr>
<tr>
<td>Booth #3 Model Area (Day 3)</td>
<td>Morning</td>
<td>1.9 \times 10^6</td>
<td>3.5 \times 10^5</td>
</tr>
<tr>
<td></td>
<td>Afternoon</td>
<td>1.7 \times 10^6</td>
<td>1.1 \times 10^5</td>
</tr>
<tr>
<td>Booth #3 Model Area (Day 4)</td>
<td>Morning</td>
<td>1.3 \times 10^6</td>
<td>1.9 \times 10^5</td>
</tr>
<tr>
<td></td>
<td>Afternoon</td>
<td>1.0 \times 10^6</td>
<td>1.6 \times 10^5</td>
</tr>
</tbody>
</table>

3.2. Air Exchange Quantification

Air speeds were measured at the central ventilation system and at the doors of the booths, during activity periods, and were used to quantify the total air flows in the WA during spraying. The total air changes per hour (ACH, h\(^{-1}\)) were then estimated by considering the volume of each of the modeled areas (to reproduce emissions from booths #1 and #3, Figure 1). The total flows (Q) for model area #1 and #3 were 16078 and 6216 m\(^3\) h\(^{-1}\), respectively with ACH values of 35 and 25 h\(^{-1}\). These values are quite high although in line with reported values in industrial environments, which typically range between 0.3-30 h\(^{-1}\) [49,50]. Additionally, air speeds were measured at the booth doors when they were open, with ACH ranging between 49–89 h\(^{-1}\) (Table S3). The latter ACH are not representative of actual working conditions, given that doors were mostly closed when the spraying guns were operating. Overall, the ACH measured indicate a high variability of the air exchange rates in the workplace, which would influence the modeling results as the ACH is, together with the emission rate, a key input parameter for the model.

3.3. Particle Emission Rates

Particle emission rates were estimated based on WA concentrations, using convolution and cyclic steady state equations (Table 2) in order to compare the results from both approaches. Results showed that emission rates from booth #1 ranged between 1.4 \times 10^{11}–3.4 \times 10^{12} min\(^{-1}\) using the convolution theorem, and between 1.3 \times 10^{12}–3.0 \times 10^{12} min\(^{-1}\) using the cyclic steady state equation. Both approaches provided similar outputs for booth #3, ranging between 7.9 \times 10^{12}–1.2 \times 10^{13} min\(^{-1}\), with the convolution theorem and between 7.9 \times 10^{12}–1.4 \times 10^{13} with the cyclic steady state. Emission rates were higher from booth #3 than from booth #1, which is consistent with the different operational procedures (HVOF vs. APS; [7]).
Table 2. One-Box modeled concentrations using the convolution theorem and the cyclic steady state (Cyclic SS) approach to calculate emission rate ($S_N$) from NanoScan data. Emission rates were calculated for each day considering all activity periods, and modelings were applied for morning (M) and afternoon (A) periods (shift) separately.

<table>
<thead>
<tr>
<th>Model Area</th>
<th>Booth #1</th>
<th>Booth #3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day 1</td>
<td>Day 2</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>M</td>
</tr>
<tr>
<td>WA NanoScan $S_N$</td>
<td>$1.4 \times 10^{11}$</td>
<td>$3.4 \times 10^{12}$</td>
</tr>
<tr>
<td>Modeled concentrations (cm$^{-3}$)</td>
<td>$1.3 \times 10^{12}$</td>
<td>$3.0 \times 10^{12}$</td>
</tr>
<tr>
<td>WA measured (cm$^{-3}$)</td>
<td>NanoScan</td>
<td>$4.2 \times 10^{11}$</td>
</tr>
<tr>
<td>DISCmini</td>
<td>$6.4 \times 10^{11}$</td>
<td>$9.6 \times 10^{11}$</td>
</tr>
<tr>
<td>Ratio (modeled/NanoScan measured)</td>
<td>Convolution</td>
<td>0.33</td>
</tr>
<tr>
<td>Ratio (modeled/DISCmini measured)</td>
<td>Cyclic SS</td>
<td>2.19</td>
</tr>
<tr>
<td>Ratio</td>
<td>Cyclic SS</td>
<td>2.66</td>
</tr>
</tbody>
</table>

* Unusually high ratios were obtained for Day 1, probably due to the low impact of particle emissions on WA concentrations (Figure S1) which led to an overestimation of low concentrations by the model.

In general, both methods provided relatively similar results despite the differences in calculations, thus supporting the robustness of the emission rates calculated. The cyclic steady state generally provided higher emission rates than the convolution theorem (from 1.8 up to 10 times higher), with the exception of Day 3 in booth #3, for which the convolution theorem provided a higher rate (by a factor of 4–16; Table 2). When using the cyclic steady state, differences between days in the same booth were smaller than when using the convolution theorem, suggesting that the convolution theorem is more case-sensitive and will, therefore, probably provide more precise modeling results.

In Koivisto et al. (2018) [15], where particle number emission rates were quantified during electrostatic spray deposition of TiO2 by using the same approaches as in the present study, emission rates near the source were $2.2 \times 10^{12}$ min$^{-1}$ (convolution theorem) and $1.1 \times 10^{12}$ min$^{-1}$ (cyclic steady state). As in the present work, emission rates calculated with the two methods were mostly comparable despite differences in the calculation methods.

The emission rates quantified for the thermal spraying activities were comparable to other emission sources in the literature, e.g., dip coating ($4.2 \times 10^{11}$ min$^{-1}$ and $6.6 \times 10^{11}$ min$^{-1}$; [40], laser printing (maximum rates between $2.4 \times 10^{9}$ and $1.0 \times 10^{13}$; [38,51,52]), in houses due to Tabaco (0.84-3.76 x $10^{11}$ min$^{-1}$) and cooking (1.8-10$^{11}$ min$^{-1}$) [53–55], or NP production in academic laboratories (1.3 x $10^{11}$–1.2 x $10^{12}$ min$^{-1}$; [56]), among others.

3.4. One-Box Model Performance

Worker area (WA) particle number concentrations were modeled by applying a one-box mass balance model [28]. The two types of emission rates calculated (using convolution theorem and cyclic steady state approach) were used as input, with the aim to test model performance under a real-world industrial scenario. The one-box model was applied to the booth #1 and #3 model areas, to predict particle number concentrations in the WA during thermal spraying from each of the booths. The model was tested for two days (including one morning and one afternoon shift, each) in each model area (#1 and #3).

Modeled particle number concentrations in the WA based on the NanoScan monitored concentrations ranged between $1.4–2.4 \times 10^4$ (convolution theorem) and $1.7–2.4 \times 10^4$ (cyclic steady state) while spraying in booth #1, and between $5.3–6.0 \times 10^4$ (convolution theorem) and $4.5–7.1 \times 10^4$ (cyclic steady state) while spraying in booth #3 (Table 2). When comparing these concentrations with actual measured NanoScan ones, on a case by case basis, results indicate that in all cases the model underestimated measured concentrations irrespective of the method used to calculate emission rates: ratios modeled/measured concentrations were < 0.5 for all of the study cases (with one exception, Figure 3a). When comparing modeled concentrations to measured DISCmini concentrations in the
WA, ratios modeled/measured were consistent with those obtained with NanoScan (<0.55, except for the booth #1, day 1), also underestimating measured concentrations (Table 2 and Figure 3a). In general, higher underestimations and variability of the measured concentrations were obtained when using the DiSCmini dataset for model validation. These differences may be attributed to the fact that both instruments (NanoScan and DiSCmini) are not directly comparable as DiSCmini (corona charging principle) monitors particle diameters between 10–700 nm while NanoScan (single particle counting) monitors 20–420 nm (Fonseca et al., 2016). It should be noted that concentrations in terms of particle number are significantly higher than in terms of mass, which is a metric more frequently used with mass balance models, and both metrics are known to represent different particle properties (e.g., size, density, etc.) and therefore have different behaviors [56].

![Graph](image.png)

**Figure 3.** Ratio modeled/measured concentrations (a), and RMSLE (modeled/measured) (b). Ratio 0.5 and 2 are marked as reference (dashed line). Cyclic SS: cyclic steady state equation.

Because of this limitation, the assessment of the root mean squared logarithmic error (RMSLE) is proposed to not over-penalize differences between predicted and actual values, when concentrations are high [36]. This is because the RMSLE mainly takes into account the ratio of change, rather than the actual concentrations. Figure 3b shows that the RMSLE (modeled/NanoScan measured) ranged between 0.4–1.4 when using convolution emission rates and 0.7–1.7 when using cyclic steady state. The same analysis using the DiSCmini dataset resulted in RMSLE (modeled/DiSCmini measured) between 0.6–1.8 when using convolution emission rates and 0.9–2.1 when using cyclic steady state (data not shown). These ratios were compared to the benchmarks proposed by Jayjock et al. (2011) [30], which representative of modeling outputs reviewed in literature. Thus, when considering the RMSLE, only one case was outside the Jayjock et al. (2011) benchmark (0.5–2): booth #3 (Day3/A) with the convolution theorem. This would mean that, according to the ranges suggested by Jayjock et al. (2011), the performance of the one-box model for the industrial scenario assessed in this work would be considered as comparable. In the literature, several authors have reported underestimations by the one-box model [31,35,36,57,58] as it assumes homogeneous concentrations through all the room. This is consistent with our results, even though the high airflows measured in the industrial scenario allowed us to assume adequate mixing, on average. However, it is possible that full mixing was not achieved at all times and during all repetitions, and this should be considered as one of the limitations of the present work.

Model underestimations could also be related to inaccurate ACH calculation or to the underestimation of emission rates including booth protection factor. Emission rates are known to be the most critical exposure determinant, and thus should be calculated based on experimental data collected as close (physically) to the source as possible with known dilution and mixing. Otherwise, large differences may be detected depending on the location and position of the monitoring
instrumentation [36]. These authors demonstrated that emission rates can be corrected by using an adjusting coefficient to compensate for unknown flow distributions. The results presented in this work, which are based on emission rates calculated from data collected at a distance from the source (>3m), support the need for a correction coefficient to improve the emission rates calculated. Unfortunately, knowledge of air mixing is a frequent issue encountered when measurements are carried out in real-world industrial scenarios.

The results were also analyzed in terms of average RMLSE across all cases (Days 1 to 4, morning and afternoon shifts), for the booth #1 and #3 scenarios (Figure 4). Results show that when emission rates were calculated using the convolution theorem, model predictions were more closely aligned with RMLSE = 1 than when the cyclic steady state equation was used, and the ratios (especially for booth #3) presented lower variability. The results obtained when applying the convolution theorem were more case-sensitive, whereas applying the cyclic steady state required lower computational efforts. Overall, differences obtained with both parametrizations were not large. Therefore, for preliminary risk assessment and based on the data from this industrial scenario, particle emission rates calculated with the cyclic steady state equation may be sufficient, whereas for a more case-specific analysis the convolution theorem may be a better approach for emission rate calculation.

![Figure 4](image-url)

**Figure 4.** Vertical box plot for RMSLE modeled/measured concentrations for booth#1 and booth#3 model areas using convolution SN (a) and Cyclic steady state SN (b). Ratio 0.5 and 2 are marked as reference (dashed line). The boundary of the box closest to zero indicates the 25th percentile and the farthest from zero the 75th percentile. The solid red line within the box indicates the median value. Error bars above and below indicate the 10th and 90th percentiles.

Finally, model performance was also evaluated with regard to the type of particles emitted, which were different in the two scenarios given that different thermal spraying techniques were used (APS in booth #1, and HVOF in booth #3). In short, particles emitted in booth #1 were mostly spherical and resulting from melting of the ceramic powder sprayed, while particles emitted in booth #3 showed more irregular morphologies resulting from mechanical impaction of the powder on the surface to be coated [7]. Modeling results for both scenarios showed only slight differences (Figure 4), which did not seem to be linked to the spraying techniques (APS and HVOF) but rather to the layout and configuration of the study area (Figure 1). In the booth #1 model area the door was always kept in a similar position (partially closed). Conversely, in the booth #3 model area, due to requirements of the spraying process the worker had to enter and exit the booth frequently, which means that the door configuration and the number of times that it was open and closed was different in every shift. The door configuration not only impacts particle transport, but also air flows (ACH). The impact of this can be clearly observed in Day 3 (Figure 2), where markedly higher concentrations were recorded in the WA during the morning (when the door was open) than in the afternoon (door closed),
while emissions at the source remained at relatively constant levels. Given that particle emission rates were calculated for full days, this intra-daily variability is considered a source of the higher variability in modeled/measured ratios (Figure 3) and RMLSE (Figure 4) observed for booth #3 (in comparison with booth #1). This result indicates that, to improve model performance, not only emission rates but also the ACH need to be calculated as precisely as possible, given that small variations can lead to significant under- or overestimations of particle concentrations and, thus, can limit the effectiveness of risk assessments and lead to impaired decision-making.

An example of the variability of model outcomes is reported in Supplementary material (Table S3 and S4), using a different door configuration (door fully open). The estimated ACH values from measured air speeds when booths doors were open ranged between 49–89 h$^{-1}$, which is approximately double than the ACH (25–35 h$^{-1}$) estimated when booths doors were closed. Modeled/measured concentrations ratios using ACH 49–89 h$^{-1}$ ranged between 0.1–0.4, indicating higher underestimations of measured concentrations than when using ACH 25–35 h$^{-1}$ (when ratios ranged between 0.2–0.7, Table 2). As door configurations and worker layout were not always constant, especially in booth #3 where the time during which the door was open/closed was different in every repetition, estimated ACH values used for the modeling (25–35 h$^{-1}$) may not be fully representative of actual ACH values for each specific repetition. In such cases, were ACH may be highly variable with time, a probabilistic approach or a sensitivity analysis as the one conducted in Ribalta et al., 2019 [33] would be highly useful.

According to the literature, mass balance models have been satisfactorily tested in real-world settings mostly in terms of particle mass [39,59–62] with ratios modeled/measured of 0.82–1.22 and 1.10 ± 2.32 during packing and pouring processes [32,33], and for vapors and sprays with ratios of 0.49–3.29 and 0.32–3.28 for chemical component emissions [30,63]. However, models have not been extensively tested for particle number concentrations, which is currently the most commonly-used metric for NP exposure, in real-work environments. In Jensen et al. [35,36], one-, two- and three-box models were tested for particle number concentrations from a brush generator in a controlled chamber experiment, with models being able to estimate concentrations within a RMSLE factor of 0.5–2 [36].

In the present work, ratios for modeled concentration were 0.2–0.7 and RMSLE 0.4–1.7, with the model clearly underestimating actual exposures. It may thus be concluded that the one-box model can provide a preliminary idea of the order of magnitude of unintentional NP concentrations, and that the accuracy of the results depends on the input parameters like ACH and particle emission rates. Therefore, the availability of a publicly-shared emission-rate library for modeling would be highly useful for preliminary risk assessments in absence of measured emission rates or particle concentrations. However, more precise modeling results require accurate quantification of the input parameters, implying that additional work in model parametrization is necessary. Model underestimations, even when ratios are within the 0.5–2 benchmark, are undesirable from a risk assessment point of view, where overestimating concentrations would be more precautionary.

4. Conclusions

An industrial scenario characterized by high concentrations of unintentionally-released NPs was selected to test the performance of a one-box mass balance model. Emission rates in terms of particle number concentration, one of the main inputs of the model, were estimated using two approaches: the convolution theorem and the cyclic steady state equation. The main conclusions extracted are:

- Nanoparticle emission rates from thermal spraying of ceramic coatings were from the booth to working area (WA) in the range $1.4 \times 10^{11}$–$1.4 \times 10^{13}$ min$^{-1}$. These emission rates are slightly higher or of a similar order of magnitude as those reported in the literature from sources such as industrial dip-coating, laser printing or even indoor cooking in homes.
- Both approaches for emission rate calculation provided comparable rates, which were slightly lower when the convolution theorem was used. The cyclic steady state approach required lower computational efforts.
• The one-box model underestimated concentrations measured in the WA irrespective of the method used for emission-rate calculation. The ratios modeled/measured concentrations were 0.2–0.7 (using the convolution theorem) and 0.2–0.5 (using the cyclic steady state equations). When correcting high concentrations by using the root mean squared logarithmic error (RMSLE), ratios were 0.4–1.4 (convolution) and 0.7–1.7 (cyclic steady state).

• Even though both model parametrizations showed similar performance on average, the use of emission rates calculated with the convolution theorem improved results on a case by case basis (results were more case-sensitive). Thus, emission rates calculated with the cyclic steady state approach would be advisable for preliminary risk assessment, while for more precise case-specific results, the convolution theorem would be the better option.

• An additional key input affecting model performance was seen to be the estimation of the air exchange per hour (ACH). This parameter was strongly impacted by the position of the door of the booth where emissions were generated, which should be taken into account carefully in modeling exercises.

• In sum, with adequate parametrization, one-box mass balance models may provide useful guidance regarding the order of magnitude of expected particle number concentrations in industrial scenarios, and thus be used as a preliminary risk assessment tools.

Supplementary Materials: The following are available online at http://www.mdpi.com/1660-4601/16/10/1695/s1, Figure S1: Booth #1, Day 1 a) shows particle number concentrations measured inside the booth by DiSCmini (DM), from worker area by NanoScan (WA) and particle emission rates solved by convolution from NanoScan WA concentrations, Figure S2: Booth #1, Day 2 a) shows particle number concentrations measured inside the booth by DiSCmini (DM), from worker area by NanoScan (WA) and particle emission rates solved by convolution from NanoScan WA concentrations, Figure S3: Booth #3, Day 4 a) shows particle number concentrations measured inside the booth by DiSCmini (DM), from worker area by NanoScan (WA) and particle emission rates solved by convolution from NanoScan WA concentrations, Table S1: Sampling day, booth, technic used (HVOF or APS), and feedstock materials summary, Table S2: Respirable mass concentration during the thermal spraying activity, Table S3: Parameterization of the single box model considering booth door open: V (m3) is volume used for modeling, Q (m3 h–1) is ventilation air volume flow through the Worker Area and ACH (h–1) is the air changes per hour calculated from measured air speeds, Table S4: One Box modeled concentrations considering booth door open, and using the convolution theorem and the cyclic steady state (Cyclic SS) approach to calculate emission rate (SN) from NanoScan data.


