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Airborne engineered nanomaterials in the workplace—a review of release and worker exposure during nanomaterial production and handling processes

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HIGHLIGHTS

• Release characteristics can be grouped by the type of occupational activities.

• Release levels may be linked to process energy.

• A better data reporting practice will facilitate exposure assessment.

• The results help prioritize industrial processes for human risk assessment.

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ABSTRACT

For exposure and risk assessment in occupational settings involving engineered nanomaterials (ENMs), it is important to understand the mechanisms of release and how they are influenced by the ENM, the matrix material, and process characteristics. This review summarizes studies providing ENM release information in occupational settings, during different industrial activities and using various nanomaterials. It also assesses the contextual information – such as the amounts of materials handled, protective measures, and measurement strategies – to understand which release scenarios can result in exposure. High-energy processes such as synthesis, spraying, and machining were associated with the release of large numbers of predominantly small-sized particles. Low-energy processes, including laboratory handling, cleaning, and industrial bagging activities, usually resulted in slight or moderate releases of relatively large agglomerates. The present analysis suggests that process-based release potential can be ranked, thus helping to prioritize release assessments, which is useful for tiered exposure assessment approaches and for guiding the implementation of workplace safety strategies. The contextual information provided in the literature was often insufficient to directly link release to exposure. The studies that did allow an analysis suggested that significant worker exposure might mainly occur when engineering safeguards and personal protection strategies were not carried out as recommended.

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1. Introduction

Engineered nanomaterials (ENMs) possess different physical and chemical properties than their bulk counterparts and, because of this, are used in manufacturing processes for a variety of applications [1]. However, during their production and use, ENMs may be released into the workplace, resulting in workers' exposure. Understanding release is important for accurately describing the exposure scenarios that are helpful for risk assessment and management [2], which are required under regulatory schemes such as REACH in the EU [3].

Release can be referred to as the detachment of nanomaterials from a body of powder, a suspension, or a solid matrix [4]. This can be expressed as a rate describing the amount of material released per unit of time. In workplaces, the release of ENMs can occur throughout their entire lifecycle-manufacturing, use, and recycling. Release mechanisms depend on the physical state of the material (powder, suspension, or solid) and the amount of energy introduced by specific processes. For powders, environmental humidity and the moisture content of the raw powder have a significant influence on the release level, as suggested by dustiness studies [5]. Liquid suspensions containing ENMs can release nanoparticles from the solution's surface when external energies are applied, such as stirring [6], sonication [6,7], centrifuging, [8] or spraying [6,9]. The release rate from liquids depends on factors such as the ENM concentration and its solubility in the solution. Release from solid matrices is mainly caused by the mechanical treatment of nanocomposites, including drilling, sawing, and sanding [10-12]. Parameters such as the ENM's concentration and distribution within the composite matrix and the process conditions (e.g., treatment type, temperature, or relative humidity), as well as ageing processes such as weathering [13], play important roles in release rates and forms (e.g. agglomerate, individual particle, mixture of ENM and matrix material).

To prevent or reduce ENM releases, it is important to understand the determinants of release related to nanomaterials, the matrix in which they are embedded (if at all), and the process and/or activity involved. Tsai et al. [14] reported that handling 100g of nano-alumina powder resulted in a much higher released particle concentration than handling 15 g. High-energy processes, such as pouring, generate more particles than less vigorous processes, such as transferring. Johnson et al. [7] found that the sonication of functionalized multi-walled carbon nanotubes (MWCNTs) in reconstituted water containing natural organic matter resulted in particle concentrations three times higher than sonicating raw MWCNTs in the same medium.

Material that was detached (i.e., released) from a powder body, a liquid, or a solid matrix can be emitted depending on the process specifications and on-site control measures in place. Fig. 1 depicts a typical occupational setting from which ENMs could be released, emitted, and transported, resulting in exposure to workers. If the release rate cannot be directly calculated from a predefined release mechanism, it may still be possible to estimate it from the information on source concentrations, near-field volume flow rates, and the release start point and duration. Some of the released particles might be captured by engineering controls (e.g., ventilation or enclosure); the escaped portion, which subsequently disperses into working environments, is called emission. Transmission describes the process during which emitted aerosols are transported to the immediate receptors, which then results in exposure.

Amongst the metrics used to characterize the release of nanomaterials, particle number and mass concentration are the two most widely used parameters for airborne ENMs in occupational settings [15], possibly due to the availability of sampling equipment and mature sampling procedures. Such data allow the creation of rankings for the release potential of common industrial processes and the study of how release is influenced by factors such as the quantity of material needed, how it is treated, the energy levels associated, and variable human factors.

In addition to the characterization of the ENMs released, such as that provided by ISO [16], a comprehensive exposure assessment should also include the necessary contextual information. Clark et al. [2] pointed out that the level of relevant detailed information in the existing literature on exposure is often insufficient for an in-depth understanding of the situation being studied. Parameters such as ventilation type, the personal protective equipment (PPE) used, sampling locations, frequency and duration of worker activity, and personal sampling data are often not fully described. This information is critical to transform upstream release data into downstream exposure estimates. Only sufficiently detailed metadata will allow the development of exposure scenarios that are valid for risk assessment purposes and that can be used for establishing health and safety strategies.

This paper reviews the information on ENM release and exposure in the scientific literature and assesses how they inform us about the related human exposure in workplaces. The availability of the contextual information needed for exposure and risk assessment was assessed to identify potential gaps in data collection and reporting. The characteristics of released ENMs-including number concentration, mean size, and morphology-were compared for different processes involved in order to facilitate a general grouping and ranking of release potential. Measurement strategies, such as the equipment types and sampling locations used in field studies, were evaluated to give a better understanding of release and exposure data. Furthermore, production capacities and amounts handled were compared across different activities and materials in order to identify processes with a possibility of high occupational exposure. Finally, the types and efficiencies of engineering controls were summarized in order to describe the overall level of protection for workers in nanotechnology workplaces.

2. Method

We conducted a systematic review of scientific publications describing real-world measurements of airborne ENM release and exposure in industry and research laboratories. The goal was to cover a wide range of relevant studies on this topic and describe the current information and knowledge about ENM release in workplaces.

The studies examined were collected from multiple literature sources. As a first step, 26 publications were identified in the NANEX database. The NANEX project's goal was to build a comprehensive library of occupational exposure scenarios for ENMs throughout their entire lifecycle [17]; it includes scientific literature and large surveys which generally contain descriptions of the material, the processes and activities, release levels of airborne nanoparticles, and subsequent exposure estimates under specific environments. The literature covered scenarios related to the production of ENMs at a research-scale, as well as in industrial settings and downstream uses. The information available was a very good fit with the context of our review. Thus, the list of literature in the NANEX database was used to target relevant publications. Another identified comprehensive library on types of nanomaterials and nano-objects used in various industrial processes was the R-Nano platform [18].

In a second step, we searched public online databases such as PUBMED and ScienceDirect. Keywords were chosen by analyzing the frequency with which they appeared in the titles of the selected NANEX publications. The most common words were *release*; *exposure*; *workplace*(*s*); *airborne*; *nanoparticle*(*s*); and *characterizations*. Combinations of these terms were then used in the searches. The names of specific materials were also used—such as *titanium dioxide*

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