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Review article

Nanomaterial exposures for worker, consumer and the general public

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ABSTRACT

Exposures to nanomaterials comprise the exposure to nano-objects, to nanostructured materials or nanocomposites being 'relatively' pristine at the place of production or 'aged' at later stages. This review presents the state of the art and current short-comings in nanomaterial exposure measurements and assessments with a strong regulatory focus. Overall, release and the study of release processes are central for understanding, modelling and minimising possible exposure, which holds true for worker, consumer and the general public exposure. Nanomaterial exposure assessment is furthest developed in the occupational field with different measurement devices, methods and significant data being already available. The biggest challenge here is harmonisation. Consumer exposure assessments are mainly based on combining release measurements and modelling using exposure scenarios since measurements on a regularly basis are not feasible. A tiered approach similar to the already established one for work places would be a significant improvement. There also is a strong need to further develop and harmonise methods. The least quantitative information is available for exposure of the general public via the environment. The measurement and analysis methods are limited and expensive in cases when manufactured nanomaterials have to be identified and quantified. Therefore, environmental nanomaterial concentrations are mostly modelled. Many parameters have to be estimated with uncertainties being often very high.

The summary of the current state of the art and challenges for nanomaterial exposure assessment for workers, consumers and of the public via the environment is performed to promote advancements in the different exposure assessment fields by facilitating cross-fertilization.

1. Introduction

Research on manufactured nanomaterial (MN) exposures of workers, consumers and via the environment of the general public has made major progress during the recent years indicated by an increase of publications from 18 in the year 2000, 1144 in 2010 to 3753 in 2016 (Table 1). Some of the health and safety research addressed was of fundamental scientific nature but also regulatory issues were addressed more and more as shown in Table 1. The term 'regulatory issues' in this review refers to laws, standards and general tools for regulation.

When looking at the regulatory areas addressed it can be noticed that most information and measurement data for engineered nanoparticle are currently available for worker exposure (e.g. Table 1). Much less is known about consumer exposure and such data have a higher uncertainty (e.g. Table 1). Exposure of the general population via the environment, as well as environmental exposure of the whole biota, is still the most challenging part due to low concentrations and limited analytical methods for engineered nanoparticles (Cornelis et al., 2014; Baalousha et al., 2016; Peijnenburg et al., 2015). The relative high number of publications listed in Table 1 for exposure via the environment is due to the high number of publications on ambient exposure to ultrafine particles, soot and other non-engineered nanoparticles. Only few articles found in the literature search for exposure via the environment were on engineered nanomaterials.

A review on nanomaterial exposure can be structured according to the field of regulations: occupational safety, consumer safety, safety of the general public and the environment. Another way of structuring the information could be according to the lifecycle of nanomaterials by discussing releases, emissions, transport processes, transformation and exposures for each life cycle stage. The focus of the latter one is from the perspective of a product whilst the first one focuses on safety and how regulation is set up. As this review intents to summarize relevant

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Table 1
Articles published per year

Key words*	Additional key words	2016	2010	2000
Nanoparticle, exposure, concentration		3753	1144	18
+ Regulatory or regulation		1174 (31%)	290 (25%)	4 (22%)[a]
	+ Work or worker or workplace	278	90	0
	+ Consumer	189	27	0
	+ Environment + Air or water or soil	547	120	2[b]

*www.scopus.com last searched 11th Sept. 2017.
[a] Note: 2001 was the first article on engineered nanoparticles related to regulation; this search include quite some literature on ultrafine and soot particles.
[b] Note: 2004 was the first article on engineered nanoparticles in the environment; this search include quite some literature on ultrafine and soot particles.

information to support regulation the information was structured according to fields of regulation. Information base for the review was focussed on reviewed publications, project reports and summaries funded by the EU, as well as literature reviews done in the framework of the European projects, especially NANoREG.

Exposure assessments rely on a basic knowledge of the measurement methods and strategies delivering the concentrations by which exposure can be determined. Other approaches are based on exposure scenarios or release processes. Modelling tools for occupational and consumer exposure are based on knowledge of release and emission. These specific models are becoming more and more available, and will also be discussed.