Funding: This research was funded by the Spanish MINECO (CGL2015-66777-C2–1-R, 2-R), and through project PCIN-2015–173-C02-01, under the frame of SIINN, the ERA-NET for a Safe Implementation of Innovative Nanoscience and Nanotechnology, by SIINN-ERANET project CERASAFE (id.:16). Additional support was provided by Generalitat de Catalunya AGAUR 2017 SGR41, the Spanish Ministry of the Environment (13CAES006), FEDER (European Regional Development Fund) “Una manera de hacer Europa”.

Acknowledgments: The authors acknowledge TM COMAS (http://www.tmcomas.com) for their committed cooperation.

Conflicts of Interest: The authors declare no conflict of interest relating to the material presented in this article.

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Discussion

Chapter 5
5. DISCUSSION

As presented in chapter 2, this Thesis sets out to address 5 objectives which are discussed in detail in this section by linking them to the key results and findings from this work. A summary of the objectives and how they were tackled is presented below and summarized in Figure 5.1. The specific results obtained, and their links to the objectives, are presented in the integrated discussion below.

1) To assess worker exposure in different real-world ceramic workplace scenarios in order to identify process parameters and material’s characteristics influencing particle emissions:

The impact of particle emissions on workplace exposure was assessed 1) at a pilot plant scale during mechanical handling of 5 ceramic materials (+2 additional materials described in section “4.1.1 Additional results”) with different particle characteristics and two energy levels (Publication I); and 2) at industrial scale during packing of a total of 8 materials and in 5 different packing lines (with different levels of enclosure and energy applied) (Publications II and III). Additionally, worker exposure was assessed in a thermal spraying industrial workshop where two spraying techniques were used (APS and HVOF) (Publication IV).

2) To evaluate decision making approaches (determination of statistically significant increases) and metrics to report worker exposure (mass, particle number concentrations and surface area):

The assessment of frequently used metrics to report worker exposure linking exposure to health effects was tackled in Publication II, a case study where a total of 7 materials were packed in 3 packing lines. Additionally, 4 decision-making approaches were evaluated and compared for particle number and mass concentrations, in the same case study.

3) To study materials dustiness as a tool for worker exposure prediction:

The potential of the dustiness index as a tool for exposure prediction was investigated by correlating dustiness indexes with exposure concentrations in two case scenarios: a pilot plant where 5 ceramic materials (+2 materials in section “4.1.1 Additional results”) were handled (Publication I), and an industrial plant where 7 materials were processed in 3 packing lines (Publication II). In addition, the relevance of the dustiness index as an
input parameter for the one- and two-box mass-balance models (1 material in 2 packing lines) was also evaluated (Publication III).

4) To evaluate mass-balance models (one- and two-box models) as worker exposure prediction tools under real-world settings:

One- and two-box mass-balance models were tested in two different scenarios, with low concentrations of coarse particles generated during mechanical handling of a granulated powder (Publication III), and with high NP concentrations emitted by a thermal spraying process (Publication IV).
5) To evaluate tools for health risk assessment such as the inhalation deposition dose ICRP model, and risk assessment and control banding tools:

Three risk assessment tools (ART, Stoffenmanager, NanoSafer), including one based on control banding (NanoSafer), were applied to two case studies where a total of 8 materials were packed in 5 different packing lines (Publications II and III). The models were also applied to the remaining case studies and the results are presented in sections 4.2.1 and 4.3.1 (“Additional results”). In addition, the ICRP inhalation deposition model was applied to the same case studies (Publications II and III).

5.1. Exposure assessment and particle emissions

Ceramic industry workplace exposure was assessed in a pilot plant and in 3 industrial settings, during handling or packing of 15 different types of powdered materials (Table 5.1; Publications I, II and III), and during a thermal process (thermal spraying).

Table 5.1 Summary of all materials subjected to mechanical handling, and their characteristics (particle shape, \(d_{50}\), and dustiness index and classification). C.D: Continuous drop. R.D: Rotating drum.

<table>
<thead>
<tr>
<th>Paper No</th>
<th>Material</th>
<th>Particle shape</th>
<th>Particle Size ((d_{50} \text{ } \mu m))</th>
<th>Dustiness, Inhalable fraction ((W_i))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Index (mg kg(^{-1}))</td>
<td>Classification</td>
</tr>
<tr>
<td>I</td>
<td>Si sand</td>
<td>Spherical</td>
<td>120</td>
<td>463</td>
</tr>
<tr>
<td></td>
<td>Quartz 1.1</td>
<td>Spherical</td>
<td>12.1</td>
<td>4593</td>
</tr>
<tr>
<td></td>
<td>Quartz 1.2</td>
<td>Spherical</td>
<td>5.8</td>
<td>3855</td>
</tr>
<tr>
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<td>Quartz 1.3</td>
<td>Spherical</td>
<td>3.4</td>
<td>3029</td>
</tr>
<tr>
<td></td>
<td>Kaolin 1.1</td>
<td>Plate-like</td>
<td>5.7</td>
<td>10012</td>
</tr>
<tr>
<td></td>
<td>Clay 1.1</td>
<td>Plate-like</td>
<td>2.7</td>
<td>16811</td>
</tr>
<tr>
<td></td>
<td>Clay 1.2</td>
<td>Plate-like</td>
<td>5.0</td>
<td>20139</td>
</tr>
<tr>
<td>II</td>
<td>Clay 2.1</td>
<td>Plate-like</td>
<td>13</td>
<td>1733</td>
</tr>
<tr>
<td></td>
<td>Clay 2.2</td>
<td>Plate-like</td>
<td>10</td>
<td>5170</td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.1</td>
<td>Plate-like</td>
<td>13</td>
<td>18886</td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.1</td>
<td>Spherical</td>
<td>31-39</td>
<td>10246</td>
</tr>
<tr>
<td></td>
<td>Quartz 2.1</td>
<td>Spherical</td>
<td>30-38</td>
<td>8891</td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.2</td>
<td>Spherical</td>
<td>22</td>
<td>9651</td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.2</td>
<td>Plate-like</td>
<td>8</td>
<td>12325</td>
</tr>
<tr>
<td>III</td>
<td>Fertilizer</td>
<td>Granulate</td>
<td>n/a</td>
<td>1026</td>
</tr>
</tbody>
</table>

- 160 -
Results showed that handling of powdered materials (d_{50} 2.7-39 \mu m) increased inhalable and respirable particle mass concentrations significantly with regard to background concentrations, resulting in potential worker exposure risks (Publications I, II and III). In the same way, thermal spraying significantly increased respirable mass concentrations (Publication IV). OEL were, however, not exceeded. Conversely, concentrations in terms of particle number did in general not show statistically significant increases with regard to background concentrations, during the mechanical activities assessed in this Thesis (handling and packing of powders, ceramic materials and fertilizers) (Publications I, II and III). Statistically significant increases in particle number concentrations resulting in impacts on worker exposure were also detected in the mechanical activities assessed, but they were linked in most cases to NP emissions from parallel activities such as driving of diesel-powered forklifts or cleaning and vacuuming activities, as well as due to outdoor air infiltration (Publications I, II and III). Conversely, thermal spraying was seen to significantly impact particle number concentrations exceeding the nano-reference recommended limit value (40000 cm^{-3}) (Publication IV). As will be further discussed below, these results evidence the need to implement different particle monitoring strategies in workplace settings, given the variety of potential particle emission sources which results in a broad variety of particle characteristics and potential metrics (e.g., particle number and mass concentrations).

On average, mean inhalable particle mass concentrations monitored in the workplaces where mechanical handling was assessed ranged between 80 and 4000 \mu g m^{-3}, and were the highest for packing of ceramic materials in line where low mitigation strategies were applied (Table 5.2) (Publication II). Respirable mass concentrations showed similar tendency as inhalable mass concentrations, and ranged between 17 and 598 \mu g m^{-3} for mechanical handling (Figure 5.2 and Table 5.2). Conversely, particle number concentrations monitored were on average closer to urban background and traffic site concentrations in Europe (e.g., 1.5-3.0x10^4 cm^{-3}, Reche et al. 2011) than in the case of particle mass. As discussed above, this is linked to the smaller number of ultrafine particle or NP sources in the industrial scenarios assessed (with the exception of the thermal spraying plant). The highest mean particle number concentrations were recorded while handling of the inorganic fertilizer (7x10^4 cm^{-3}) and during thermal spraying with concentrations reaching averages of 10^6 and 10^5 cm^{-3} in booths and worker area, respectively (Figure 5.3 and Table 5.2) (Publication III and IV). For the thermal process, respirable mass concentrations ranged between 90-160 and 130-700 \mu g m^{-3} in
the worker area and inside the booths, respectively (Publication IV). Finally, mean particle diameters within the monitoring range of the portable SMPS NanoScan (20-420 nm) and MiniWras (10 nm-35 μm) ranged between 40 and 90 nm (Figure 5.4 and Table 5.2), while for most of the materials it was approximately 30-50 nm which was attributed to infiltration of ambient air urban ultrafine particles.

**Figure 5.2** Bar plot for mean respirable mass concentrations measured for each case and material. Respirable mass concentrations were monitored with the Grimm mini-LAS.

Particle mass concentration was therefore identified as the most relevant metric for the scenarios assessed in this Thesis. At a fine temporal resolution, mass concentrations showed a cyclic behaviour, with major increases, which exceeded the 8h occupational exposure limits during short periods of time coinciding with each repetition of the specific activity under study. Major particle releases were also detected during accidents (Publication I and II). Particle mass concentrations usually showed relatively fast decreases to background levels after cessation of the activity, as opposed to particle number concentrations which progressively accumulated over time (Publication I). The impact of such short-term high particle mass concentrations would be undetected if only 8h TWAs were monitored and potentially significant impacts on worker’s health would be under-reported. Therefore, this work highlights that time-resolved monitoring of particle metrics, at least particle mass and number concentrations, is essential. In addition, these results also support the conclusions by Koponen et al. (2015), who pointed out the need to consider the number of repetitions as a critical issue in worker
exposure assessment given that cycles are usually marked by a peak concentration at the beginning. Similar cyclic patterns were observed in the scenarios assessed in this Thesis.

**Mean Particle Number Concentration**

![Bar plot for mean particle number concentrations measured for each material and case. Particle number concentration was monitored with the CPC except for publication III where NanoScan SMPS was used. Dashed line indicates the nano-reference value for particle number.](image)

**Figure 5.3** Bar plot for mean particle number concentrations measured for each material and case. Particle number concentration was monitored with the CPC except for publication III where NanoScan SMPS was used. Dashed line indicates the nano-reference value for particle number.

**Mean Particle Size**

![Bar plot for mean particle size measured for each case and material. Particle size was monitored with the NanoScan SMPS except for publication II where MiniWras was used.](image)

**Figure 5.4** Bar plot for mean particle size measured for each case and material. Particle size was monitored with the NanoScan SMPS except for publication II where MiniWras was used.
Table 5.2 Summary of measured airborne particle concentrations. "Case": for Publication I, this refers to low and high energy settings; for Publication II, this refers to low, medium and high mitigation strategies applied along the packing line. *: device with asterisk was used (NanoScan, MiniWras). Concentrations given are for worker area measurements.

<table>
<thead>
<tr>
<th>Paper N°</th>
<th>Material /Process</th>
<th>Case</th>
<th>Particle number (cm³)</th>
<th>Particle size (nm)</th>
<th>Particle mass (Grimm mini-LAS) (μg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CPC *NanoScan</td>
<td>NanoScan *MiniWras</td>
<td>Respirable</td>
</tr>
<tr>
<td>I</td>
<td>Si sand</td>
<td>Low</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>40498</td>
<td>43.4</td>
<td>39.1</td>
</tr>
<tr>
<td></td>
<td>Quartz 1.1</td>
<td>Low</td>
<td>30310</td>
<td>53.4</td>
<td>70.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>28059</td>
<td>53.4</td>
<td>48.0</td>
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<tr>
<td></td>
<td>Quartz 1.2</td>
<td>Low</td>
<td>15033</td>
<td>54.2</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>23091</td>
<td>47.2</td>
<td>29.3</td>
</tr>
<tr>
<td></td>
<td>Quartz 1.3</td>
<td>Low</td>
<td>21756</td>
<td>55.0</td>
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</tr>
<tr>
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<td></td>
<td>High</td>
<td>34214</td>
<td>46.4</td>
<td>37.9</td>
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<td></td>
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<td>24002</td>
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<tr>
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<td></td>
<td>High</td>
<td>20880</td>
<td>44.1</td>
<td>87.4</td>
</tr>
<tr>
<td></td>
<td>Clay 1.1</td>
<td>Low</td>
<td>16156</td>
<td>57.7</td>
<td>156.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>12944</td>
<td>53.9</td>
<td>232.2</td>
</tr>
<tr>
<td></td>
<td>Clay 1.2</td>
<td>Low</td>
<td>11374</td>
<td>78.2</td>
<td>301.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>9163</td>
<td>71.2</td>
<td>295.8</td>
</tr>
<tr>
<td>II</td>
<td>Clay 2.1</td>
<td>Low</td>
<td>36216</td>
<td>*53.5</td>
<td>157.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>41448</td>
<td>*83.5</td>
<td>425.5</td>
</tr>
<tr>
<td></td>
<td>Clay 2.2</td>
<td>Low</td>
<td>35530</td>
<td>*82.5</td>
<td>137.0</td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.1</td>
<td>Low</td>
<td>39464</td>
<td>*82.7</td>
<td>322.0</td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.1</td>
<td>Medium</td>
<td>35713</td>
<td>*78.5</td>
<td>181.0</td>
</tr>
<tr>
<td></td>
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<td>Medium</td>
<td>39464</td>
<td>*82.7</td>
<td>322.0</td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.2</td>
<td>High</td>
<td>31263</td>
<td>*92.0</td>
<td>495.0</td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.2</td>
<td>High</td>
<td>61250</td>
<td>*71.5</td>
<td>95.0</td>
</tr>
<tr>
<td>III</td>
<td>Fertilizer</td>
<td>Small bags</td>
<td>*72123</td>
<td>45.1</td>
<td>298.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Big bags</td>
<td>*68120</td>
<td>52.0</td>
<td>598.0</td>
</tr>
<tr>
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<td>APS</td>
<td>Booth #1</td>
<td>60000</td>
<td>40.0</td>
<td>152.0</td>
</tr>
<tr>
<td></td>
<td>HVOF</td>
<td>Booth #3</td>
<td>200000</td>
<td>39.6</td>
<td>135.5</td>
</tr>
</tbody>
</table>

On the other hand, the relevance of monitoring particle metrics in the worker breathing zone was identified. This is not only necessary to accurately determine worker exposure,
but also to obtain key information about the activity, materials and particle emissions generated. For example, in the packing line with low mitigation strategies (Publication II), where low dustiness materials were usually packed, the gravimetrically-determined respirable mass concentrations monitored were similar in the breathing zone and in the worker area (monitored 1.5-2 m away from the worker). Conversely, in the packing line with medium mitigation strategies, where materials being packed had higher dustiness levels, the respirable mass concentrations (also gravimetrically determined) in the breathing zone were higher than in the worker area, pointing out that workers were highly exposed specifically while closing the bag, when the extraction system was switched off. This piece of information, key in the design of measures to effectively reduce worker exposure, could only be obtained by simultaneously monitoring exposure concentrations in the breathing zone and in the worker area. Once again, this result evidences the value of carrying out experimental measurements of a wide variety of particle metrics, simultaneously in different locations, to achieve detailed and effective workplace exposure assessments which can in turn be used for efficient risk management as well as for model calibration and validation.

On the topic of exposure mitigation measures, several strategies were identified in the industrial environments assessed:

1) Source enclosure was evidenced to be an effective mitigation strategy in the workplaces and for the activities assessed, given that a clear inverse relationship was observed between exposure concentrations and degree of enclosure during packing of ceramic materials (Publication II). This was also observed in Publication IV, where particle number concentrations in the worker area during thermal spraying were significantly lower when the door connecting the booth and worker area was closed, compared to when it was partially open. This result is especially relevant due to the fact that it refers to particle number (not mass) concentrations. The results from this work show that, for the scenarios assessed, physical enclosures such as sliding doors or degree of isolation of the source are effective tools to reduce exposures to both particle number and mass concentrations, at a relatively low cost.

2) Modifying energy settings was seen to constitute another potentially effective mitigation strategy, for the mechanical activities assessed (handling and packing of powders and ceramic materials). For example, during handling of materials at high energy in a pilot plant (Publication I) particle emissions were from 26% up to 37%
higher than when handling was carried out with low energy. The subsequent reduction in particle exposures was thus significant. However, the feasibility of operating at lower energy and/or the increased industrial cost resulting from the longer time required for processing of the materials at lower energy should be considered and quantified.

3) Finally, results evidenced that particle morphology may significantly influence the resulting particle emissions during handling of raw materials (Publication 1). When considering materials with similar primary particle diameter (e.g., Kaolin 1.1, 5.7 \( \mu m \); Clay 1, 2.7 \( \mu m \); Quartz 1.2, 5.8 \( \mu m \); and Quartz 1.3, 3.4 \( \mu m \)), handling of plate-like materials (e.g., Clays) resulted in significantly higher workplace exposure concentrations in terms of particle mass when compared to mostly spherical particles materials (e.g., Quartz) (Figure 5.5) (Publication 1). In addition, plate-like materials dustiness was also generally higher than for spherical materials (Table 5.1). Thus, particle shape was pointed out as a factor to be considered when planning effective measures to reduce worker exposure. In this regard, when plate-like materials are handled, high effective measures should be implemented to adequately protect workers from exposure. As a limitation, it must be noted that particle monitoring instruments are calibrated based on spherical particles, and thus their performance when challenged with plate-like particles may decrease and this may have influenced the data collected and the conclusions extracted in this work.

