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Uncertain Risks of Nanomaterials and Unknown Hazards: Comparison of Nanomaterials Risk Assessment Tools

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Abstract **-**The amount of nanomaterials and associated products manufactured nowadays is rapidly increasing. This raises the issue of the final fate of such products after use and the consequent release of nanomaterials into the environment, and together with this, the potential risks due to their accumulation in the human body, animals and plants. It is of vital importance to resolve these questions as the behaviour of nanomaterials is likely to differ from that of bulk materials of analogous composition. We have compared a variety of existing tools and methodologies for environmental risk assessment of nanomaterials that have been developed at national and international level. Each of these tools considers various aspects when dealing with nanomaterial risk assessment. They provide support in acquiring the information required for performing risk evaluation and risk management decisions during different stages of the life cycle, from design and use to recycling and/or disposal of manufactured products containing nanoparticles. Our eventual aim is to strengthen the existing methodologies by identifying the uncertainties when applying these tools to the five different types of nanotechnology-based products studied, that is, nano-silver, zinc oxide, titanium dioxide, carbon nanotubes and nanocellulose.

Keywords**:** Nanomaterials, Risk assessment, Product life cycle, Environmental impact, Health hazards.

1. Introduction

In addition to known hazards, such as air pollution and exposure to industrial chemicals, other new types of environment-related health risks are emerging. New technologies, such as nanotechnology, may cause risks to human health and the environment at scales that we are not yet able to ascertain (Hoet, 2004). At the moment, work is undertaken to quantify risk factors that have an impact on human health and well-being.

When a new technology is developing is difficult to gather information concerning its new and particular features because they are in the process of being determined and scarce data is available. In particular for nanotechnology only limited information on the behaviour, transformation and final fate of nanomaterials in the environment is available at the moment (Moore, 2006; Nowack, 2012). Also data on amounts produced and disposed of during the life cycle of the product containing nanomaterials is necessary to help regulators to carry out proper risk assessment for nanomaterials (Piccinno, 2012). Appropriate analytical methods are required to reliably detect nanoparticles in various compartments and determine their physico-chemical properties. Concentration data alone is inadequate to quantify the risk of nanomaterials, but needs to be supplemented by accurate measurement of parameters affecting transport and aggregation (Ulrich, 2012; Gottschalk, 2011).

The stability and features of commercial products containing engineered nanoparticles greatly depend on their capacity not to suffer modifications, such as aggregation, that can change their properties. More importantly, the formation of aggregates will also influence the behaviour of such products when they are released into the environment during any time in their life cycle (Wiesner, 2009).

Currently available risk assessment methodologies for nanomaterials which have been developed by different organizations in countries worldwide are identified. These methodologies have been subjected to a critical analysis in which we have studied the features of each tool in order to establish how they work and the information required by each of them during all the life cycle steps. We have also looked at the feasibility of these methodologies for potential users both inside and outside the manufacturing industry. In addition, the uncertainties and gaps of the studied methodologies have also been determined.

Of the methodologies identified, two of them are deemed to have more interesting features and to be more suitable for environmental risk assessment of nanomaterials. These two methodologies are the Swiss Precautionary Matrix for Synthetic Nanomaterials (Höck, 2013) and the Environmental Defense and DuPont Nano Risk Framework (Environmental Defense - DuPont Nano Partnership, 2007). Both of them have been applied to real cases and the results obtained are discussed.

2. Materials and Methods

The selected materials were grouped according to their similarities in composition and shape but with different levels of toxicity/hazard to allow comparison: two particulates (nano-ZnO and nano-TiO_2), two fibre-like materials (nanocellulose and carbon nanotubes) and metallic nanoparticles (nano-Ag). Nano-ZnO shows visible transparency that together with its photocatalytic activity make it an optimal component to be included in coatings, sunscreens, cosmetics, solar cells, electronic constituents and pigment for paints (Ma, 2013). Nano-TiO_2 is used in paints as a consequence of its photocatalytic activity. It is also found in cosmetics, sunscreen and food packaging materials (Wiesner, 2006). Nanocellulose is a nontoxic natural biodegradable polymer, with chemical functionality, thermal stability and moisture absorption properties. It can also be chemically functionalized and may find applications in a wide range of consumer products as for example paper and textiles as well as medical applications and nanocomposites (Martins, 2012). Carbon nanotubes are used to enhance the mechanical properties of composite materials thanks to their high strength and also as flame retardant for textiles. Due to their semiconducting properties they are also applied in electronic components (Popov, 2004). Nano-Ag acts as an antimicrobial agent which is used in household products, clothes and paints (Christensen, 2010).