Exposures that could probably cause health concerns in the workplace where nanomaterials are produced or handled were the starting point of experimental research. Exposure measurements and assessments from industrial workplaces were first conducted at the end of the last and beginning of this century (Maynard et al., 2004 and Kuhlbusch et al., 2004). The basic questions in the first years approximately until 2008 were:

- How can we identify nanomaterials in air?
- How can we quantify nanomaterials in air?
- How can we differentiate manufactured from natural or incidentally generated nano-sized materials?

These questions were first investigated at workplaces for the reasons that (a) the kind of nanomaterial to identify and quantify was clearly defined, (b) the concentrations were the highest to be expected and hence likely of highest relevance and (c) well defined conditions were available facilitating the use of experimental measurement set-ups.

From 2004 onwards research about consumer exposures gained higher interest (Hoet et al., 2004 and Scopus search). The main focus was to be able to understand exposure and the possible effects of nanomaterials for consumers, and thus to deflect possible public concern. To achieve this, it was important to build on knowledge gained from workplaces, especially with regard to measurement methods. Several issues of concern related to exposure measurements and assessment beyond measurement methods were identified to be relevant in particular for consumer and environmental exposure.

Consumers can be potentially exposed to nanomaterials in products during different phases of the product lifecycle: production, processing, use phase, end-of-lifecycle. Assessment of consumer exposure to MN is complex, primarily because important information is often lacking. These relates to detailed information on the use of MN in consumer goods as well as to technical difficulties during measurement, in particular for liquid or solid products. Additionally, information on release during use and thus exposure is also not readily available.

Exposure via the environment is still the least developed area with respect to exposure measurements and assessment despite being addressed already in 2003 (Colvin, 2003). The reasons are simple but also demonstrate the current limitations in our knowledge. The first problem is the identification of the MN in the environment. In matrices like natural waters, particle agglomerates in ambient air, or soil it is unclear how a specific manufactured nanomaterial can clearly be identified and quantified due to the complexity of the matrix but also partially due to a high natural particle background. Measurement methods for these complex matrices with multiple influencing side factors are most demanding. Thus, any measurement method and strategy for assessing environmental exposure will need careful evaluation before it is ready to be used in regulatory settings.

The historical development of MN exposure assessments was also influenced by risk management options available for the protection of humans. Release and exposure conditions can be very well regulated and specific personal safety measures assured at workplaces. The possible uses of nanomaterial products by consumer are much broader and personal safety measures cannot be assured. Exposure assessments for the public have to consider all releases and environmental transformation processes. Hence they are presented and discussed in separate sections.

2. Release

Fragments of nanomaterials or nanoparticles have to be released before any exposure may occur. The conceptual approach of release as a prerequisite of exposure to nanomaterials started around 2008 (e.g. Müller and Nowack, 2008) discussing release into the environment for environmental exposure modelling. Subsequent discussions of nanomaterial safety research showed that the release processes are relevant in all exposure areas. Hence one key development in this field in recent years is summarised in the so-called Framework of Release (MARINA, 2014). Strictly speaking, the Framework of Release is a combination of existing concepts and tools linked in a framework to facilitate their regulatory development and use.

The basic concept is straight forward: A possible risk is only present if an exposure is possible. Release (separation from a larger unit) of nanomaterials or fragments of nanomaterials from powders, composites, suspensions or other nanomaterials is a prerequisite for any exposure. The step following release is the emission and transport of the released material into e.g. an airborne state which then can lead to an exposure of workers, consumers, public or the environment.

The framework of release encompasses four specific points:

The release processes: mechanical, thermal, chemical and mixed processes.

a) Test methods to simulate a process and to derive information on the effect of a given release process to a given material.
b) Linking a test method to an explicit activity or environmental process (see Table 2).

Table 2
Activity type and simulation methods: example for dustiness and de-agglomeration

Activity type
Pouring
Mixing/Stirring
Bagging
Pelletizing
Ball milling
Injection moulding
High energy close operations (leaks)

→ Shear stress →

Principle	Simulation Method
Dustiness	Continuous drop
	Rotating drum
	Vortex
Deagglomeration	Rheogram
	Critical orifice
	High speed aerosolization