![Inhalable particle mass concentration: Publication 1](image)

**Figure 5.5** Bar plot for mean inhalable mass concentrations measured for spherical (ca. spherical) and plate-like shaped materials in Publications 1. Inhalable mass concentrations were monitored with the Grimm mini-LAS.
5.2. Metrics and tools for exposure assessment

5.2.1. Metrics for exposure assessment

One major topic of discussion in exposure monitoring is the selection of the most adequate metrics to report exposure concentrations. In this PhD Thesis, particle number and mass (respirable and inhalable fractions) concentrations were monitored in different scenarios where micro- and NPs were emitted. When monitoring exposures to micron-sized particles due to mechanical handling, usually no significant increases in particle number concentration were detected due to the activity under study. However, monitoring particle number concentrations together with electron microscope (TEM and SEM) coupled with EDX helps to identify, through particle size and chemical composition analysis, the influence of other emission sources (e.g. parallel activities, or outdoor infiltration) which affected particle number concentrations (Publications I, II and III). Conversely, when monitoring high NP concentrations such as in the thermal spraying scenario, particle emissions were seen to affect both particle number and mass concentrations, specifically the respirable mass fraction (Publication IV). One key result was the observation by using electron microscope imagery that NPs may form aggregates, which can potentially affect particle mass concentrations, and as a result particle mass may also be an efficient metric even in scenarios where NPs are the dominant particle type (Publication I, II and III). Thus, considering the results obtained, simultaneous monitoring of particle number and mass concentrations should be encouraged for exposure assessment together with the use of microscope images and EDX technic, which were seen to be key to correctly identify sources, processes and external outdoor influence.

5.2.2. Statistical significance of particle impacts on exposure

Once particle emission impacts on exposure concentrations are detected, it is necessary to quantify their statistical significance to assess their relevance with regard to worker exposure and health risk. The nanoGEM approach (Asbach et al. 2012) has been widely used in research projects and industrial settings due to its simplicity and reliability, and it focuses on particle number concentrations. The need for a comparable approach to be applied to particle mass was identified in this work, and therefore a number of methods was tested for particle emissions in 7 packing cases (Publication II): 1) nanoGEM (Asbach et al. 2012); 2) the ARIMA models (proposed as “golden standard” by EN
nanoGEM approach proved useful for particle mass concentrations, although it was seen to underestimate the statistical significance in some of the cases when compared to traditional statistical tests results. Thus, the use of the nanoGEM approach for particle mass concentrations could be encouraged considering its limitations. The nanoGEM approach usefulness for particle number concentrations was confirmed. The ARIMA model was seen to be the least conservative when compared to the traditional statistical tests and the nanoGEM approach, and it was the most complex to apply as it requires specific expert statistical knowledge. Thus, the design of a user-friendly and specific approach tailored to particle mass concentrations would be advisable, possibly based on the nanoGEM strategy.

5.3. Dustiness as an exposure prediction tool

Discussions regarding the use of the dustiness index as a tool for exposure prediction are ongoing (Evans et al. 2013, Levin et al. 2014, Dubey et al. 2017), given that some authors found correlations with exposure (Heitbrink et al. 1989, Breum et al. 2003, Brouwer et al. 2006) whereas others did not (Heitbrink et al. 1990, Class et al. 2001, Fonseca et al. 2018). Therefore, studying which parameters affect this correlation is paramount in order to establish the potential of dustiness as an exposure prediction tool. In this PhD Thesis the correlation between dustiness and exposure during mechanical handling processes was studied at pilot plant (Publication I) and industrial scale (Publication II).

High degrees of correlation were found between dustiness and exposure concentrations during mechanical handling in a pilot plant ($R^2 = 0.77-0.97$; Publication I) and during packing at industrial scale ($R^2 = 0.27-0.80$; Publication II). Thus, the results from this work point out dustiness as a useful tool for exposure prediction. However, certain limitations were brought to light:

1) Dustiness-exposure correlations were seen to be stronger when the characteristics of the materials dominated over process characteristics. This refers, for example, to the influence of mitigation strategies: at industrial scale, a high correlation dustiness-exposure was found for a packing line with low mitigation strategies ($R^2 = 0.80$), whereas no correlation was identified for packing lines with
medium and high levels of mitigation ($R^2 = 0.27$) (Publication II). This may explain the apparent contradictory results reported in the literature regarding dustiness correlation with exposure. Thus, for industrial activities where the main driver of exposure was the material being handled/packed, high correlations between dustiness and exposure concentrations were obtained and therefore, in these scenarios the dustiness index may be considered a useful tool for exposure prediction. In addition, dustiness can be used as a preliminary assessment tool to estimate whether mitigation strategies will be needed or not.

2) **Particle morphology plays a role in modifying dustiness.** The analysis of the different types of materials tested evidenced that Clays (plate-like shaped primary particles) were outliers in the correlation plots between dustiness and exposure concentrations, when compared with relatively spherical particles (Publication I). In addition, it was found that the highest exposure concentrations and dustiness indexes were measured for materials with very different specific surface area (SSA) values [e.g. Kaolin (K1) and Quartz (Q1), 9.6 and 1.4 m$^2$ g$^{-1}$, respectively] and different particle shapes (e.g. platy Kaolin and spherical Quartz) (Publication I), although when comparing different Quartzes and Kaolin samples separately, good correlations between dustiness and SSA were found (López-Lilao et al. 2015, 2016). This confirms the difficulty to establish a general relationship between dustiness and the physical-chemical properties of materials, as well as the need to assess the links between dustiness and exposure differentiating by material characteristics or groups. Instrumental limitations should also be considered (i.e., instrument performance when challenged with non-spherical particles). Further research is necessary in this direction.

3) **The selection of the dustiness method was found to be essential for material characterization, especially if dustiness is to be used as input parameter in models.** The highest correlation between dustiness and exposure concentrations during mechanical handling in a pilot plant (where material suffered rotation) was obtained for the R.D method, with the high energy setting ($R^2 = 0.99$) (Publication I, Additional results “section 4.1.1”). Conversely, when the C.D method was used for the same purpose, the correlation was slightly weaker (Publication I). This indicates that dustiness is a better predictor of exposure when using the dustiness method which mimics the actual activity being assessed better. This may also be an explanation to the apparent contradictory results reported in literature regarding the ability of dustiness to predict...
worker exposure. In addition, although a strong correlation between the two available methods (C.D and R.D) was found when considering the inhalable fraction ($R^2 = 0.78$), which was previously reported in Evans et al. (2017) for the R.D and the venturi test, dustiness classifications in categories when using one or another method are not always comparable (Table 5.1). Specifically, materials are usually categorized as having a lower level of dustiness when using the R.D compared to the C.D.

Considering the results obtained, it may be concluded that dustiness could be considered a promising tool for worker exposure prediction in industrial settings such as the ones assessed in this work, as long as certain factors are taken into consideration: the selection of the dustiness method, the physical characteristics of the materials tested, and influence of process characteristics (e.g., enclosure) which might prevail over material properties as determinants of exposure in workplace settings.

Finally, the use of dustiness as input for mass-balance models was assessed in Publication III. The results obtained are presented and discussed in the following section.

5.4. Mass-balance models performance

One- and two-box mass-balance models were applied to two real-world scenarios with the aim to test their efficacy for different industrial environments. The two scenarios under study were 1) a mechanical process (packing of a fertilizer in small and big bags) where low concentrations of mainly coarse particles were emitted (Publication III); and 2) a thermal spraying process (APS and HVOF) where high concentrations of unintentionally-released NP were monitored (Publication IV).

For the mechanical process, the one- and the two-box models predicted mass concentrations within a ratio modelled/measured between 0.82 and 1.22 for all four study cases. Typically, a benchmark of 0.5-2.0 is considered for this kind of models (Jayjock et al. 2011). While both models provided relatively accurate results, the two-box model showed a slightly better performance when the layout of the industrial scenario resembled more closely a two-box model (Publication III). For the thermal spraying scenario, where only the one-box approach was tested, the model underestimated the particle number concentrations monitored (ratios ranging 0.2-0.7, and RMSLE ratios
0.4-1.7; \textit{Publication IV}). Even though these ratios fall within the 0.5-2.0 benchmark in 13/14 of the cases, it may be concluded that the performance of the one-box model was poorer for the high particle concentration (\textit{Publication IV}) than for the low particle concentration (\textit{Publication III}) scenario. The causes for these differences are various and linked not only to the concentrations monitored, but also to the input particle data and the characterization of the airflows inside each of the industrial plants. This evidences the difficulties of particle modelling in real-world industrial scenarios, and the need for experimental measurements to validate modelling approaches.

The addition of outdoor and background concentrations to the models increased modelling precision and overall performance, which is a step-forward in mass-balance model application in real-scenarios (\textit{Publication III} and \textit{Publication IV}). Therefore, correctly monitoring and assessing outdoor and background concentrations is essential, as they can have an impact on worker exposure which needs to be contemplated during the application and evaluation of models.

After assessing the performance of the mass-balance models under high and low concentrations, and in terms of particle number and mass concentrations, it may be concluded that both the one- (even with its simplifications) and the two-box models may be useful tools for exposure assessment in industrial settings. However, modelling results are highly dependent on the parametrization, which is still sometimes not fully understood and for which experimental data are frequently lacking. Thus, a discussion on two of the most relevant parameters (particle emission rates and air flow characterization), as well as their implications regarding model performance, was developed in \textit{Publication III} and \textit{IV}, and is summarized below.

\subsection*{5.4.1. Dustiness and measurement-based particle emission rates}

Three different methods were evaluated to quantify particle emission rates: dustiness-based, measurement-based convolution theorem, and measurement based cyclic steady state equation.

For mechanical processes in which powdered materials are handled, emission rates can be calculated by using the material’s dustiness index as input parameter. While Koivisto \textit{et al.} (2015) showed that this method has certain weaknesses, in this PhD Thesis good modelling predictions were obtained when using dustiness to calculate emission rate (\textit{Publication III}). One limitation (see 5.3) was the need to include an energy factor (H)
to transpose the energy applied during the dustiness test to the energy applied during the process under study. This \( H \) parameter is not yet parametrized and gives rise to different interpretations which will also depend on the dustiness method used. Therefore, for a correct and standardized application of dustiness in mass-balance models, the most urgent need regarding calculation dustiness-based emission rates identified in Publication III is to establish guidelines which specify 1) which dustiness test should be used for each type of industrial activity; and 2) \( H \) values depending on the energy applied in the process, which could be calculated by using calibration dustiness-exposure curves for specific types of processes and groups of materials, according to what was discussed in section 5.3.

When emissions cannot be estimated based on the dustiness index (e.g. process-generated or unintentionally-released NP) emission rates must be estimated based on experimentally-monitored particle concentrations. Here, two methods with different degrees of complexity were assessed: the convolution theorem and the cyclic steady state equation (Publication IV). Although emission rates obtained with both methods were comparable, using the convolution theorem improved modelling results on a case by case basis, providing more case-sensitive modelling results. Therefore, although both provided acceptable modelling results, using the cyclic steady state equation would be advisable for preliminary exposure assessment whereas for more precise and case-specific results the convolution theorem would be better option. In sum, even though the calculation of emission rates using dustiness (Publication III) and particle monitoring (with convolution theorem or cyclic steady state, Publication IV) present some limitations and their parametrization still needs improvements, they provided acceptable modelling results which justify their use.

5.4.2. Air flow parametrization

Air flow characterization (general air exchange rate, AER, and NF-FF air flow (\( \beta \))) was paramount to obtain accurate modelling results. In the setting assessed in Publication III the NF-FF \( \beta \) values were unknown, and thus literature values were used with the support of a sensitivity analysis. The selection of the NF-FF \( \beta \) values impacted modelling results strongly for the small bags scenario, with ratios (modelled/measured) varying broadly from 0.68 using the lowest \( \beta \) and up to 1.89 using the highest \( \beta \). In Publication IV, ratios (modelled/measured) presented a narrower range 0.18-0.67 when using experimentally measured air speeds. These results evidenced that, to achieve good
model performance, air flows (incoming and internal flows) should be calculated or estimated as precisely as possible, given that small variations can lead to significant under- or overestimations of particle concentrations (Publication III and IV) and thus to impaired decision-making limiting the effectiveness of mass-balance models as exposure and risk assessment tools.

As a final conclusion regarding parametrization, literature data for particle emission rates and air flows were proved useful for modelling. Thus, reporting experimental data from exposure studies to publicly-accessible databases or libraries would be highly beneficial for modelling usability and expansion.

### 5.5. Risk assessment tools performance

Exposure assessment is at times not sufficient for decision making, and health risk assessment is required. However, there are yet not enough studies assessing the toxicology, exposure and health impacts of particles or of aerosol mixtures of micron-sized particles and NPs. As a result, several relatively user-friendly tools have been developed. In this PhD Thesis two types of tools were tested: an inhalation deposition model (ICRP model), and three risk assessment and control banding based tools (ART, Stoffenmanager and NanoSafer).

#### 5.5.1. ICRP Inhalation deposition model

The ICRP deposition model, which requires as input experimentally-monitored particle size distributions, provides information regarding the regions in the respiratory tract where inhaled particles would deposit, irrespective of their chemical composition. As a result, an evaluation of the potential respiratory health risk can be conducted depending on how deep particles reach in the respiratory tract. In this Thesis, the ICRP model was applied for exposures monitored during packing of 7 ceramic materials (Publication II) and 1 inorganic fertilizer (Publication III) (Table 5.3). Particles emitted during packing of ceramic materials (packing lines with low, medium and high mitigation strategies; Publication II), deposited mainly in the head-airways 27-41%, with deposition increases when compared with background regional surface area deposition of 2-23%. Surface area deposition on tracheobronchial and alveolar regions were 7-10% and 51-64%, respectively, suffering decreases during packing when compared to background
deposition in the same regions of 1-5% and 1-18%, respectively. Similarly, during big bags packing of the inorganic fertilizer (Publication III), even though main deposition was again the alveolar region 52-62% due to forklifts activity influence, particles deposition increased in the head airways by 8% and decreased in the alveolar region by 7%. Thus, reduced effects on health due to packing emitted particles may be expected when comparing with case studies dominated by alveolar deposition, as in the case of the small bags packing of the inorganic fertilizer, where deposited particles during packing increased when compared to background deposition in the alveolar region by up to a 3% and decreased in head airways and trachea bronchial regions by up to 2% and 5%, respectively. Similarly, during thermal spraying, emitted particles were seen to deposit mainly in the alveolar region with 54-70% considering surface area (Salmatonidis et al. 2019) with an increased tracheobronchial deposition when compared to the other types of particles assessed (7-15%, Table 5.3). However, it should be noted that such models do not consider particle morphology or chemistry which can have an impact on health-respiratory disease.

Table 5.3 Calculated dose rates in surface area, and regional deposition in percentages on head airways, trachea bronchi and alveolar for cases in Publication II, III and in Salmatonidis et al. 2019.* values not published.

<table>
<thead>
<tr>
<th>Paper Nº</th>
<th>Material</th>
<th>Case</th>
<th>Deposited Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total [μm² min⁻¹]</td>
</tr>
<tr>
<td>II</td>
<td>Clay 2.1</td>
<td>Low</td>
<td>9.7x10⁵</td>
</tr>
<tr>
<td></td>
<td>Clay 2.2</td>
<td>Low</td>
<td>6.7x10⁵</td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.1</td>
<td>Low</td>
<td>1.2x10⁶</td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.1</td>
<td>Medium</td>
<td>1.1x10⁶</td>
</tr>
<tr>
<td></td>
<td>Quartz 2.1</td>
<td>Medium</td>
<td>5.4x10⁵</td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.2</td>
<td>High</td>
<td>8.6x10⁵</td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.2</td>
<td>High</td>
<td>9.0x10⁵</td>
</tr>
<tr>
<td>III</td>
<td>Fertilizer</td>
<td>Small bags</td>
<td>4.3-6.0x10⁵</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Big bags</td>
<td>3.3-7.6 x10⁶</td>
</tr>
<tr>
<td></td>
<td>APS*</td>
<td>Booth #1</td>
<td>3.9x10⁵</td>
</tr>
<tr>
<td></td>
<td>HVOF</td>
<td>Booth #3</td>
<td>3.6.3x10⁵</td>
</tr>
</tbody>
</table>

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Particle deposition in the respiratory tract was studied in terms of particle number, mass and surface area. Absolute values and percentages were different for each metric, but results regarding the region in which emitted particles deposited were similar regardless of the metric used. Particle surface area was the metric which represented particle deposition in the respiratory tract in a more balanced and consistent way. The use of such models, which are relatively easy to use and only require knowledge on particle size distribution, is encouraged during exposure assessment as their outcomes provide risk information useful for decision making.

5.5.2. Risk assessment and control banding tools

Risk assessment and control banding based tools are designed to help users to estimate health risks due to exposure to airborne particles (Tielemans et al. 2008a, Kristensen et al. 2010, Fransman et al. 2011, ECHA 2016). They are mainly used in the framework of risk assessment of chemical hazards under the REACH regulation by private-sector industries. In this Thesis, two risk assessment tools (ART, Stoffenmanager) and one risk assessment tool based on control banding (NanoSafer) were applied to test their performance and usability on case studies of industrial packing of 7 ceramic materials (Publication II) and 1 inorganic fertilizer (Publication III). As discussed in previous sections, it should be noted that the NanoSafer tool was originally designed to assess risks from NP exposures, not from micron-sized particles, and therefore the cases presented in this work are not the ideal target for this tool, which is still under testing and calibration processes.