3. Discussion

Many organisations are now actively involved in developing methodologies and techniques to improve tools for environmental risk assessment, including the EPA (Environmental Protection Agency, 1998), OECD (OECD Environment Directorate, 2012), WHO (Web-1), ECHA (Aitken, 2011) and ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals, 2009). A major problem related to the use of risk assessment is the lack of specific data for nanomaterials and that the data which is available is often subject to uncertainty. Nanomaterials have unique properties which cause them to behave in a different way from their chemical analogues in bulk form. The nanomaterial special properties derive from (i) their quantum properties, which impact on their electronic properties, magnetism and colour, in addition to (ii) their high surface to volume ratio, which affects the catalytic activity, chemical reactivity and solubility (Linkov, 2009).

Risk assessment may be carried out to determine the effects of a substance on human health (Health Risk Assessment) and ecosystems (Ecological Risk Assessment), while Environmental Risk Assessment examines the risks resulting from industrial activity to ecosystems, animals and humans. It comprises health risk assessments, ecological or ecotoxicological risk assessments, and specific industrial applications of risk assessment.

Existing risk assessment tools for nanomaterials (Table 1) have been subjected to a critical analysis to establish how they work in practice and the information required by each of them during all the life cycle steps. We have also looked at the feasibility of these tools for potential users. In addition, the uncertainties and gaps of the studied tools have also been determined. Two tools, the Precautionary Matrix and the Nano Risk Framework, have been selected to perform environmental risk assessment for several typical manufactured products containing engineered nanomaterials (ENM).

Table 1. Available methods for risk assessment of nanomaterials.

Assessment method	Source	Website
Precautionary Matrix for Synthetic Nanomaterials	Federal Offices of Public Health and Environment (FOPH & FOEN) - Switzerland	www.bag.admin.ch/nanotechnologie/12171/12174/12175/index.html?lang=en
Nano Risk Framework	DuPont and Environmental Defense - USA	www.nanoriskframework.com/
Risk Assessment of manufactured nanomaterials	New Energy and Industrial Technology Development Organization (NEDO) - Japan	www.aist-riss.jp/main/modules/product/nano_rad.html?ml_lang=en
NanoCommission Assessment Tool	German Federal Ministry for the Environment, Nature Conservation & Nuclear Safety	www.bmu.de/en/service/publications/downloads/details/artikel/responsible-use-of-nanotechnologies-1/
Precautionary Strategies for Managing Nanomaterials	German Advisory Council on the Environment	www.umweltrat.de/SharedDocs/Downloads/EN/02_Special_Reports/2011_09_Precautionary_Strategies_for_managing_Nanomaterials_KFE.pdf?__blob=publicationFile
SafeNano Scientific Services	Institute of Occupational Medicine (IOM) - UK	www.safenano.org/
Cenarios -Certifiable Nanospecific Risk Management and Monitoring System	The Innovation Society (Switzerland)	http://www.innovationsgesellschaft.ch/images/publikationen/Factsheet_CENARIOS_english_arial2.pdf
REACH Implementation Project on Nanomaterials (RIPoN)	European Chemicals Agency (ECHA)	http://ec.europa.eu/environment/chemicals/nanotech/reach-clp/ripon_en.htm
Work Health & Safety Assessment Tool for Handling Engineered Nanomaterials	Safe Work Australia	http://www.safeworkaustralia.gov.au/sites/swa/about/publications/pages/at201008workhealthandsafetyassessmenttool
Stoffenmanager Nano 1.0	Netherlands Ministry of Social Affairs and Employment	http://nano.stoffenmanager.nl/
NanoSafer	The Industries Council of Occupational Health and Safety (Denmark)	http://nanosafer.i-bar.dk
ANSES	French National Agency for Food Safety, Environment and Labor	http://www.anses.fr/Documents/AP2008sa0407RaEN.pdf

Both of the tools studied require information on their potential uses because these have a direct impact on their possible hazards and exposure effects. The physico-chemical characterization of the nanomaterial is also a key feature when carrying out risk assessment (Figure 1). Hazard identification and exposure assessment complete the necessary parameters to study when carrying out risk assessment (Rickerby, 2014).