The two risk assessment tools (ART and Stoffenmanager) generally overestimated (ratio modelled/measured > 1) the experimentally-measured exposures (ART Bayesian, by 82% and Stoffenmanager, by 64%) although in some occasions underestimations (ratio modelled/measured < 1) were also detected (Stoffenmanager, 36%, and ART Mechanistic model, 73%). No clear pattern was detected. When compared with the 0.5-2.0 benchmark, the results from the ART Mechanistic and Bayesian models were within the benchmark in 27% of the cases, while the results from Stoffenmanager matched the benchmark in 64% of the cases assessed. The control banding tool NanoSafer (designed for nanomaterials assessment) overestimated monitored exposure respirable mass concentration for all the ceramic materials within a factor 13-120 and 1.1-38 when NF and FF modelled concentrations were considered, respectively (Publication II). Conversely, for the fertilizer packing NanoSafer NF concentrations overestimated monitored
concentrations by a factor 1.1 up to 6.8. In sum, results evidenced a better performance of Stoffenmanager for the cases assessed (mechanical handling of powders; packing) (Table 5.4), even though a pattern to understand the causes of the under or overestimations of the model was not identified.

**Table 5.4** Ratio of modelled/measured concentrations considering ART (C.D based), Stoffenmanager and NanoSafer model outputs, and 8h TWA values. Acceptable ratio limits (0.5-2.0; benchmark by Jayjock *et al.* 2011). Bold and green: within the limits. Red: overestimation. Yellow: underestimation. Calculations were made by considering C.D dustiness index.

<table>
<thead>
<tr>
<th>Paper No</th>
<th>Material</th>
<th>ART Mechanistic</th>
<th>ART Bayesian</th>
<th>Stoffenmanager</th>
<th>NanoSafer NF-FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>Clay 2.1</td>
<td>0.2</td>
<td>1.5</td>
<td>1.9</td>
<td>13-1.1</td>
</tr>
<tr>
<td></td>
<td>Clay 2.2</td>
<td>4.2</td>
<td>6.0</td>
<td>2.9</td>
<td>42-3.5</td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.1</td>
<td>1.2</td>
<td>2.7</td>
<td>1.9</td>
<td>75-6.3</td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.1</td>
<td>0.9</td>
<td>2.4</td>
<td>2.6</td>
<td>74-6.2</td>
</tr>
<tr>
<td></td>
<td>Quartz 2.1</td>
<td>0.7</td>
<td>2.6</td>
<td>1.6</td>
<td>97-8.1</td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.2</td>
<td>0.6</td>
<td>1.5</td>
<td>0.3</td>
<td>120-38</td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.2</td>
<td>1.7</td>
<td>5.2</td>
<td>0.8</td>
<td>64-20</td>
</tr>
<tr>
<td>III</td>
<td>Small Bags 1</td>
<td>&lt; 0.01</td>
<td>0.1</td>
<td>0.5</td>
<td>1.2-0.02</td>
</tr>
<tr>
<td></td>
<td>Small Bags 2</td>
<td>&lt; 0.01</td>
<td>0.1</td>
<td>0.5</td>
<td>1.8-0.03</td>
</tr>
<tr>
<td></td>
<td>Big Bags 1</td>
<td>0.3</td>
<td>1.8</td>
<td>1.2</td>
<td>6.8-1.1</td>
</tr>
<tr>
<td></td>
<td>Big Bags 2</td>
<td>0.4</td>
<td>2.1</td>
<td>1.4</td>
<td>6.7-1.1</td>
</tr>
</tbody>
</table>

The results from Stoffenmanager were relatively more stable for the same industrial process but different material, whereas the ART and NanoSafer models provided different results. For example, for Clay 2.1, Clay 2.2 and Kaolin 2.1, which are materials packed in the same line, ART and NanoSafer results ranged from an acceptable range, to over- and underestimations. Conversely, ART and NanoSafer are more versatile as they provide the user with the option to introduce a dustiness index value or level, as opposed to Stoffenmanager, which only has the option to introduce the type of material. In NanoSafer, health and safety and nano-specifications have high influence in the resulting scores, which are later transposed to estimated concentrations (section 3.6.2). In ART, what seems to have more importance were material-related inputs. The models usually
require a dustiness index or level, but it is not possible to differentiate between the different dustiness methods used. As shown in section 5.3, dustiness classification and correlation with exposure is different when using one or another dustiness test. This has implications regarding the energy factor needed to translate dustiness to exposure (section 5.4), which is also dependent on the dustiness method used.

In order to assess the relevance of the selection of the method to quantify dustiness (C.D or R.D), the ART models (mechanistic and Bayesian) were applied using both types of dustiness calculations, with the results shown in Table 5.5. R.D based ART Bayesian estimated concentrations were within the 0.5–2.0 benchmark by 46% whereas C.D based ART Bayesian only by 27%. However, C.D based ART Bayesian overestimated monitored exposures by 82%, from which overestimations with a ratio > 3 represent a 64%, while R.D ART Bayesian underestimated exposures with the same percentage (82%), which is considered detrimental for modelling. Thus, highly different estimated exposure concentrations results were obtained when using C.D or R.D dustiness indexes, pointing out the need to use the dustiness test which best represents the activity object of study.

Table 5.5 Ratio of modelled/measured concentrations considering ART (C.D based) and ART (R.D based) model outputs, and 8h TWA values. Acceptable ratio limits (0.5–2.0; benchmark by Jayjock et al. 2011). Bold and green: within the limits. Red: overestimation. Yellow: underestimation.

<table>
<thead>
<tr>
<th>Paper No</th>
<th>Material</th>
<th>Ratio modelled/measured</th>
<th>ART Bayesian (C.D dustiness)</th>
<th>ART Bayesian (R.D dustiness)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>Clay 2.1</td>
<td>1.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Clay 2.2</td>
<td>6.0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.1</td>
<td>2.7</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.1</td>
<td>2.4</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Quartz 2.1</td>
<td>2.6</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feldspar 2.2</td>
<td>1.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kaolin 2.2</td>
<td>5.2</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Small Bags 1</td>
<td>0.1</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Small Bags 2</td>
<td>0.1</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Big Bags 1</td>
<td>1.8</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Big Bags 2</td>
<td>2.1</td>
<td>0.65</td>
<td></td>
</tr>
</tbody>
</table>
In general, a lack of harmonization between risk assessment tools was evidenced through this work, regarding input parameters (e.g., dustiness method) and types of outputs (exposure concentrations vs. scores). This is in agreement with other authors who pointed out a lack of comparability between tools (Liguori et al. 2016, Sánchez Jiménez et al. 2016), as well as transparency in some cases (Koivisto et al. 2018), which limit a more wider-spread application of these tools. For example, NanoSafer is the only tool which considers cyclic processes, while room volume and air exchange values cannot be entered as specific measured values (only default drop down values) in ART or Stoffenmanager. As discussed above, these parameters were experimentally seen to be major determinants of worker exposure. In addition, even though tools were designed to be used by non-experts possibly in private-sector industries, expert criteria are required during the selection of certain of the options, and slight differences between processes are difficult to introduce in the models. As a result, and based on this work, it may be concluded that there is a clear need for evaluation, calibration and harmonization of risk assessment tools, especially when they are applied to real-world industrial settings.
Chapter 6

Conclusions
6. CONCLUSIONS

This PhD Thesis addresses worker exposure to airborne particles emitted during industrial and semi-industrial (pilot plant) activities (mechanical handling and thermal processes) in the ceramic sector. It aims to contribute to the harmonization of exposure assessment (in terms of metrics and decision making), the evaluation of dustiness as an exposure prediction tool, and the performance understanding of mass-balance models and risk assessment tools. The main conclusions extracted from this work are presented following the same structure as the Objectives and Discussion chapters.

Exposure assessment and particle emissions

- Mechanical handling of ceramic materials at pilot-plant and industrial-scale significantly impacted worker exposure in terms of particle mass; therefore these activities should always be performed under control to minimise particle emissions and avoid exceeding current occupational limits, set out for mass concentrations.

- Thermal processes (thermal spraying and diesel engines) significantly increased particle exposures in terms of particle number and mass concentrations and in some cases exceeded the nano-reference values.

- Modifying the degree of source enclosure (engineering control measure) and the energy applied to the process (process modification) were identified as effective strategies to reduce worker exposure. Nevertheless, in existing industrial scenarios the application of process modifications is usually limited or not feasible due to technical reasons, and thus they should be implemented during the process design phase.

- Packing of ceramic materials using low mitigation strategies was identified as the process assessed in this Thesis with the highest impact on worker exposure in terms of mass. However, monitored mass concentrations did not exceed the established Spanish OEL values, and were even lower than 50% of the OEL. Thus, the need for a revision of current OELs was identified as they do not promote the application of mitigation strategies when workers are exposed to high particle mass concentrations.
Chapter 6. Conclusions

Metrics and tools for exposure assessment

- Simultaneously monitoring of particle number and mass concentrations when assessing worker exposure should be encouraged regardless of the case study and the type and size of particles expected (nano/coarse), since in scenarios where only micron-sized particles where expected, significant nano-sized particle concentrations in terms of number were also monitored, and vice versa. This highlights the fact that, in industrial settings, the main process is frequently not the only emission source, and the influence of external or secondary sources may have major implications on exposure.

- For regulatory purposes, exposure to particle mass concentrations is currently evaluated by comparison with OEL values. In this work, OEL values were not exceeded in any case even though high particle mass increases were detected. For these increases (e.g., exposure impacts not exceeding OELs, or having shorter duration) the need for a specific mass-tailored and user-friendly approach to identify statistically significant increases was identified. Such an approach would be comparable to the one already available for particle number concentrations.

Dustiness as a predictor tool

High correlation was found between the dustiness index and exposure concentrations in several exposure scenarios, indicating that dustiness could be a promising tool for worker exposure prediction and even for mass-balance models and risk assessment tools application. However, this correlation is not straightforward and several limitations were identified:

- The correlation was stronger when considering only materials with similar characteristics (e.g., primary particle shape). Other particle parameters such as surface area (SSA) or primary particle size ($d_{50}$) were not seen to have a clear influence on the correlation between dustiness and exposure.

- The correlation between dustiness and exposure was stronger when materials characteristics dominated over process characteristics. It has been observed that, in industrial scenarios, engineering controls (e.g., enclosure, or local exhaust ventilation) are stronger determinants of exposure than the material's dustiness, hence their parametrization is paramount to wider the application of the dustiness index.
Each dustiness method selected provides different classification levels for the same materials. In addition, better correlation dustiness-exposure was obtained when the dustiness method applied was similar to actual process under study. Therefore, the method used to calculate the dustiness index should always be reported and adequately selected.

Mass-balance models

The one- and two-box models tested showed good performance for low mass concentrations and high particle number concentrations. Therefore, for scenarios comparable to those assessed in this PhD Thesis, box models could be recommended as tools for exposure assessment. The two-box model showed higher accuracy than one-box model when the layout of the modelled area was similar to that of a standard two-box model.

- The performance of the one- and two-box models resulted in higher accuracy when including outdoor and background concentrations in the model domain, especially when clear impacts of outdoor infiltration and parallel processes were detected.
- When estimating emission rates based on the dustiness index, an urgent need to establish and harmonize guidelines to select the appropriate dustiness method and to estimate the handling energy factor (H) was identified.
- Emission rates estimated from measurements (using the convolution theorem and the cyclic steady state equation) provided good modelling results. Using convolution theorem-based emission rates showed higher case-sensitive modelling results, and thus this option should be preferred when higher precision modelling is required, especially in time-variable emission sources. Conversely, cyclic steady state-based rates would be better option for preliminary exposure assessments and for modelling constant continuous or constant discontinuous emission sources, due to the lower computational efforts required.
- The application of the mass-balance models requires accurate air flowrate data. In this regard the experimental determination of air flowrates should be preferred to the application of theoretical values, despite the great experimental difficulties encountered in some real-world industrial scenarios to its experimental determination.
• The usefulness of libraries reporting values regarding dustiness indexes, energy factors, emission rates and local control efficacy among others, for modelling, was highlighted, due to the complexity of measuring many of these parameters in real-world scenarios.

Risk assessment

• The ICRP inhalation deposition model was a useful and user-friendly tool to provide information regarding health risk assessment, as it provided particle regional deposition values which can be transposed to respiratory health risks and requires only particle size distribution as input.

• From all the tools tested (ART, Stoffenmanager and NanoSafer), Stoffenmanager provided the most precise prediction of airborne concentrations emitted during mechanical handling (industrial packing) of ceramic materials and fertilizers. However, ART and NanoSafer were more versatile tools with more options to customise the assessments. The results from NanoSafer were not directly comparable as this model was developed for nanoparticle risk assessment. In spite of providing useful information for implementing mitigation measures, the results obtained in this work show that these risk assessment tools should currently be considered as semiquantitative models in term of exposure prediction.

• The dustiness index seems to be the parameter with the largest impact on concentrations modelled with ART. Nevertheless, the method used to determine the dustiness index should be clearly specified in risk assessment analyses, as very different results are obtained as a function of the method (rotating drum or continuous drop).

• A lack of harmonization between tools, and therefore limitations in comparability, were detected. Inputs and outputs are different between tools, which limits comparability. In addition, different tools which are recommended by the ECHA provide, for the same case study, very different results and conclusions regarding exposure risks. Therefore, these tools should be carefully used, and their parametrization reported, to ensure the adequate interpretation of their output results. Another potential use would be to assess expected risk reductions derived from introducing mitigation strategies and work guidelines in workplaces.
7. Limitations and future research

From the results obtained in this PhD Thesis, several open questions and gaps have been identified which require further research:

- A general limitation encountered in exposure assessment studies is that the calibration of monitoring instruments is based on spherical particles, and thus their performance when challenged with non-spherical particles may vary, ultimately influencing the results and conclusions extracted. Additional tests at laboratory-scale and industrial facilities should be carried out to further the understanding of instruments performance when monitoring non-spherical or even fibrous particles.

- Even though some light was provided in this PhD Thesis regarding the use of dustiness as an exposure prediction tool, still difficulties remain regarding the relationship between dustiness and the physic-chemical properties of materials, as well as regarding the links between dustiness and exposure differentiating by material characteristics or groups. Therefore, dustiness still needs to be further studied and understood to be widely used for exposure assessment purposes. The extension of this work to nano-powders, currently underway, will make a very relevant contribution to this field of research.

- The energy factor (H), needed to transpose dustiness energy to the activity under study, requires definition and standardization in order to be widely used for exposure modelling.

- One- and two-box mass-balance models proved to be useful for exposure modelling. However, experimental data (particle monitoring in real-world scenarios) is still necessary for model validation. Furthermore, models are not yet at a stage where they can be widely applied in industrial settings, as they require detailed expert knowledge and experimentally determined particle concentrations for model calibration.

- The performance of mass-balance models and risk assessment tools was evaluated in this PhD Thesis using the benchmark proposed by Jayjock et al. (2011). The accuracy for these tools should be further assessed, and harmonised if the tools are meant to be used in industrial settings for comparable exposure and risk assessment. This would need to be carried out for different particle metrics, at least particle number and mass concentrations.
- Specifically for the case of risk assessment and control banding tools, a clear need for evaluation, calibration and harmonization of tools was identified, as different tools, which are proposed by the ECHA, provided different outcomes for the same case scenarios, leading to different conclusions, especially if they are not properly used.

- The need for a user-friendly decision making approach to statistically significant impacts on exposure in terms of particle mass was identified.

- Certain of the potential mitigation strategies identified in this PhD Thesis involve process modifications, and thus their application in industrial scenarios is limited. Implementation of mitigation strategies to reduce worker exposure should preferably be introduced during the process design phase, in order to include exposure considerations in the design. This is currently not the case in some European regions, in contrast to environmental considerations, which must be included as per current regulations. For example, modifying process energy was identified as a potential mitigation strategy. However, the increased industrial cost resulting from the longer time required for processing of the materials at lower energy should be evaluated and quantified. Therefore, the use of modelling tools to simulate worker exposure to micron- and nano-sized particles in industrial processes design should be fostered.
Chapter 8

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ANNEX A. GLOSSARY, ACRONYMS AND SYMBOLS

Glossary

Background (BG) and pre-activity: it refers to temporal background concentrations usually measured before and/or after the process of study.

Breathing zone (BZ): measurements next to worker at height of the nose and mouth of the worker.

Coarse particles: particles > 2.5 μm.

Control banding: approach based on “computational” hazard and exposure for the control of workplace exposure.

Dustiness: measure of the tendency of a powdered material to release particles in response to a mechanical or aerodynamic stimulus.

d50: median diameter (50th percentile).

dlaser: diameter of a sphere of same diameter as the cross-sectional area of the particle μm.

dstockes: diameter of a sphere of same diameter as the cross-sectional projection area of the particle μm.

Emission rate: amount of particles (mass or particle number) released by a process per unit of time.

Fine particles: particles between 0.1 and 2.5 μm.

Indoor: refers to spatial background concentrations measured during the process at a point where process particles do not affect measurements but at the same times representative of the space where the process is taking place.

Inhalable: mass fraction of total airborne particles which is inhaled through the nose and mouth. It has 100% penetration for small particles (< 10 μm), dropping to 50% for 100 μm particles and has no median cut-off aerodynamic diameter.

Alveolar macrophages: specialized cells of the immune system (located in the lung alveoli) involved in detection, phagocytosis and destruction of anything that does not have the type of proteins specific to healthy body cells on its surface (e.g. cellular debris, small particles, bacteria or cancer cells). They initiate inflammation by releasing cytokines (molecules that activate other cells).

Mass-balance models: models based on a set of mass balance equations including information of the source (contaminant generation), particle transport, deposition and coagulation.

NanoGEM approach:
Mean concentration > BG ± 3 · (σBG); described in Asbach et al., 2012.

Nanomaterial: natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm.

Nanoparticles (NP): particles < 100 nm according to nanotechnology field classification.

Nucleation: particle formation from gaseous precursors.

Outdoor: refers to measurements conducted outdoors next to the industrial unit entrance through which outdoor infiltration occur.

PM10: describes inhalable particles, with diameters that are generally 10 μm and smaller.
**PM$_{2.5}$:**  particulate matter with diameters generally 2.5 μm and smaller.

**Respirable:** mass fraction of inhaled particles penetrating to the unciliated airways with a median aerodynamic diameter of 4.25 μm and 1.5 GSD.

**Risk assessment tools:** empirical models, based on dimensionless exposure modifying factors to calculate an exposure score which is further converted to an exposure value by using calibration factors.

**Silicosis:** occupational illness which is a form of pneumoconiosis (fibrogenic lung disease) caused by inhalation of crystalline silica dust, and is marked by inflammation and scarring in forms of nodular lesions in the upper lobes of the lungs.

**Thoracic:** mass fraction of inhaled particles penetrating beyond the larynx. The curve has a median diameter of 11.64 μm and geometric standard deviation (GSD) of 1.5.

**Tiered approach:** assessment strategy for the determination of exposure to nanoparticles in workplaces which consists of several hierarchical tiers.

**UFP:** Ultrafine particles; particles < 100 nm according to aerosol research field classification.

**Worker Area (WA):** measurements on a similar distance and position similar to where the worker is standing. The location can be considered representative of worker exposure but not be considered strictly breathing zone.
Acronyms

**ACGIH:** American Conference of Governmental Industrial Hygienists

**ACH:** Air Changes per Hour

**AER:** Air Exchange Ratio

**Ag:** Silver

**Al₂O₃:** Aluminium oxide

**APS:** Atmospheric Plasma Spraying

**AR:** Aspect Ratio

**ARIMA:** Autoregressive Integrated Moving Average

**ART:** the Advanced Reach Tool

**Au:** Gold

**BAuA:** Bundesanstalt für Arbeitsschutz und Arbeitsmedizin “Federal Institute for Occupational Safety and Health”

**BET:** Brunauer–Emmett–Teller theory

**BG:** Background

**BZ:** Breathing zone

**CCOHS:** Canadian Centre for Occupational Health and Safety

**C.D.:** Continuous Drop dustiness

**CEN:** European Committee for Standardization

**CPC:** Condensation Particle Counter

**CNT:** Carbon nanotubes

**DiSCmini:** Diffusion Size Classifier miniature

**DNEL:** Derived No-Effect Level

**DMA:** Differential Mobility Analyser

**ECH:** European Chemical Agency

**EDX:** Energy Dispersive X-ray

**EEA:** European Environmental Agency

**EN:** European Norm

**ENP:** Engineered Nanoparticles

**ER:** Emission Rate

**FF:** Far-Field

**GSD:** Geometrical Standard Deviation

**Grimm mini-LAS:** Grimm mini Laser Aerosol Spectrometer

**H:** Energy factor

**HEPA:** High Efficiency Particulate Filter

**HR:** Hausner Ratio

**H₂SO₄:** Sulfuric acid

**HVOF:** High Velocity Oxy-Fuel coating spraying

**ICRP:** International Commission on Radiological Protection

**IFA:** Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung “Institute for Occupational Safety and Health of the German Social Accident Insurance”

**IGF:** Institut für Gefahrstoff-Forschung “Institute for the Research on Hazardous Substances”

**INSHT:** Instituto Nacional de Seguridad e Higiene en el Trabajo

**ISO:** International Organization for Standardization

**ITC:** Instituto de Tecnología Cerámica “Institute of Ceramic Technology”

**LC:** Local Controls
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDSA</td>
<td>Lung Deposited Surface Area</td>
</tr>
<tr>
<td>LEV</td>
<td>Local Exhaust Ventilation</td>
</tr>
<tr>
<td>MAK</td>
<td>Maximum workplace concentrations</td>
</tr>
<tr>
<td>MNs</td>
<td>Manufactured Nanomaterials</td>
</tr>
<tr>
<td>NF</td>
<td>Near-Field</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
</tr>
<tr>
<td>NIOSH</td>
<td>National Institute for Occupational Safety and Health</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Nitrogen Oxides</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>NRCWE</td>
<td>National Research Center for the Working Environment</td>
</tr>
<tr>
<td>NRV</td>
<td>Nano-Reference Values</td>
</tr>
<tr>
<td>OECD</td>
<td>Organisation for Economic Co-operation and Development</td>
</tr>
<tr>
<td>OEL</td>
<td>Occupational Exposure Limits</td>
</tr>
<tr>
<td>OPC</td>
<td>Optical Particle Counter</td>
</tr>
<tr>
<td>OPS</td>
<td>Optical particle Sizer</td>
</tr>
<tr>
<td>PEL</td>
<td>Permissible Exposure Limits</td>
</tr>
<tr>
<td>PGNP</td>
<td>process-generated nanoparticles</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>PPE</td>
<td>Personal Protection Equipment</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle Size Distribution</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td>RCS</td>
<td>Respirable Crystalline Silica</td>
</tr>
<tr>
<td>R.D</td>
<td>Rotating Drum dustiness</td>
</tr>
<tr>
<td>REACH</td>
<td>Registration, Evaluation, Authorization and Restriction of Chemicals</td>
</tr>
<tr>
<td>REL</td>
<td>Recommended Exposure Limit</td>
</tr>
<tr>
<td>RMSLE</td>
<td>Root Mean Squared Logarithmic Error</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SER</td>
<td>Social Economic Council of the Netherlands</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>SMPS</td>
<td>Scanning Mobility Particle Sizer</td>
</tr>
<tr>
<td>SSA</td>
<td>Specific Surface Area</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TLV</td>
<td>Threshold Limit Values</td>
</tr>
<tr>
<td>TNO</td>
<td>Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek “Netherlands Organisation for Applied Scientific Research”</td>
</tr>
<tr>
<td>TSP</td>
<td>Total Suspended Particles</td>
</tr>
<tr>
<td>UFP</td>
<td>Ultrafine particles</td>
</tr>
<tr>
<td>UNE</td>
<td>Una Norma Española</td>
</tr>
<tr>
<td>US-OSHA</td>
<td>United States - Occupational Safety and Health Administration</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>WA</td>
<td>Worker Area</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>Wᵢ</td>
<td>Dustiness inhalable fraction</td>
</tr>
<tr>
<td>Wᵣ</td>
<td>Dustiness respirable fraction</td>
</tr>
<tr>
<td>8h TWA</td>
<td>8-hours' time weighted average</td>
</tr>
</tbody>
</table>
Symbols in equations

\( \text{ACH} \): Air changes per hour (h\(^{-1}\))

\( \text{C}_\text{e} \): concentration during a specific operation

\( \text{C}_\text{i} \): initial and incoming concentration (N: cm\(^{-3}\) or M: \(\mu\)g m\(^{-3}\))

\( \text{C}_\text{nf} \): near field concentrations (N: cm\(^{-3}\) or M: \(\mu\)g m\(^{-3}\))

\( \text{C}_\text{ff} \): far field concentrations (N: cm\(^{-3}\) or M: \(\mu\)g m\(^{-3}\))

\( \bar{C} \): mean concentration (cm\(^{-3}\))

\( \text{Cc} \): slip correction factor

\( \text{Db} \): mobility diameter

\( \text{D}_\text{r} \): respirable or inhalable dustiness index of a material (mg kg\(^{-1}\) or particles kg\(^{-1}\))

\( \frac{dM}{dt} \): mass flow of the process (kg min\(^{-1}\))

\( \text{H} \): handling energy factor (-)

\( \text{LC} \): protection factor of localized controls (-)

\( \text{M} \): mass concentration (\(\mu\)g m\(^{-3}\)).

\( \text{N} \): number concentration (cm\(^{-3}\)).

\( \text{N}_\text{bg} \): background particle concentration

\( \text{Q} \): flow (m\(^3\) h\(^{-1}\))

\( \text{Q}_\text{LC} \): local control flow (m\(^3\) h\(^{-1}\))

\( \text{S and S}_{\text{Na}} \): Emission source or emission rate in particle concentration per time unit (mg or particles min\(^{-1}\))

\( s \): air speed (m s\(^{-1}\))

\( \text{SSA} \): specific surface area of the nanomaterial (m\(^2\) g\(^{-1}\))

\( t \): time (usually min)

\( \text{V} \): volume (m\(^3\))

\( \text{V}_\text{nf} \): near-field volume (m\(^3\))

\( \text{V}_\text{ff} \): far-field volume (m\(^3\))

\( d\): diameter

\( \beta \): flow rate between near-field and far-field (m\(^3\) min\(^{-1}\))

\( \gamma \): total particle decay rate (min\(^{-1}\))

\( \delta \): scattering parameter for air (0.905)

\( \delta_{\text{nano}} \): specific density of the nanomaterial (g cm\(^{-3}\))

\( \varepsilon_{\text{c}} \): protection factor due to enclosure (-)

\( \lambda \): ventilation rate (min\(^{-1}\))

\( \lambda_{\text{air}} \): mean free path for air (0.066 \(\mu\)m)

\( \rho_{\text{eff}} \): effective density (g cm\(^{-3}\))

\( \sigma \): standard deviation
Supplementary Materials

Annex B
ANNEX B. Supplementary materials

1. Supporting Information Publication I: On the relationship between exposure to particles and dustiness during handling of powders in industrial settings

Figure S1 Micrographs of the original materials. (a) Q2 and (b) K1.

Method

Rotating drum

1. Inlet
2. Dust generation section (drum)
3. Dust collection
4. Foams and filter

Continuous drop

1. Sample tank
2. Metering device
3. Drop pipe
4. Sampling head for the respirable aerosol fraction
5. Sampling head the inhalable aerosol fraction

Figure S2 Pictures and description of the dustiness methods used, rotating drum and continuous drop.
Figure S3 Time series of PM$_{2.5}$ in terms of µg/m$^3$ monitored with Grimm on the worker area and the outdoor measurement points for the materials S1, Q1, Q2, Q3 and K1. Note that the Y axis is in log scale. Worker Area is represented in red and outdoor in green. Background and activity periods are divided with a dotted black line.
Figure S4 Time series of particle number concentration (monitored with CPC) and inhalable mass fraction in log scale (monitored with Grimm) for S1, Q1, Q2 and K1 materials. Background, exhaust, cleaning and handling repetitions for low and high energy settings are marked with colour bars at the bottom of the each graph (green, black, blue and red respectively). The three first red lines correspond to low energy settings and the last three ones to the high energy settings.

Potential mitigation strategies – Case study

The general room air extraction system was tested as a potential mitigation measure. Particle number and mass concentrations were then monitored. The extraction system was used three of the four days of the sampling campaign during approximately one hour during midday, when no other processes were ongoing. Figures 2 and S3 show that during when the air extraction system of the room was ON there was reduction of the inhalable mass fraction (coarse particles) as well as the respirable fraction. Other studies such as Cena and Peters, (2011); Douwes et al. (2017) and Jensen et al. (2015) also pointed out the relevance of the exhaust ventilation system on the removal of particles, although they used a local exhaust system. Contrarily, ultrafine particle concentrations during the time when the room air extraction system was ON did not decrease, and they even
increased during one day (when Q1 material was assessed, Figure 2 and Figure S1). Mean and maximum particle number concentrations during the time when room extraction system was ON were 42686 and 51461 #/cm$^3$, respectively. Figure S1 shows the particle size distribution in the worker area for materials S1 and Q1. In both cases the highest concentrations for particles in the range 20 – 50 nm were reached during the time when the air extraction system was ON. For the first day (10/10/2016 – S1 material) the increasing trend in nanoparticles concentration started minutes before the extraction system was switched ON, while for the second day (11/10/2016 – Q1) the increase in nanoparticles concentration was produced during the air extraction system period. The particle size range monitored, from 20 to 50 nm, points to outdoor road traffic emissions as the source of these particles, as this is the typical size range of these emissions (Brines et al., 2015) and the main door of the plant was open all the time during the tests. Therefore, the air extraction system showed a clear decrease in coarse particle concentrations, but did not favour ultrafine particle reduction.

Figure S5 Particle size distribution (particle range from 10 to 420 nm) measured with the NanoScan for two of the sampling days 10/10/2016 and 11/10/2016, corresponding to materials S1 and Q1 respectively. Extraction system periods are marked with a white line under. Note that the particle number concentration colour scale is different for each graph.
Figure S6 EDX spectrum analysis for TEM images presented in figure 7. EDX images correspond a) to 7a; b) to 7b and 7c; c) to 7d; d) to 7e; e) to 7f; f) to 7g; g) to 7h; h) to 7i; i) to 7j; j) to 7k; k) to 7l; l) to 7m; m) to 7n; n) to 7o.

Table S1 Materials chemical composition. Note: sand chemical composition was proportioned by the supplier.

<table>
<thead>
<tr>
<th>Material</th>
<th>S1</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>K1</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI 1050°C</td>
<td>NDA</td>
<td>0.3</td>
<td>0.63</td>
<td>0.40</td>
<td>12.8</td>
</tr>
<tr>
<td>SiO₂</td>
<td>32</td>
<td>99</td>
<td>98.4</td>
<td>99.6</td>
<td>49.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>NDA</td>
<td>0.60</td>
<td>0.80</td>
<td>0.02</td>
<td>36.7</td>
</tr>
<tr>
<td>TiO₂</td>
<td>NDA</td>
<td>0.03</td>
<td>0.06</td>
<td>0.01</td>
<td>0.11</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>NDA</td>
<td>0.03</td>
<td>0.04</td>
<td>0.01</td>
<td>0.42</td>
</tr>
<tr>
<td>CaO</td>
<td>NDA</td>
<td>0.08</td>
<td>0.09</td>
<td>0.01</td>
<td>0.11</td>
</tr>
<tr>
<td>MgO</td>
<td>NDA</td>
<td>0.01</td>
<td>0.02</td>
<td>&lt; 0.01</td>
<td>0.09</td>
</tr>
<tr>
<td>K₂O</td>
<td>NDA</td>
<td>0.1</td>
<td>0.07</td>
<td>0.01</td>
<td>0.59</td>
</tr>
<tr>
<td>Na₂O</td>
<td>NDA</td>
<td>0.01</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>65</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
**Table S2** TWA results for all materials and for inhalable and respirable mass fractions. For each material, temporal background concentrations, handling under low energy settings and handling under high energy settings are used for the calculation. TWA xh (µg/m³): worker exposure during all the measurements period including temporal background, handling under low energy and under high energy settings. Note there are different sampling periods for each material. TWA 8h (µg/m³): worker exposure using the temporal background concentrations to complete the 8h TWA. Limit values: inhalable 10000 µg/m³ and respirable 3000 µg/m³. Equation used:

\[ TWA = \frac{t_1c_1 + t_2c_2 + \ldots t_nc_n}{t_1 + t_2 + \ldots t_n} \]

where: \( c_n \) is the mean concentration during a specific operation and \( t_n \) is the time of the specific operation.

<table>
<thead>
<tr>
<th>Material</th>
<th>S1</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>K1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TWA_{xh}</strong> / TWA_{8h}</td>
<td>TWA_{2.5h}</td>
<td>TWA_{8h}</td>
<td>TWA_{4.1h}</td>
<td>TWA_{8h}</td>
<td>TWA_{3.5h}</td>
</tr>
<tr>
<td><strong>Inhalable fraction</strong></td>
<td>591.4</td>
<td>256.5</td>
<td>242.2</td>
<td>152.8</td>
<td>134.4</td>
</tr>
<tr>
<td><strong>Respirable fraction</strong></td>
<td>106.9</td>
<td>42.6</td>
<td>56.9</td>
<td>39.4</td>
<td>24.3</td>
</tr>
</tbody>
</table>
Table S3 Mean particle number and mass concentration (inhalable and respirable fraction) in the worker area during cleaning operations for each material and their respective background concentrations. Statistically significant differences found after applying the exposure > 3σ+BG are marked in bold.

<table>
<thead>
<tr>
<th>Material</th>
<th>Number concentration</th>
<th>Inhalable mass</th>
<th>Respirable mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Background Cleaning</td>
<td>Background Cleaning</td>
<td>Background Cleaning</td>
</tr>
<tr>
<td>SI</td>
<td>10620 (9179-16431)</td>
<td>9869 (7615-12995)</td>
<td>92.1 (14.6-1168.3)</td>
</tr>
<tr>
<td>Q1</td>
<td>42686 (25420-51461)</td>
<td>24176 (17865-35288)</td>
<td>39.6 (19.0-300.0)</td>
</tr>
<tr>
<td>Q2</td>
<td>29226 (16645-47210)</td>
<td>22153 (13591-81248)</td>
<td>15.2 (3.8-135.1)</td>
</tr>
<tr>
<td>Q3</td>
<td>33064 (24959-43430)</td>
<td>42131 (30647-64444)</td>
<td>34.1 (15.0-343.6)</td>
</tr>
<tr>
<td>K1</td>
<td>46421 (30470-53894)</td>
<td>31131 (15048-77386)</td>
<td>13.0 (5.8-34.7)</td>
</tr>
</tbody>
</table>
2. Supplementary material Publication II: Health risk assessment from exposure to particles during packing in working environments

Figure S1 Packing lines images.

Method

1. Sample tank
2. Metering device
3. Drop pipe
4. Sampling head for the respirable aerosol fraction
5. Sampling head the inhalable aerosol fraction

Figure S2 Pictures and description of the continuous drop dustiness method used for dustiness determination.
During packing of Clay 1, total particle number concentration measured with the CPC (34535-37898 cm$^{-3}$) was similar to pre-activity concentrations (42410±32660 cm$^{-3}$). The same was true for the respirable mass fraction (144-166 μg m$^{-3}$ during packing vs. 212±260 μg m$^{-3}$ during background). Contrarily, the inhalable mass fraction was higher (1370-1847 μg m$^{-3}$) than pre-activity concentrations (986±1000 μg m$^{-3}$) with increases between 384 and 861 μg m$^{-3}$ although they were not statistically significant. Clear peaks can be identified for each bag being packed which coincide approximately with the start of the pouring process. Breathing zone and worker area respirable dust concentrations were 101 μg m$^{-3}$ and 182 μg m$^{-3}$ respectively. Particle mean diameter (NanoScan) during packing was 50.8-55.9 nm.
Figure S4  Particle concentration at the WA during packing of Kaolin 1: (a) particle number concentration time series (CPC and DM; DiSCmini); (b) particle size distribution time series measured with the MiniWras, solid black line shows MiniWras $d_{50}$; (c) mass concentration time series measured by Grimm mini-LAS. Black vertical lines indicate start (solid line) and stop (dashed line) of the each batch.