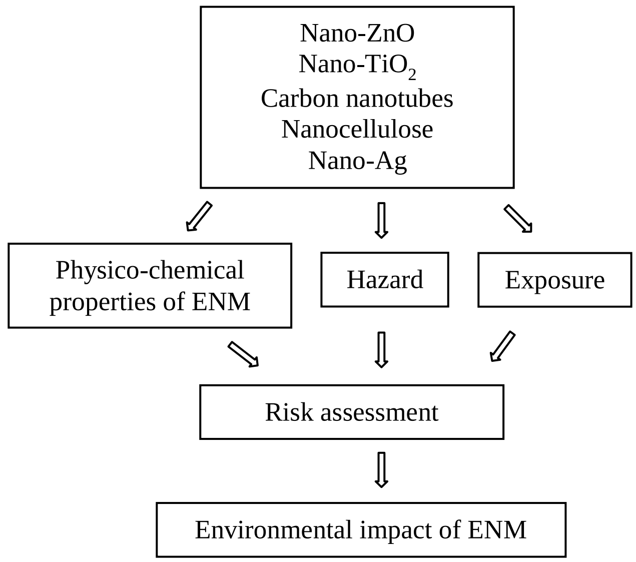

Fig. 1. Basic scheme for the risk assessment and environmental impact of ENM.

The Precautionary Matrix for nanomaterials consists of a questionnaire structured in distinct sections. It enables determination of risks during every step of the life-cycle. The Nano Risk Framework enables preliminary identification of health, safety and environmental risks of nanomaterials. It allows evaluation for each stage of the nanomaterial life-cycle and to include new data when they become available. Risk assessment of the five manufactured products containing nanomaterials described above have been performed applying both methodologies.

The evaluation criteria of the Precautionary Matrix do not consider the chemical composition of each nanomaterial as such and, for this reason, they have been classified according to their physical state (or carrier material) and, in this way, different input is generated. The carrier material of a specific nanomaterial may change during the life cycle of the product (from the manufacturing process, use and final disposal). On the other hand, this classification may be applied to different materials in the same physical state and with the same reactivity. When analysing the five materials using this tool we find that the same result is obtained for nano-TiO_2 and carbon nanotubes if we consider they both are in solid form. They both are highly reactive so they have been grouped together but the different shape of the material, 35 nm nanoparticle *vs*. fibre, has not been taken into account, although it has been reported that carbon nanotubes may show toxicity due to their fibre-like shape and by analogy with asbestos (Poland, 2008). The results obtained for nano-Ag and nano-TiO_2 are the same when considering they are in a liquid matrix, because their redox, catalytic and ROS-formation behaviour are regarded to be equal for both nanomaterials. As for nano-ZnO slightly higher values in the final evaluation are obtained than for nano-Ti O_2, as nano-ZnO is classified with high ROS-formation behaviour and high induction of inflammation reactions by the Precautionary Matrix developers (Höck, 2013).

The applicability of both methodologies to real case scenarios of manufactured nanomaterial containing products presented significant obstacles due to the lack of relevant information to complete the required questionnaires. The Nano Risk Framework requires a very detailed set of information which is difficult to gather due to lack of availability of such data on literature, which may vary from those of their bulk equivalents and also because the manufacturing companies producing nanomaterials are not willing to disclose commercially sensitive information. Production volume is one of the subjects that is difficult to obtain data about (Piccinno, 2012). The scarcity of relevant data in literature about physico-chemical characterization, toxicity and final fate is related to the insufficiency of standardized and validated methods to generate the necessary input. Because of this, we consider that the Precautionary Matrix is the system which enables the completion of a nanomaterial risk assessment in a more rapid way as it requires less amount of data and also allows approximations to be made more easily when data are insufficient. The data requirements are simplified and the decision analysis is facilitated as it offers a graphical output showing where the risk limits have been established and highlighting where the uncertainties are. However, only an initial risk assessment is possible when applying the Precautionary Matrix because it does not consider toxicity data and this causes the results to be rather generic as they are independent of the chemical composition of the nanomaterial.

4. Conclusion

Traditional chemical risk assessment methodologies show limitations when applied to nanomaterials. This is due to the challenges arising from the unique properties of nanomaterials and their different behaviour in comparison to conventional chemicals. Each of the nano-specific methodologies take into account the new properties of nanomaterials at some level. Only preliminary risk assessments are possible at the moment due to the high degree of uncertainty associated with the determination of toxicology, ecotoxicology, biopersistance in the environment and data on final fate of nanomaterials.

There are still many data gaps and little information is available on the material inputs and environmental releases due to the manufacture of nanomaterials.

Exposure, environmental fate and transport will be crucial in determining the overall environmental impact of nanomaterials but there are no standard accepted methods for assessing their environmental fate. Models for predicting the fate, transport, and human health impacts of conventional environmental contaminants thus need to be modified to take into account the specific properties of nanomaterials, which may differ from those of their bulk analogues. A major difficulty in performing risk assessment is that the estimated nanomaterial concentrations in the environmental compartments are subject to wide variability, due to the uncertainties in the production volume of the nanomaterials and the product life cycles, with the result that the potential exposures are largely unknown.

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