During packing of Kaolin 1, total particle number concentration measured with the CPC (40565–42331 cm$^{-3}$) was significantly higher than pre-activity concentrations (15721±2185 cm$^{-3}$). Inhalable (2647–4705 μg m$^{-3}$) and respirable (242–609 μg m$^{-3}$) mass fractions were also significantly higher than pre-activity concentrations (92±114 and 18±9 μg m$^{-3}$ for inhalable and respirable mass fractions) with increases of 2554–4613 and 224–591 μg m$^{-3}$ for the inhalable and respirable fractions. Peaks of particles around 5 μm at the start of each bag being pack are easily recognizable which coincide with the action of manually place the pallet in the packing area. Breathing zone and worker area respirable dust concentrations were 36 μg m$^{-3}$ and 321 μg m$^{-3}$ respectively. Mean particle dimeter (MiniWras) during packing was 79.7-86.5 nm.
During packing of Quartz 1, total particle number concentration measured with the CPC suffered a statistically significant increase during packing of batch 2 (46670±17666 cm$^{-3}$) compared to pre-activity (23291±6988 cm$^{-3}$) contrarily to what happened during batch 3 in which particle number concentrations remained the same (24755±4862 cm$^{-3}$). No increases of respirable (153-209 μg m$^{-3}$) and inhalable (1150-1714 μg m$^{-3}$) particle mass were observed during packing compared to pre-activity concentrations (353±351 μg m$^{-3}$ for respirable and 3529±3324 μg m$^{-3}$ for inhalable) although peaks can be identified at the beginning of some bags being packed. The fact that not significant increases were detected is mostly because before the packing process, maintenance processes were carried out, and even though a period between maintenance processes and packing was left, was not enough for concentrations to stabilize. If we compare inhalable mass fraction in the WA and indoor, 1432 μg m$^{-3}$ in the WA vs. 851 μg m$^{-3}$ indoor clear influence in mass concentrations in the WA due to packing are detected.
Figure S6 Particle concentration at the WA during packing of Kaolin 2: (a) particle number concentration time series (CPC and DM; DiSCmini); (b) particle size distribution time series measured with the MiniWras, solid black line shows MiniWras $d_{50}$; (c) mass concentration time series measured by Grimm mini-LAS. Black vertical lines indicate start (solid line) and stop (dashed line) of each batch.

During packing of Kaolin 2 statistically significant increases of particle number concentration were monitored (54292-71996 cm$^{-3}$) when comparing with pre-activity concentrations (9567±7230 cm$^{-3}$). However, this increase was due to outdoor and indoor influences (diesel forklifts activity). No increases on particle mass concentrations were also observed.
Figure S7 SEM images from particles collected in the worker area during materials packing.
Table S1 Materials particle size distribution and chemical composition. PSD: particle size distribution. L.O.I: loss of ignition.

<table>
<thead>
<tr>
<th>Material</th>
<th>PSD</th>
<th>Chemical analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_{10}$ (μm)</td>
<td>$d_{50}$ (μm)</td>
</tr>
<tr>
<td>Clay 1</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>Feldspar 1</td>
<td>4-5</td>
<td>31-39</td>
</tr>
<tr>
<td>Quartz 1</td>
<td>4-5</td>
<td>30-38</td>
</tr>
<tr>
<td>Clay 2</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Kaolin 1</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>Feldspar 2</td>
<td>4</td>
<td>22</td>
</tr>
<tr>
<td>Kaolin 2</td>
<td>3</td>
<td>8</td>
</tr>
</tbody>
</table>

Table S2 Intercomparison results.*Low degree of agreements between CPC and MW is due to differences in the measurement ranges and technics.

<table>
<thead>
<tr>
<th>Number (CPC as Reference)</th>
<th>Mass Concentration (MiniWras as Reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
<td>2d-R$^2$</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>MD1</td>
<td>0.78</td>
</tr>
<tr>
<td>MD2</td>
<td>0.73</td>
</tr>
<tr>
<td>MD3</td>
<td>0.73</td>
</tr>
<tr>
<td>MD4</td>
<td>0.79</td>
</tr>
<tr>
<td>MW</td>
<td>0.41*</td>
</tr>
</tbody>
</table>
Table S3 Mean particle number concentrations (cm$^{-3}$), size (nm), lung deposited surface area (μm cm$^{-2}$) (DiSCmini) and mean inhalable, thoracic and respirable mass (μg m$^{-3}$) in the worker area, indoor and outdoor locations for each day. Means were calculated considering the two/three batches. WA: worker area. LDSA: lung deposited surface area.

<table>
<thead>
<tr>
<th>Sampling</th>
<th>DiSCmini</th>
<th>Mini-LAS (μg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N$_{tot}$ (cm$^{-3}$)</td>
<td>Size (nm)</td>
</tr>
<tr>
<td>Clay 1_L</td>
<td>WA</td>
<td>27564</td>
</tr>
<tr>
<td></td>
<td>Indoor</td>
<td>34189</td>
</tr>
<tr>
<td></td>
<td>Outdoor</td>
<td>40605</td>
</tr>
<tr>
<td>Feldspar 1_M</td>
<td>WA</td>
<td>40053</td>
</tr>
<tr>
<td></td>
<td>Indoor</td>
<td>50546</td>
</tr>
<tr>
<td></td>
<td>Outdoor</td>
<td>30776</td>
</tr>
<tr>
<td>Quartz 1_M</td>
<td>WA</td>
<td>29746</td>
</tr>
<tr>
<td></td>
<td>Indoor</td>
<td>33934</td>
</tr>
<tr>
<td></td>
<td>Outdoor</td>
<td>35961</td>
</tr>
<tr>
<td>Clay 2_L</td>
<td>WA</td>
<td>23558</td>
</tr>
<tr>
<td></td>
<td>Indoor</td>
<td>19113</td>
</tr>
<tr>
<td></td>
<td>Outdoor</td>
<td>28643</td>
</tr>
<tr>
<td>Kaolin 1_L</td>
<td>WA</td>
<td>48424</td>
</tr>
<tr>
<td></td>
<td>Indoor</td>
<td>35016</td>
</tr>
<tr>
<td></td>
<td>Outdoor</td>
<td>47618</td>
</tr>
<tr>
<td>Feldspar 2_H</td>
<td>WA</td>
<td>21784</td>
</tr>
<tr>
<td></td>
<td>Indoor</td>
<td>27615</td>
</tr>
<tr>
<td></td>
<td>Outdoor</td>
<td>25541</td>
</tr>
<tr>
<td>Kaolin 2_H</td>
<td>WA</td>
<td>81257</td>
</tr>
<tr>
<td></td>
<td>Indoor</td>
<td>68377</td>
</tr>
<tr>
<td></td>
<td>Outdoor</td>
<td>57085</td>
</tr>
</tbody>
</table>

Table S4 Quartz 1 respirable crystalline silica results for the dustiness test

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (μg)</th>
<th>RCS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Quartz</td>
</tr>
<tr>
<td>Filter 1</td>
<td>940</td>
<td>915</td>
</tr>
<tr>
<td>Filter 2</td>
<td>470</td>
<td>475</td>
</tr>
</tbody>
</table>
Annex A: ARIMA models analysis

ARIMA models analysis and its results are presented here. Only two cases of the ARIMA analysis performed are shown due to space reasons. One example of an ARIMA disagreeing with the other tests used (nanoGEM, t test and MW “U” test) and one agreeing is shown.

Case 1) Feldspar 2 inhalable fraction concentration.

ARIMA model used was (1,0,0)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Standard Error</th>
<th>t Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>642.86</td>
<td>4527.3</td>
<td>0.141996</td>
</tr>
<tr>
<td>AR(1)</td>
<td>0.773193</td>
<td>0.0155994</td>
<td>49.5651</td>
</tr>
<tr>
<td>Beta1</td>
<td>1881.05</td>
<td>4372.37</td>
<td>0.430214</td>
</tr>
<tr>
<td>Variance</td>
<td>7.47912e+06</td>
<td>152236</td>
<td>38.9059</td>
</tr>
</tbody>
</table>

Beta1 is < 1.95 therefore concentrations during process are not significantly higher than concentrations during pre-activity.
This result differs from the ones obtained by using the nanoGEM approach, the t test and the MW “U” test which conclude that concentrations during packing are significantly higher than pre-activity.

Case 2) Kaolin 1 inhalable fraction concentration.

ARIMA model used was (1,0,1)

Regression with ARIMA(1,0,1) Error Model:
Conditional Probability Distribution: Gaussian

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Standard Error</th>
<th>t Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-10</td>
<td>2016.28</td>
<td>-0.00495962</td>
</tr>
<tr>
<td>AR(1)</td>
<td>0.899713</td>
<td>0.106432</td>
<td>8.49399</td>
</tr>
<tr>
<td>MA(1)</td>
<td>-0.775286</td>
<td>0.156427</td>
<td>-4.97538</td>
</tr>
<tr>
<td>Beta1</td>
<td>3525.06</td>
<td>1541.25</td>
<td>2.28909</td>
</tr>
<tr>
<td>Variance</td>
<td>1.325955e+07</td>
<td>837807</td>
<td>15.8265</td>
</tr>
</tbody>
</table>

Beta1 is > 1.95 therefore concentrations during process are significantly higher than concentrations during pre-activity.
This result is in agreement with results obtained by using the nanoGEM approach, the \( t \) test and the MW “U” test which conclude that concentrations during packing are significantly higher than pre-activity.

Annex B: Web-based modelling tools output results

Web-based modelling tools reports are shown here. Only two cases for each tool are shown due to space reasons, one for packing line L and one for packing line M.

ART

a) Kaolin 1, Packing line L

<table>
<thead>
<tr>
<th>Details for Activity (untitled)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission sources:</td>
</tr>
<tr>
<td>Near field</td>
</tr>
<tr>
<td>Far field ✓</td>
</tr>
<tr>
<td>Duration (mins): 162</td>
</tr>
</tbody>
</table>

**Operational Conditions**

- **Substance emission potential**: Powders, granules or pelleted material
- **Dustiness**: 18886 mg/kg for inhalable fraction
- **Moisture content**: Dry product (< 5 % moisture content)
- **Powder weight fraction**: 0.9

**Activity emission potential**

- **Activity class**: Falling powders
- **Situation**: Transferring 100 – 1000 kg/minute
- **Handling type**: Routine transfer
- **Drop height**: Drop height > 0.5 m
- **Containment level**: Open process

**Surface contamination**

- **Process fully enclosed?**: No
- **Effective housekeeping practices in place?**: Yes

**Dispersion**

- **Work area**: Indoors
- **Room size**: Large workrooms only

**Risk Management Measures**

- **Localised controls**
  - **Primary**: Fixed capturing hood (90.00 % reduction)
  - **Secondary**: No localized controls (0.00 % reduction)
  - **Segregation**: No segregation (0.00 % reduction)
  - **Personal enclosure**: No personal enclosure (0.00 % reduction)

- **Dispersion**
  - **Ventilation rate**: 10 air changes per hour (ACH)
Predicted exposure levels

ART predicts air concentrations in a worker’s personal breathing zone outside of any Respiratory Protection Equipment (RPE). The use of RPE must be considered separately.

Mechanistic model results

The predicted 75th percentile full-shift exposure is 1.8 mg/m³.

The inter-quartile confidence interval is 0.98 mg/m³ to 3.3 mg/m³.

Bayesian model results

<table>
<thead>
<tr>
<th>Data source</th>
<th>Proj. Ref.</th>
<th>No. of site</th>
<th>No. of workers</th>
<th>No. of records</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagging fine powder with bagging machine with integrated LEV</td>
<td>V7657/02/01</td>
<td>1</td>
<td>2</td>
<td>9</td>
</tr>
</tbody>
</table>

Totals 1 2 9

The predicted 75th percentile full-shift exposure is 4.1 mg/m³.

The inter-quartile confidence interval is 3 mg/m³ to 5.5 mg/m³.
b) Feldspar 1, Packing line M

Details for Activity Feldspar 1

<table>
<thead>
<tr>
<th>Emission sources:</th>
<th>Near field</th>
<th>Far field</th>
<th>Duration (mins):</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>✓</td>
<td>243</td>
</tr>
</tbody>
</table>

**Far-field exposure**

**Operational Conditions**

<table>
<thead>
<tr>
<th>Substance emission potential</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance product type</td>
<td>Powders, granules or palliatized material</td>
</tr>
<tr>
<td>Dustiness</td>
<td>10246 mg/kg for inhalable fraction</td>
</tr>
<tr>
<td>Moisture content</td>
<td>Dry product (&lt; 5 % moisture content)</td>
</tr>
<tr>
<td>Powder weight fraction</td>
<td>0.9</td>
</tr>
</tbody>
</table>

**Activity emission potential**

<table>
<thead>
<tr>
<th>Activity class</th>
<th>Falling powders</th>
</tr>
</thead>
<tbody>
<tr>
<td>Situation</td>
<td>Transferring 100 - 1000 kg/minute</td>
</tr>
<tr>
<td>Handling type</td>
<td>Routine transfer</td>
</tr>
<tr>
<td>Drop height</td>
<td>Drop height &gt; 0.5 m</td>
</tr>
<tr>
<td>Containment level</td>
<td>Handling that reduces contact between product and adjacent air. Notes: This does not include processes that are fully contained by localised controls (see next questions).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface contamination</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Process fully enclosed?</td>
<td>No</td>
</tr>
<tr>
<td>Effective housekeeping practices in place?</td>
<td>Yes</td>
</tr>
</tbody>
</table>

**Dispersion**

<table>
<thead>
<tr>
<th>Work area</th>
<th>Indoors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room size</td>
<td>Large workrooms only</td>
</tr>
</tbody>
</table>

**Risk Management Measures**

**Localised controls**

<table>
<thead>
<tr>
<th>Primary</th>
<th>Fixed capturing hood (98.00 % reduction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary</td>
<td>No localized controls (0.00 % reduction)</td>
</tr>
<tr>
<td>Segregation</td>
<td>No segregation (0.00 % reduction)</td>
</tr>
<tr>
<td>Personal enclosure</td>
<td>No personal enclosure (0.00 % reduction)</td>
</tr>
</tbody>
</table>

**Dispersion**

| Ventilation rate | 19 air changes per hour (ACH) |
**Predicted exposure levels**

ART predicts air concentrations in a worker's personal breathing zone outside of any Respiratory Protection Equipment (RPE). The use of RPE must be considered separately.

**Mechanistic model results**

The predicted 75th percentile full-shift exposure is 1.6 mg/m³.

The inter-quartile confidence interval is 0.86 mg/m³ to 3.1 mg/m³.

**Bayesian model results**

<table>
<thead>
<tr>
<th>Data source</th>
<th>Proj. ref.</th>
<th>No. of citations</th>
<th>No. of workers</th>
<th>No. of records</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagging fine powder with bagging machine with integrated LEV</td>
<td>V7607/02/01</td>
<td>1</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td></td>
<td>1</td>
<td>2</td>
<td>9</td>
</tr>
</tbody>
</table>

The predicted 75th percentile full-shift exposure is 4 mg/m³.

The inter-quartile confidence interval is 2.9 mg/m³ to 5.5 mg/m³.

**Stoffenmanager**

a) Kaolin 1, Packing line L

### Información básica

<table>
<thead>
<tr>
<th>Producto</th>
<th>Kaolin 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Departamento</td>
<td>Stoffenmanager</td>
</tr>
<tr>
<td>Nombre de la evaluación de riesgos</td>
<td>A_K1</td>
</tr>
</tbody>
</table>

### Resultados de la estimación de la exposición

<table>
<thead>
<tr>
<th>Componente</th>
<th>Polvo inhalable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentración de la tarea (mg/m³)</td>
<td>8.73</td>
</tr>
<tr>
<td>Concentración media diaria (mg/m³)</td>
<td>2.95</td>
</tr>
</tbody>
</table>

### Resultados de las estimaciones de exposición

<table>
<thead>
<tr>
<th>Componente</th>
<th>Kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Número CAS</td>
<td>1332-58-7</td>
</tr>
<tr>
<td>Concentración de la tarea (mg/m³)</td>
<td>7.86</td>
</tr>
<tr>
<td>Indice de Caracterización de Riesgo Tarea</td>
<td>2.62</td>
</tr>
<tr>
<td>Valor límite (mg/m3) + tipo</td>
<td>3 mg/m3 TWA-8 horas</td>
</tr>
<tr>
<td>Concentración media diaria (mg/m3)</td>
<td>2.65</td>
</tr>
<tr>
<td>Indice de Caracterización de Riesgo Día</td>
<td>0.88</td>
</tr>
<tr>
<td>Valor límite (mg/m3) + tipo</td>
<td>3 mg/m3 TWA-8 horas</td>
</tr>
<tr>
<td>Concentración en el producto inicial (%)</td>
<td>90</td>
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</tbody>
</table>

### Características del producto

<table>
<thead>
<tr>
<th>Indicaciones de peligro H</th>
<th>Productos extremadamente pulverulentos</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulverulencia del producto</td>
<td></td>
</tr>
</tbody>
</table>

### Proceso de trabajo o tarea

| Proceso de trabajo o tarea | Packing Euroarce (Hall L-Packing line L and M) |
### Annex B. Supplementary Materials

<table>
<thead>
<tr>
<th>Actividad</th>
<th>Manipulación de productos con una velocidad/fuerza relativamente alta que puede provocar cierta dispersión de polvo</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROC</td>
<td>PROC8b: Transferencia de sustancias o preparados (carga / descarga) en instalaciones específicas.</td>
</tr>
<tr>
<td>Duración (minutos)</td>
<td>162</td>
</tr>
<tr>
<td>Frecuencia de la tarea</td>
<td>2-3 días a la semana</td>
</tr>
<tr>
<td>Actividad en el área de respiración</td>
<td>No</td>
</tr>
<tr>
<td>Múltiples trabajadores</td>
<td>-</td>
</tr>
<tr>
<td>Evaporación, secado o curado después de la actividad</td>
<td>-</td>
</tr>
<tr>
<td>Protección respiratoria</td>
<td>Sin protección</td>
</tr>
<tr>
<td><strong>Lugar de trabajo</strong></td>
<td></td>
</tr>
<tr>
<td>Lugar de trabajo</td>
<td>Euroarce packing hall 1</td>
</tr>
<tr>
<td>Volumen del recinto de trabajo</td>
<td>Volumen superior 1000 m$^3$</td>
</tr>
<tr>
<td>Ventilación del recinto de trabajo</td>
<td>Ventilación general (ventanas y puertas abiertas)</td>
</tr>
<tr>
<td>Limpieza periódica del área de trabajo</td>
<td>Sí</td>
</tr>
<tr>
<td>Inspección y mantenimiento periódico</td>
<td>Sí</td>
</tr>
<tr>
<td>Medidas de control en la fuente</td>
<td>Sistema de extracción localizada</td>
</tr>
<tr>
<td>Separación del trabajador</td>
<td>El trabajador no trabaja en una cabina.</td>
</tr>
</tbody>
</table>

b) Feldspar 1, Packing line M

<table>
<thead>
<tr>
<th>Información básica</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Producto</strong></td>
<td>Feldspar 1</td>
</tr>
<tr>
<td><strong>Departamento</strong></td>
<td>Stoffenmanager</td>
</tr>
<tr>
<td><strong>Nombre de la evaluación de riesgos</strong></td>
<td>B_F1</td>
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<table>
<thead>
<tr>
<th>Componente</th>
<th>Polvo inhalable</th>
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<tbody>
<tr>
<td>Concentración de la tarea (mg/m3)</td>
<td>8,73</td>
</tr>
<tr>
<td>Concentración media diaria (mg/m3)</td>
<td>4,42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Componente</th>
<th>Feldspar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Número CAS</td>
<td>68476-25-5</td>
</tr>
<tr>
<td>Concentración de la tarea (mg/m3)</td>
<td>7,86</td>
</tr>
<tr>
<td>Indice de Caracterización de Riesgo Tarea</td>
<td>2,62</td>
</tr>
<tr>
<td>Valor límite (mg/m3) + tipo</td>
<td>3 mg/m3 TWA-8 horas</td>
</tr>
<tr>
<td>Concentración media diaria (mg/m3)</td>
<td>3,98</td>
</tr>
<tr>
<td>Indice de Caracterización de Riesgo Día</td>
<td>1,33</td>
</tr>
<tr>
<td>Valor límite (mg/m3) + tipo</td>
<td>3 mg/m3 TWA-8 horas</td>
</tr>
<tr>
<td>Concentración en el producto inicial (%)</td>
<td>90</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Características del producto</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Indicaciones de peligro H</td>
<td></td>
</tr>
<tr>
<td>Pulverulencia del producto</td>
<td>Productos extremadamente pulverulentos</td>
</tr>
</tbody>
</table>

<p>| Proceso de trabajo o tarea   | Packing Euroarce (Hall 1-Packing line L and M) |</p>
<table>
<thead>
<tr>
<th>Actividad</th>
<th>Manipulación de productos con una velocidad/fuerza relativamente alta que puede provocar cierta dispersión de polvo</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROC</td>
<td>PROC8b: Transferencia de sustancias o preparados (carga / descarga) en instalaciones específicas.</td>
</tr>
<tr>
<td>Duración (minutos)</td>
<td>243</td>
</tr>
<tr>
<td>Frecuencia de la tarea</td>
<td>2-3 días a la semana</td>
</tr>
<tr>
<td>Actividad en el área de respiración</td>
<td>No</td>
</tr>
<tr>
<td>Múltiples trabajadores</td>
<td>-</td>
</tr>
<tr>
<td>Evaporación, secado o curado después de la actividad</td>
<td>-</td>
</tr>
<tr>
<td>Protección respiratoria</td>
<td>Sin protección</td>
</tr>
</tbody>
</table>

**Lugar de trabajo**

<table>
<thead>
<tr>
<th>Lugar de trabajo</th>
<th>Euroarce packing hall 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volumen del recinto de trabajo</td>
<td>Volumen superior 1000 m³</td>
</tr>
<tr>
<td>Ventilación del recinto de trabajo</td>
<td>Ventilación general (ventanas y puertas abiertas)</td>
</tr>
<tr>
<td>Limpieza periódica del área de trabajo</td>
<td>Sí</td>
</tr>
<tr>
<td>Inspección y mantenimiento periódico</td>
<td>Sí</td>
</tr>
<tr>
<td>Medidas de control en la fuente</td>
<td>Sistema de extracción localizada</td>
</tr>
<tr>
<td>Separación del trabajador</td>
<td>El trabajador no trabaja en una cabina.</td>
</tr>
</tbody>
</table>
NanoSafer Control Banding Report for Airborne Occupational Exposure Assessment
version 1.1

Assessment prepared by

<table>
<thead>
<tr>
<th>Name:</th>
<th>Address:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Phone:</td>
<td>E-mail:</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Date: Tuesday, Dec 4, 2018</td>
<td></td>
</tr>
</tbody>
</table>

Assessment of

<table>
<thead>
<tr>
<th>Material assessed:</th>
<th>Kaolin 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Producer:</td>
<td>SICA SL</td>
</tr>
<tr>
<td>Classified as nanomaterial consisting of:</td>
<td>Nancoobject</td>
</tr>
<tr>
<td>Work situation assessed:</td>
<td>Packing Line L</td>
</tr>
<tr>
<td>Process type:</td>
<td>Powder Handling</td>
</tr>
</tbody>
</table>

Result of assessment

<table>
<thead>
<tr>
<th>Estimated hazard level 0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>The hazard level is estimated based on High aspect ratio material: No</td>
</tr>
<tr>
<td>A high volume specific surface area of 41.60 m²/cm³</td>
</tr>
<tr>
<td>Of the analogue bulk material: 3 mg/m³</td>
</tr>
<tr>
<td>Solubility: Insoluble (&lt; 1 g/L)</td>
</tr>
<tr>
<td>Presence of surface coating: No</td>
</tr>
<tr>
<td>Known hazards of analogue bulk material</td>
</tr>
<tr>
<td>Estimated time-resolved exposure index</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Near-field Acute</th>
<th>Near-field Daily</th>
<th>Far-field Acute</th>
<th>Far-field Daily</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.29</td>
<td>4.151</td>
<td>1.067</td>
<td>0.3498</td>
</tr>
<tr>
<td>EBS: Very high exposure</td>
<td>EBS: Very high exposure</td>
<td>EBS: Very high exposure</td>
<td>EBS: Moderate exposure potential</td>
</tr>
</tbody>
</table>
Note: the local control (exhaust ventilation) was estimated to reduce particle emissions by 90%. A factor of 0.1 was applied to the respirable dustiness input parameter.
b) Feldspar 1, Packing line M

NanoSafer Control Banding Report for Airborne Occupational Exposure Assessment

Assessment prepared by

Name: 
Address: 
Phone: 
E-mail: 
Date: Tuesday, Dec 4, 2016

Assessment of

Material assessed: Feldspar 1
Producer: SAMCA
Classified as nanomaterial consisting of: Nanoobject

Work situation assessed: Packing Line M
Process type: Powder Handling

Result of assessment

Estimated hazard level 0.6
The hazard level is estimated based on
High aspect ratio material: No
OEL of analogue bulk material: 3 mg/m³
Solubility: Insoluble (< 1 g/L)
Presence of surface coating: No
Known hazards of analogue bulk material
H373 May cause damage to organs through prolonged or repeated exposure

Estimated time-resolved exposure index

Near-field Acute
15.24
EB5: Very high exposure

Near-field Daily
5.566
EB5: Very high exposure

Far-field Acute
0.9588
EB4: High exposure potential

Far-field Daily
0.4690
EB3: Moderate exposure potential
Note: the local control (exhaust ventilation) was estimated to reduce particle emissions by 90%. A factor of 0.1 was applied to the respirable dustiness input parameter.
3. Supplementary material Publication III: Testing the performance of one and two box models as tools for risk assessment of particle exposure during packing of inorganic fertilizer

Figure S1 Images of the small and big bags packing lines plus instrument location.

Figure S2 DiSCmini, NanoScan, MiniWras and CPC number concentration during an intercomparison previous to the packing measurements. We can observe that the MiniWras, unlike CPC, NanoScan and DiSCmini cannot detect an increase of particles under 45-50 nm of diameter.
Figure S3 Particle concentration in the packing area (WA) during small bags day 1 (SB1): (a) particle number concentration time series; (b) particle size distribution time series measured with the MiniWras and the NanoScan, solid black line shows DiSCmini (DM) $D_{50}$; (c) mass concentration time series. Red vertical lines indicate start (solid line) and stop (dashed line) of the packing operation and horizontal black and blue lines on the top of the graphs indicate diesel and electric forklifts activity respectively.

Figure S4 Particle concentration in the packing area (WA) during big bags day 2 (BB2): (a) particle number concentration time series; (b) particle size distribution time series measured with the MiniWras and the NanoScan, solid black line shows DiSCmini (DM) $D_{50}$; (c) mass concentration time series. Red vertical lines in (a) and (c) indicate start (solid line) and stop (dashed line) of the packing operation and horizontal black and blue lines on the top of the graphs indicate diesel and electric forklifts activity respectively.
Table S1 Mean number concentration and particle size for background (pre-activity) and packing process measured with the DiSCmini in the worker area, indoor and outdoor measurement locations. *NaN: information not available due to technical problems. Values in bold indicate a statistically significant differences compared with background concentrations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Process</th>
<th>Worker area (WA)</th>
<th>Indoor</th>
<th>Outdoor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Number (cm³)</td>
<td>Size (nm)</td>
<td>Number (cm³)</td>
</tr>
<tr>
<td>SB1</td>
<td>Background</td>
<td>115845</td>
<td>38</td>
<td>126803</td>
</tr>
<tr>
<td></td>
<td>Packing</td>
<td>72263</td>
<td>32</td>
<td>81903</td>
</tr>
<tr>
<td>SB2</td>
<td>Background</td>
<td>130834</td>
<td>28</td>
<td>*NaN</td>
</tr>
<tr>
<td></td>
<td>Packing</td>
<td>78200</td>
<td>37</td>
<td>*NaN</td>
</tr>
<tr>
<td>BB1</td>
<td>Background</td>
<td>145232</td>
<td>33</td>
<td>117211</td>
</tr>
<tr>
<td></td>
<td>Packing</td>
<td>113087</td>
<td>37</td>
<td>102988</td>
</tr>
<tr>
<td>BB2</td>
<td>Background</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Packing</td>
<td>41955</td>
<td>44</td>
<td>45277</td>
</tr>
</tbody>
</table>

Table S2 Mean particle mass concentration for background (pre-activity) and packing processes measured with the Grimm – mini LAS laser spectrometer in the indoors and outdoors locations. Values are in µg m⁻³. Values in bold indicate a statistically significant differences compared with background concentrations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Process</th>
<th>Indoor</th>
<th>Outdoor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inhalable</td>
<td>Thoracic</td>
</tr>
<tr>
<td>SB1</td>
<td>Background</td>
<td>2063</td>
<td>1630</td>
</tr>
<tr>
<td></td>
<td>Packing</td>
<td>1142</td>
<td>771</td>
</tr>
<tr>
<td>SB2</td>
<td>Background</td>
<td>1232</td>
<td>878</td>
</tr>
<tr>
<td></td>
<td>Packing</td>
<td>1599</td>
<td>1144</td>
</tr>
<tr>
<td>BB1</td>
<td>Background</td>
<td>1537</td>
<td>1120</td>
</tr>
<tr>
<td></td>
<td>Packing</td>
<td>1514</td>
<td>1269</td>
</tr>
<tr>
<td>BB2</td>
<td>Background</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Packing</td>
<td>1171</td>
<td>902</td>
</tr>
</tbody>
</table>
Table S3  Calculated dose rates in particle number, $n$ and mass, $m$ and regional deposition in percentages to head airways, trachea bronchi and alveolar regions.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Day 1 - Small Bags 1</th>
<th>Day 2 - Small Bags 2</th>
<th>Day 3 - Big Bags 1</th>
<th>Day 4 - Big Bags 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BG</td>
<td>Packing</td>
<td>BG</td>
<td>Packing</td>
</tr>
<tr>
<td>$\dot{n}_{10}$ [min$^{-1}$]</td>
<td>770</td>
<td>857</td>
<td>834</td>
<td>1035</td>
</tr>
<tr>
<td>$\dot{n}$, Head airways [%]</td>
<td>11.7</td>
<td>12.6</td>
<td>12.1</td>
<td>11.5</td>
</tr>
<tr>
<td>$\dot{n}$, Trachea bronchi [%]</td>
<td>19.1</td>
<td>20.4</td>
<td>20.0</td>
<td>19.4</td>
</tr>
<tr>
<td>$\dot{n}$, Alveolar [%]</td>
<td>69.2</td>
<td>67.0</td>
<td>68.0</td>
<td>69.1</td>
</tr>
<tr>
<td>$\dot{m}_{10}$ [μg min$^{-1}$]</td>
<td>24.0</td>
<td>22.1</td>
<td>20.1</td>
<td>26.4</td>
</tr>
<tr>
<td>$m$, Head airways [%]</td>
<td>90.8</td>
<td>93.5</td>
<td>92.0</td>
<td>92.4</td>
</tr>
<tr>
<td>$m$, Trachea bronchi [%]</td>
<td>3.6</td>
<td>2.6</td>
<td>3.3</td>
<td>3.1</td>
</tr>
<tr>
<td>$m$, Alveolar [%]</td>
<td>5.7</td>
<td>3.9</td>
<td>4.8</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table S4  Stoffenmanager report for the small bags case scenario.

<table>
<thead>
<tr>
<th>Basic information</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>YaraMila COMPLEX</td>
</tr>
<tr>
<td>Department</td>
<td>Stoffenmanager</td>
</tr>
<tr>
<td>Name risk assessment</td>
<td>BCL packing small bags</td>
</tr>
</tbody>
</table>

| Results exposure estimation       |                                |
| Component                         | Inhalable dust                 |
| Task concentration (mg/m$^3$)      | 1.80                           |
| Daily average concentration (mg/m$^3$) | 0.90                        |

| Results exposure estimations       |                                |
| Component                         | Ammonium nitrate               |
| CAS-number                        | 6484-52-2                      |
| Task concentration (mg/m$^3$)      | 0.36                           |
| Risk Characterization Ratio Task  | < 0.01                         |
| Limit value (mg/m$^3$)            | 37.6 mg/m$^3$ TWA-8 hours | European Chemicals Agency (ECHA) |
| Daily average concentration (mg/m$^3$) | 0.18                        |
| Risk Characterization Ratio Day   | < 0.01                         |
| Limit value (mg/m$^3$)            | 37.6 mg/m$^3$ TWA-8 hours | European Chemicals Agency (ECHA) |
| Concentration in initial product (%) | 20                          |

| Component                         | Potassium nitrate             |
| CAS-number                        | 7757-79-1                     |
| Task concentration (mg/m$^3$)      | 0.27                           |
| Risk Characterization Ratio Task  | < 0.01                         |
| Limit value (mg/m$^3$)            | 36.7 mg/m$^3$ TWA-8 hours | European Chemicals Agency (ECHA) |
| Daily average concentration (mg/m$^3$) | 0.14                        |
| Risk Characterization Ratio Day   | < 0.01                         |
| Limit value (mg/m$^3$)            | 36.7 mg/m$^3$ TWA-8 hours | European Chemicals Agency (ECHA) |
### Concentration in initial product (%)

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration in initial product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium fluoride</td>
<td>15</td>
</tr>
</tbody>
</table>

### CAS-number

<table>
<thead>
<tr>
<th>Task concentration (mg/m³)</th>
<th>Risk Characterization Ratio Task</th>
<th>Limit value (mg/m³)</th>
<th>Daily average concentration (mg/m³)</th>
<th>Risk Characterization Ratio Day</th>
<th>Limit value (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,054</td>
<td>0,011</td>
<td>5 mg/m³ TWA-8 hours</td>
<td>0,027</td>
<td>&lt; 0,01</td>
<td>5 mg/m³ TWA-8 hours</td>
</tr>
</tbody>
</table>

### Product characteristics

<table>
<thead>
<tr>
<th>H-statements</th>
<th>Dustiness product</th>
</tr>
</thead>
<tbody>
<tr>
<td>H272: May intensify fire; oxidiser</td>
<td>Granules/grains/flakes</td>
</tr>
<tr>
<td>H319: Causes serious eye irritation</td>
<td></td>
</tr>
</tbody>
</table>

### Process

<table>
<thead>
<tr>
<th>Process</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCL packing small bags</td>
<td>Handling of products where due to high pressure, speed or force, large quantities of dust are generated and dispersed</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PROC</th>
<th>Duration (minutes)</th>
<th>Frequency of the task</th>
<th>Activity in breathing zone</th>
<th>Multiple employees</th>
<th>Evaporation, drying or curing after activity</th>
<th>Respiratory protection</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROCO: Other</td>
<td>240</td>
<td>4-5 days a week</td>
<td>No</td>
<td>-</td>
<td>-</td>
<td>No protection</td>
</tr>
</tbody>
</table>

### Workplace

<table>
<thead>
<tr>
<th>Workplace</th>
<th>Volume of the working room</th>
<th>Ventilation working room</th>
<th>Regular cleaning of work area</th>
<th>Regular inspection and maintenance</th>
<th>Control measures at the source</th>
<th>Segregation of employee</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCL packing hall (Small Bags)</td>
<td>Volume over 1000 m³</td>
<td>General ventilation (open windows and doors)</td>
<td>Yes</td>
<td>Yes</td>
<td>Containment of the source</td>
<td>The employee does not work in a cabin.</td>
</tr>
</tbody>
</table>

### Conclusion

<table>
<thead>
<tr>
<th>Checked for substitution</th>
<th>Result of the substitution test / Reason for waiving a substitution</th>
<th>Control measures</th>
<th>Responsible person</th>
<th>Date risk assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>□ Yes □ No</td>
<td>Control measures sufficient</td>
<td>□ Control measures not sufficient</td>
<td>□ Further investigation required</td>
</tr>
</tbody>
</table>

---
### Table S5 Stoffenmanager report for the big bags case scenario.

#### Basic information

<table>
<thead>
<tr>
<th>Product</th>
<th>YaraMila COMPLEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Department</td>
<td>Stoffenmanager</td>
</tr>
<tr>
<td>Name risk assessment</td>
<td>BCL big bags</td>
</tr>
</tbody>
</table>

#### Results exposure estimation

<table>
<thead>
<tr>
<th>Component</th>
<th>Inhalable dust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task concentration (mg/m³)</td>
<td>4.11</td>
</tr>
<tr>
<td>Daily average concentration (mg/m³)</td>
<td>2.06</td>
</tr>
</tbody>
</table>

#### Results exposure estimations

<table>
<thead>
<tr>
<th>Component</th>
<th>Ammonium nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS-number</td>
<td>6484-52-2</td>
</tr>
<tr>
<td>Task concentration (mg/m³)</td>
<td>0.82</td>
</tr>
<tr>
<td>Risk Characterization Ratio Task</td>
<td>0.022</td>
</tr>
<tr>
<td>Limit value (mg/m³)</td>
<td>37.6 mg/m³ TWA-8 hours</td>
</tr>
<tr>
<td>Daily average concentration (mg/m³)</td>
<td>0.41</td>
</tr>
<tr>
<td>Risk Characterization Ratio Day</td>
<td>0.011</td>
</tr>
<tr>
<td>Limit value (mg/m³)</td>
<td>37.6 mg/m³ TWA-8 hours</td>
</tr>
<tr>
<td>Concentration in initial product (%)</td>
<td>20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Potassium nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS-number</td>
<td>7757-79-1</td>
</tr>
<tr>
<td>Task concentration (mg/m³)</td>
<td>0.62</td>
</tr>
<tr>
<td>Risk Characterization Ratio Task</td>
<td>0.017</td>
</tr>
<tr>
<td>Limit value (mg/m³)</td>
<td>36.7 mg/m³ TWA-8 hours</td>
</tr>
<tr>
<td>Daily average concentration (mg/m³)</td>
<td>0.31</td>
</tr>
<tr>
<td>Risk Characterization Ratio Day</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Limit value (mg/m³)</td>
<td>36.7 mg/m³ TWA-8 hours</td>
</tr>
<tr>
<td>Concentration in initial product (%)</td>
<td>15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Calcium fluoride</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS-number</td>
<td>7789-75-5</td>
</tr>
<tr>
<td>Task concentration (mg/m³)</td>
<td>0.12</td>
</tr>
<tr>
<td>Risk Characterization Ratio Task</td>
<td>0.025</td>
</tr>
<tr>
<td>Limit value (mg/m³)</td>
<td>5 mg/m³ TWA-8 hours</td>
</tr>
<tr>
<td>Daily average concentration (mg/m³)</td>
<td>0.062</td>
</tr>
<tr>
<td>Risk Characterization Ratio Day</td>
<td>0.012</td>
</tr>
<tr>
<td>Limit value (mg/m³)</td>
<td>5 mg/m³ TWA-8 hours</td>
</tr>
<tr>
<td>Concentration in initial product (%)</td>
<td>3</td>
</tr>
</tbody>
</table>

#### Product characteristics

<table>
<thead>
<tr>
<th>H-statements</th>
<th>H272: May intensify fire; oxidiser</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H319: Causes serious eye irritation</td>
</tr>
<tr>
<td>Dustiness product</td>
<td>Granules/grains/flakes</td>
</tr>
</tbody>
</table>
### Process

<table>
<thead>
<tr>
<th>Process</th>
<th>BCL packing big bags</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity</td>
<td>Handling of products where due to high pressure, speed or force, large quantities of dust are generated and dispersed</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PROC</th>
<th>PROC0: Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration (minutes)</td>
<td>240</td>
</tr>
<tr>
<td>Frequency of the task</td>
<td>4-5 days a week</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Activity in breathing zone</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiple employees</td>
<td>-</td>
</tr>
<tr>
<td>Evaporation, drying or curing after activity</td>
<td>-</td>
</tr>
</tbody>
</table>

| Respiratory protection | No protection |

### Workplace

<table>
<thead>
<tr>
<th>Workplace</th>
<th>BCL packing hall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of the working room</td>
<td>Volume over 1000 m³</td>
</tr>
<tr>
<td>Ventilation working room</td>
<td>General ventilation (open windows and doors)</td>
</tr>
<tr>
<td>Regular cleaning of work area</td>
<td>Yes</td>
</tr>
</tbody>
</table>

| Regular inspection and maintenance | Yes |
| Control measures at the source | No control measures at the source |
| Segregation of employee | The employee does not work in a cabin |

### Conclusion

| Checked for substitution | □ Yes □ No |
| Result of the substitution test / Reason for waiving a substitution | |

| Control measures | □ Control measures sufficient |
|------------------| □ Control measures not sufficient |
| Responsible person | |
| Date risk assessment | |

| Control measures | □ Control measures sufficient |
|------------------| □ Control measures not sufficient |
| Responsible person | |
| Date risk assessment | |

---

**Annex B. Supplementary Materials**
4. Supplementary material Publication IV: Modeling of high nanoparticle exposure in an indoor industrial scenario with a one-box model

**Figure S1.** Booth #1, Day 1 a) shows particle number concentrations measured inside the booth by DiSCmini (DM), from worker area by NanoScan (WA) and particle emission rates solved by convolution from NanoScan WA concentrations. Blue line shows when the DM concentration was $>10^5$ cm$^{-3}$ indicating that the plasma spray was ON and green line when the DM concentration was $<10^5$ cm$^{-3}$ indicating that the plasma spray was OFF. Figure b) shows the particle size distributions measured by the NanoScan in the WA.

**Figure S2.** Booth #1, Day 2 a) shows particle number concentrations measured inside the booth by DiSCmini (DM), from worker area by NanoScan (WA) and particle emission rates solved by convolution from NanoScan WA concentrations. Blue line shows when the DM concentration was $>10^5$ cm$^{-3}$ indicating that
the plasma spray was ON and green line when the DM concentration was <10^5 cm\(^{-3}\) indicating that the plasma spray was OFF. Figure b) shows the particle size distributions measured by the NanoScan in the WA.

**Figure S3** Booth #3, Day 4 a) shows particle number concentrations measured inside the booth by DiSCmini (DM), from worker area by NanoScan (WA) and particle emission rates solved by convolution from NanoScan WA concentrations. Blue line shows when the DM concentration was >10^5 cm\(^{-3}\) indicating that the plasma spray was ON and green line when the DM concentration was <10^5 cm\(^{-3}\) indicating that the plasma spray was OFF. Figure b) shows the particle size distributions measured by the NanoScan in the WA.

**Table S1** Sampling day, booth, technic used (HVOF or APS), and feedstock materials summary. A: afternoon; M: morning. APS: atmospheric plasma spraying; HVOF: High Velocity Oxy-Fuel.

<table>
<thead>
<tr>
<th>Day n°</th>
<th>Booth Model area</th>
<th>Spraying Technique</th>
<th>Shift</th>
<th>Feedstock Material</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>#1</td>
<td>APS</td>
<td>A</td>
<td>Amdry 6228 &amp; ANVAL 50/50</td>
<td>Al(_2)O(_3) B2TiO(_3) &amp; Cr/Ni</td>
</tr>
<tr>
<td>Day 2</td>
<td>#1</td>
<td>APS</td>
<td>M and A</td>
<td>Amdry 6228 &amp; ANVAL 50/50</td>
<td>Al(_2)O(_3) B2TiO(_3) &amp; Cr/Ni</td>
</tr>
<tr>
<td>Day 3</td>
<td>#3</td>
<td>HVOF</td>
<td>M and A</td>
<td>WOKA 3702-1</td>
<td>WC 20Cr3C2 7Ni</td>
</tr>
<tr>
<td>Day 4</td>
<td>#3</td>
<td>HVOF</td>
<td>M and A</td>
<td>WOKA 3702-1</td>
<td>WC 20Cr3C2 7Ni</td>
</tr>
</tbody>
</table>
Table S2 Respirable mass concentration during the thermal spraying activity. Statistically significant increases are marked in bold.

<table>
<thead>
<tr>
<th>Day</th>
<th>Period</th>
<th>Inside Booth</th>
<th>Worker Area (WA)</th>
<th>Inactivity (Background)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Respirable</td>
<td>Respirable</td>
<td>Respirable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(µg m⁻³)</td>
<td>(µg m⁻³)</td>
<td>(µg m⁻³)</td>
</tr>
<tr>
<td>Booth #1 Model Area (Day 1)</td>
<td>Afternoon</td>
<td>n/a</td>
<td>172</td>
<td>53</td>
</tr>
<tr>
<td>Booth #1 Model Area (Day 2)</td>
<td>Morning</td>
<td>130</td>
<td>161</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Afternoon</td>
<td>169</td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>Booth #3 Model Area (Day 3)</td>
<td>Morning</td>
<td>698</td>
<td>142</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Afternoon</td>
<td>709</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Booth #3 Model Area (Day 4)</td>
<td>Morning</td>
<td>522</td>
<td>171</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Afternoon</td>
<td>367</td>
<td>136</td>
<td></td>
</tr>
</tbody>
</table>

Table S3 Parameterization of the single box model considering booth door open: V (m³) is volume used for modelling, Q (m³ h⁻¹) is ventilation air volume flow through the Worker Area and ACH (h⁻¹) is the air changes per hour calculated from measured air speeds.

<table>
<thead>
<tr>
<th>Model Area</th>
<th>V, [m³]</th>
<th>Q, [m³h⁻¹]</th>
<th>ACH, [h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>465</td>
<td>32155</td>
<td>69</td>
</tr>
<tr>
<td>#3</td>
<td>250</td>
<td>12291</td>
<td>49</td>
</tr>
</tbody>
</table>
Table S4 One Box modelled concentrations considering booth door open, and using the convolution theorem and the cyclic steady state (Cyclic SS) approach to calculate emission rate ($S_N$) from NanoScan data.

<table>
<thead>
<tr>
<th>Day</th>
<th>Calculated $S_N$ in WA (min$^{-1}$)</th>
<th>Shift</th>
<th>Modelled concentrations (cm$^3$)</th>
<th>WA measured (cm$^3$)</th>
<th>Ratio (modelled/measured)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Conv.</strong></td>
<td><strong>Cyclic SS</strong></td>
<td><strong>Conv.</strong></td>
<td><strong>Cyclic SS</strong></td>
<td><strong>Conv.</strong></td>
</tr>
<tr>
<td><strong>Booth #1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model Area (Day 1)</td>
<td>1.4x10$^{11}$</td>
<td>1.3x10$^{12}$</td>
<td>A</td>
<td>1.4x10$^4$</td>
<td>1.6x10$^4$</td>
</tr>
<tr>
<td>Model Area (Day 2)</td>
<td>3.4x10$^{12}$</td>
<td>3.0x10$^{12}$</td>
<td>M</td>
<td>1.9x10$^5$</td>
<td>1.9x10$^4$</td>
</tr>
<tr>
<td>Model Area (Day 3)</td>
<td>1.2x10$^{13}$</td>
<td>7.9x10$^{12}$</td>
<td>M</td>
<td>3.9x10$^4$</td>
<td>3.3x10$^4$</td>
</tr>
<tr>
<td>Model Area (Day 4)</td>
<td>7.9x10$^{12}$</td>
<td>1.4x10$^{13}$</td>
<td>M</td>
<td>4.7x10$^4$</td>
<td>5.5x10$^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Booth #3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model Area (Day 3)</td>
<td>7.9x10$^{12}$</td>
<td>1.4x10$^{13}$</td>
<td>M</td>
<td>4.5x10$^4$</td>
<td>5.1x10$^4$</td>
</tr>
</tbody>
</table>
Annex

Additional Scientific Contributions
ANNEX C. Additional scientific contributions

Peer-reviewed research publications


Conference attendance as oral presenter


cuantificación de emisiones y exposición, I Jornada de Jóvenes Investigadores en la UJI (ITC-UJI) (ICV-CSIC).

ACKNOWLEDGEMENTS

This Thesis would not have been possible without the cooperation and help of many people to whom I would like to express my gratitude.

Primeramente quiero agradecer a la Dra. Mar Viana (IDAEA) y al Profesor Eliseo Monfort (ITC), los directores de esta tesis, por confiar en mí des de un inicio, aunque este tema fuera completamente nuevo para mí, y por ofrecerme la gran oportunidad de realizar esta tesis. Muchas gracias a los dos por vuestra apoyo, consejos y correcciones a lo largo de estos tres años. He de decir que no puedo estar más agradecida de haberos tenido a los dos como directores, no solo sois grandes profesionales de los cuales he podido aprendido muchísimo a nivel laboral, sino que además habéis estado a mi lado siendo mucho más que mis directores de tesis. Gracias a los dos por vuestra cercanía, humildad y comprensión en todo momento. En especial, quiero agradecer a Mar por el día a día y las charlas que nada tiene que ver con el trabajo, por haber resuelto dudas y problemas, y en definitiva por estar disponible siempre que lo he necesitado. Gracias por haber hecho este camino mucho más fácil. Agrair també al tutor de la Universitat de Barcelona, Dr. Alex Tarancón, per acceptar ser part d’aquest tesi i per el suport ofert durant aquest temps.

I would like to offer my special thanks to Dra. María Cruz Minguillón (IDAEA) and Dr. Joonas Koivisto, for given me valuable support and advice during this last years. Without them this Thesis would not have been possible. Muchas gracias MariCruz por tus exhaustivas correcciones y excelentes aportaciones que me han ayudado a realizar un trabajo mucho mejor. Gracias por haber estado cuando lo he necesitado y por revisar esta tesis. Agradecerte també por las visitas al despacho y tus charlas con ese toque teatral que nos han animado los días en el despacho. To Joonas, thank you for given me the opportunity to learn so much about exposure modelling, for sharing your knowledge on modelling and exposure assessment, for your support, and for solving all my doubts, that were not few!

Having reached this point, I would also like to thank all the people from the National Research Center for the Working Environment (NRCWE) as well as from the Instituto de Tecnologia Ceramica (ITC) with whom I had the pleasure to work, for the fruitful collaborations and for making me feel so welcomed.
Un especial agradecimiento se lo debo a la Dra. Ana López-Lilao (ITC) y a Sara Estupiñá (ITC), así como a la Dra. Ana Sofía Fonseca (NRCWE). A Ana y Sara, mis compañeras de campaña con las que hemos pasado largas pero estupendas horas de muestreos, gracias! Ha sido genial poder trabajar a vuestro lado y aprender tanto de vosotras. Muchas gracias a las dos por haber dedicado tantas horas a este proyecto, sin vosotras, vuestro esfuerzo y dedicación, esta tesis no habría sido posible. En especial, gracias Ana por haberme enseñado tanto sobre dustiness y por haber estado siempre dispuesta a ayudarme y escucharme. A Sara, gracias por todas las horas que has pasado en planta piloto haciendo ensayos de dustiness. A Sofia, muchas gracias tanto por tu ayuda profesional y tus aportaciones a esta tesis, como por haberte cuidado tantísimo en Copenhague, pase unos grandes días a vuestro lado.

I would also like to express my gratitude to Dr. Dirk Dahmann (IGF) and Dr. Aureli Tobias for their valuable advice and contributions to this Thesis.

Agrair també al grup de TEM del CCiTUB, en especial al Joan Mendoza per estar sempre disposat a ajudar-me amb les mostres.

Un especial agradecimiento se lo debo a todo el grupo del IDAEA-EGAR. Muchas gracias a todas y todos por crear este fantástico ambiente de trabajo. Ha sido genial poder compartir todo este tiempo con vosotros. Gracias! os deseo lo mejor. En especial, quiero agradecer a todas mis compañeras y compañeros de despacho por crear ese “cálido” ambiente tan característico del 1543. Gracias a los que estáis y a las que os habéis ido. Agradecer también a Diana, por sus visitas y charlas, a Garay y Elena por la ayuda con los papeles de viajes imposibles y a Xavi y Andrés por las revisiones finales de esta tesis.

A la meva família i amics, gràcies per estar sempre al meus costat, preocupar-vos per mi, i per donar-me tants bons moments. To Felix, thank you for helping me with the design of this thesis, but most importantly for your constant support and understanding. I am so grateful to have you in my life.

Finalment, agrair a la meva mare tot el que ha fet i fa per mi. Gràcies per haver confiat sempre en mi, per animar-me i consolar-me quan ha fet falta, i per ser la persona en la que sempre podré confiar. Gràcies per haver-me donat tant, no seria on sóc sense el teu esforç.
FUNDING SOURCES

The work presented in this Thesis was carried out with the financial support from the Spanish MINECO (CGL2015-66777-C2-1-R, 2-R), and through project PCIN-2015-173-C02-01, under the frame of SIINN, the ERA-NET for a Safe Implementation of Innovative Nanoscience and Nanotechnology, by SIINN-ERANET project CERASAFE (id.:16). Additional support was provided by Generalitat de Catalunya AGAUR 2017 SGR41, the Spanish Ministry of the Environment (I3CAES006), FEDER (European Regional Development Fund) “Una manera de hacer Europa”. Special thanks are due to the following companies: Bulk Cargo Logistics, S.A., Euroarce Samca, and TM COMAS for their committed cooperation.